



GUIDELINES FOR THE NITRATE SELECTIVITY
FROM ION-EXCHANGE RESINS
HAVING A QUATERNARY AMMONIUM GROUP
AS A BINDING SITE

by

Philippe Guarilloff

M. Sc.

A thesis presented for the degree of
Doctor of Philosophy

The University of Adelaide
Department of Chemistry
South Australia

April, 1994

Awarded 1994

TABLE of CONTENTS

	page
Chapter 1 Introduction	1
Chapter 2. Materials and Methods	6
2.1 Materials	7
2.2 Physical-Chemistry Measurements	18
2.3 NMR Spectroscopy	30
2.4 EMF Experimentation	38
Chapter 3 Study of the Anion/Monomer Association	47
3.1 Introduction	47
3.2 Physical-Chemistry Properties	48
3.3 Spin Lattice Relaxation Times T_1	61
Chapter 4. Study of the Anion/Linear Polymer Association	78
4.1 Physical-Chemistry Measurements	78
4.2 NMR Spectroscopy	81
4.3 EMF Experimentation	84
Chapter 5. Study of the Anion/Cross-Linked Polymer Association	110
5.1 Presentation	110
5.2 Properties of the Cross-Linked Polymers	111
5.3 EMF Experimentation	119
5.4 Selectivity Survey	136
5.5 Conclusion	151
Chapter 6. Conclusion	166
References	171

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any other university and to my best knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of this thesis.

I consent to this thesis being made available for photocopying and loan.

Ph. Guarilloff

ACKNOWLEDGMENTS

I wish to express my gratitude to my supervisors, Drs Barry J. Steel and Tom Kurucsev, for their guidance, support and general understanding during the course of this research.

Special thanks to Gary Owens for his help and constructive talks.

My appreciation to my colleagues and friends from the University of Adelaide, and also to the technical staff of the department.

An Australian European Awards Program Scholarship followed by a University of Adelaide Overseas Postgraduate Research Scholarship are gratefully acknowledged.

THESIS SUMMARY

The aim of this project was to determine the basis for the high selectivity towards nitrates of certain quaternary ammonium ion-exchange resins. An affinity for nitrates by polymers having quaternary ammonium functional groups had been previously reported [1].

The cations chosen were benzyltrialkylammonium, and the alkyl group varied from methyl to n-pentyl. These were called the monomer analogues, since the polymers were synthesised from the monomers which were vinylbenzyltrialkylammonium chloride salts. Conductance data showed that the ion-pairing was consistently larger for nitrates and sulphates than for chlorides [2].

A systematic approach was adopted. The ion-pairing of the monomers, the linear polymers, and the cross-linked polymers were measured with some of the most common anions found in drinking water sources such as nitrate, chloride and sulphate. An appraisal of the nitrate affinity was carried out over a large range of monomer and polymer "concentrations".

Monomers and polymers were not commercially available. Vinylbenzyltrialkylammonium chloride salts were initially synthesised, and polymers were formed by radical polymerisations. The cross-linker was divinylbenzyl (DVB).

^{14}N relaxation times, T_1 , were measured to appraise the nitrate association with the monomers up to concentrations close to saturation. The rate of chemical exchange for the ion-pair formation was compared to the rate of the molecular reorientation along the C_3 axis of the nitrate ion. Densities and viscosities were measured to convert molalities to molarities and to correct the T_1 . Apparent molal volumes and hydration numbers of the monomers, in chloride and nitrate forms, were calculated. The association of the soluble linear polymers was measured by ^{14}N relaxation times of the nitrate ion and by the use of ion specific electrodes, I.S.E., for nitrates, chlorides and sulphates. Densities and viscosities were also measured, the size of the linear polymers was estimated from these viscosity measurements.

Two sets of cross-linked polymers were prepared. The cross-linking degrees were found to be 9.0 and 21.4 % (mol/mol), using microanalysis and water retention methods. Chloride, nitrate and sulphate association with the cross-linked polymers were measured using the same I.S.E. potentiometric devices.

The results obtained confirmed the trends for nitrate monomer associations observed previously [2]. The polymerisation increased the nitrate affinity which was also enhanced by larger alkyl substituent on the quaternary ammonium functional group and by a higher cross-linking degree.

[1] M.B. Jackson & B.A. Bolto, *Reactive polymers*, **12**, p. 277-290, 1990.

[2] B.J. Steel et al., *Aust. J. Chem.*, **43**, p. 1983-90, 1990.

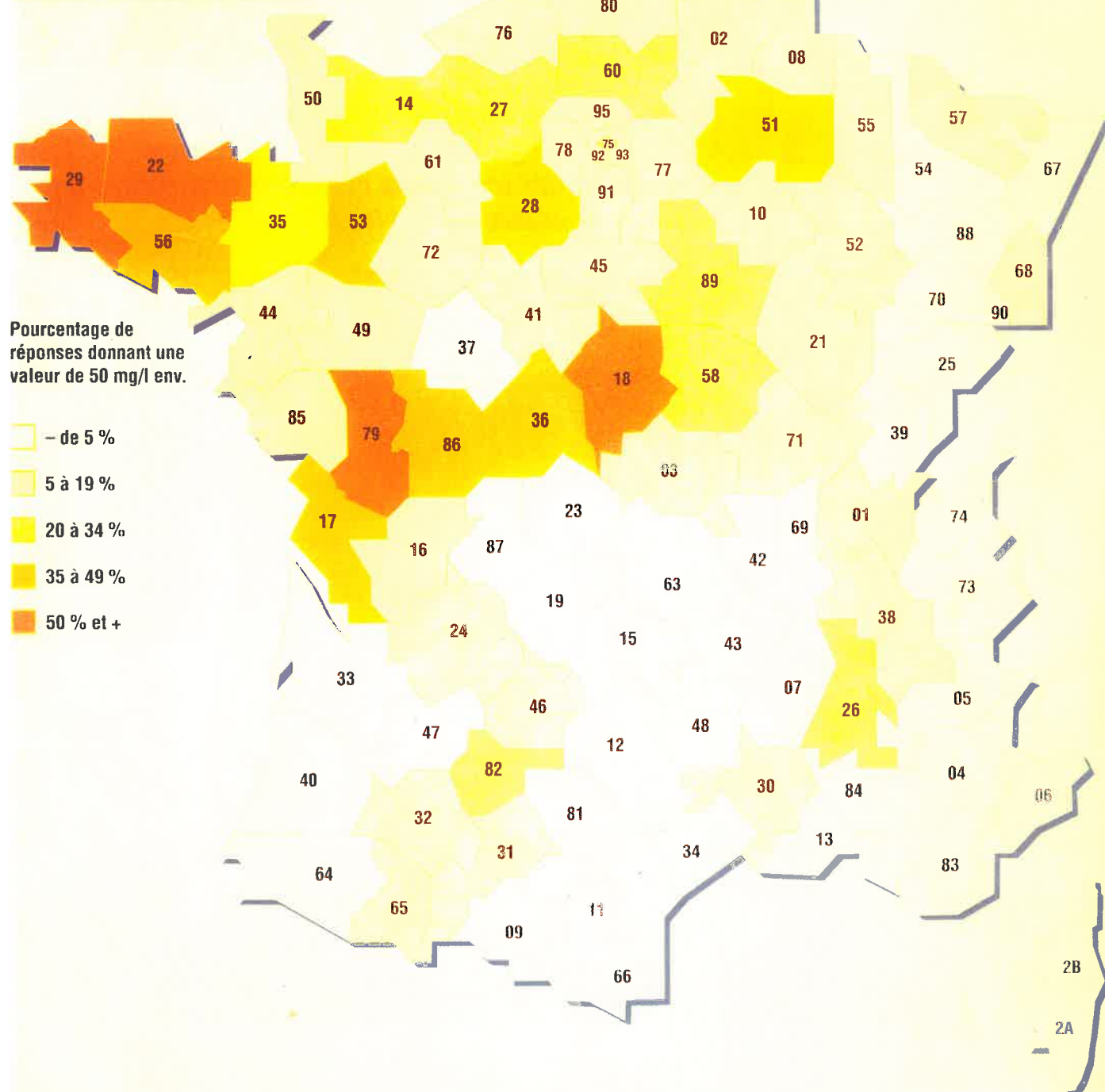


INTRODUCTION

Levels of nitrate in ground water have steadily increased in the developed countries, over the past 20 years [1-3]. Chemical fertiliser, livestock and human excrements and various other waste products provide the majority of the salts entering underground aquifers. Ground water is the main source for drinking water in rural areas and it can be contaminated by leaching nitrates [2,4] which poses a potentially serious hazard. When ingested by humans, nitrates can be reduced by gastrointestinal microflora to very reactive nitrites. Those can oxidise the ferrous iron (II) of the haemoglobin heme into the ferric iron (III) state and give methaemoglobin [3-6]. Methaemoglobin is unable to fix and to transport oxygen to the tissues leading to a lethal poisoning for infants [5,6] known as the "blue baby" syndrome. Only 10 % of the total ferrous state (haemoglobin) oxidised to ferric state (methaemoglobin) is sufficient to turn a baby blue [6]. In addition, stomach and oesophageal cancer-causing effects have been reported [7,8].

Nitrates are present in vegetables [1,2,10]. The nitrate levels in carrots, spinach, beets, lettuce, celery or radish are markedly increased in the processed baby food for example. It is necessary to control nitrate ingestion level from the water consumption. The European community has adopted a regulation that nitrate levels do not exceed more than 50 mg of nitrate (NO_3^-) per dm^3 or 11.3 mg nitrate -N per dm^3 in any drinkable water [9]. The guideline value is set at 25 mg of nitrate NO_3 per dm^3 or less. An extensive survey, based on 30 000 measurements [10], has recently been published by an independent French consumer magazine. The nitrate level of the water supplied for domestic consumption was measured all over the country in April 1993. A map, included next page, illustrates the inventory of the analysis results which revealed a nitrate level above the 50 mg dm^{-3} . Among the 96 French départements, 38 départements had less

La carte de France des nitrates



MAP 1-1: PERCENTAGE OF TAP WATER WHICH CONTAINED MORE THAN 50 mg dm⁻³ OF NITRATE IN FRANCE, TEST CONDUCTED WITH 30 000 SAMPLES IN APRIL 1993

than 5 % of their water tested with a nitrate level above 50 mg dm^{-3} , 37 departements had between 5 and 19 % of their water tested above 50 mg dm^{-3} , 10 departements had between 20 and 34 % of the water tested above the limit, 7 departements had between 35 and 49 % of their water tested above the limit and 4 departements had more than half of their sample above 50 mg dm^{-3} .

The chemical water is very cheap. In South Australia, it is delivered at an average cost of \$1 a 1 tonne. The treatment must be cheap and simple because of the large volume needed. About 1 % of the treated water delivered to customers is really ingested. During summer in Adelaide, up to 80% of the same water is used to water gardens. In spite of this, all the water has to be of potable quality.

Nitrate concentrations can be decreased using different methods. Among them, chemical reduction suffers from the high stability of nitrate ions, chemical precipitation from the high solubility of most of the nitrate salts. Reverse osmosis is hindered by the small size of the nitrate. It is not reliable for an on demand operation and requires a large amount of storage water before and after the operation as the system cannot be interrupted. The protection of the membrane and the complexity of the instrumentation restricts the use of reverse osmosis at a local level [18]. Electrodialysis is expensive to run [4,18]. Degradation by microorganisms is hardly sustaining on a continuous process as it is a slow process and requires higher concentration of contaminants to obtain a complete degradation [11]. Thus, the physicochemical adsorption remains the most feasible and simple way of removing nitrates [21]. It is flexible, relatively economical and ecologically friendly if resins are properly regenerated.

In spite of these promising aspects, the commercially available ion-exchange resins preferentially adsorb the highly charged ions dissolved in water. In this way, sulphates are preferred to nitrates [13]. Clifford and Walter [14] attributed this to the presence of two closely-spaced functional groups containing positive charges. The saturation of the resins by less harmful ions such as sulphates or chlorides impaired the adsorption

method. A resin highly selective towards nitrates would sharply decrease the frequency of the regeneration step. Furthermore, anions of a prime importance for life could still be preserved in such purified water.

Nitrates rarely associate. Robinson & Stokes [17^a] appraised that at 0.1 M, only 3 % of dissolved potassium nitrate would be associated (because of its single charge and relatively large size). Nevertheless, higher association was observed [15] for some quaternary ammonium ions when polymerised. The ion-pairing of benzyltrialkylammonium cations with chlorides, nitrates and sulphates was studied by Steel et al. [12]. The association constants were low for all these ions where monovalent ion association increased with the length of the alkyl group, while bivalent ions association decreased.

Polymerisation usually enhances the properties observed for the monomers [16]. The selectivity of nitrates by polymers including some quaternary ammonium functional groups have been discussed in the literature [13-15, 18]. This type of hydrophobic chain attached to the quaternary ammonium ions was reported to be a significant factor by Bolto & Jackson [13] and Clifford & Weber [14] for nitrate selectivity. The latter did an extensive selectivity study of 30 commercially available basic anion exchange resins. As for the matrix, the nature and the location of the functional group was found to be important. A tertiary ammonium, incorporated in the polymer chain with short organic groups attached, maximised the selectivity for divalent anions. Jackson & Bolto [15] have recently shown that the nitrate selectivity is strongly enhanced by the hydrophobicity of a resin. However, it does not depend on how this character is provided, on the length of the alkyl group or on the location of the functional group. As Gutter reported [18], the highest nitrate selectivity was obtained when $n\text{Bu}_3\text{N}^+$ was attached to a cross-linked polystyrene backbone. Clifford and Weber disagreed with this particular latter point [14], arguing that cross-linking is a minor factor for selectivity phenomena. These independent studies did not yields similar results, and so no general rules for the nitrate selectivity were established.

A clarification is needed to provide a complete understanding of the nitrate affinity for these weak-base ion-exchange resins. Using benzyltrialkylammonium cations, the association of chlorides, nitrates and sulphates with monomer analogues, linear and cross-linked polymers were measured. The study intend to determine the importance of each factors such as the role of the hydrophobic alkyl chain fixed on the quaternary ammonium binding site, the weight of the matrix on the linear and the cross-linked polymers and the effect of the cross-linking degree on the nitrate selectivity. From the acquisition of a new data, we would like to find some fundamental rules which govern the selectivity from vinylbenzyltrialkylammonium polymers towards nitrates of different anions studied have to be established. A discussion about the different systems studied, involving chlorides and sulphates, could reveal more general trends which might lead, in the future, to the design of some tailor made resins towards other anions.

presentation,
objectif
plan à l'heure ?

MATERIALS AND METHODS

2-1 MATERIALS

2-1-1 The monomeric analogues

2-1-1-1 The chloride salts

Benzyltrimethylammonium chloride: was available from Fluka as "purum" grade material. It was recrystallised from acetone/ether, and dried in vacuum oven. Silver chloride gravimetric analysis have been carried out with triplicate samples and indicated a purity of 100.15 % $\pm$ 0.05.

Benzyltriethylammonium chloride: was available from Fluka as "purum" grade material. It was recrystallised from acetone/ether twice, and dried in vacuum oven. Silver chloride gravimetric analysis was done with triplicate samples and indicated a purity of 99.80 % $\pm$ 0.16.

Benzyltripropylammonium chloride: Fluka "purum" grade tripropyl amine (10.5336 g, 74 mmol) was refluxed and stirred with benzyl chloride (12.0286 g, 95 mmol) for 46 hours at 70 °C. The orange solid obtained was dissolved in ethanol and precipitated from anhydrous ether twice. When dried in a vacuum oven, 11.6016 g of a snowy product was obtained, the yield product was 59 %. Microanalysis gave C, 70.4; H, 10.3; N, 5.1; and calculated for C₁₆H₂₈ClN was C, 71.2; H, 10.4; N, 5.2 %. The melting point was 194-195 °C (lit. [22] 189-192 °C). ¹H nmr (CDCl₃), δ 7.37, s, aromatic H; 4.85, s, benzyl methylene; 3.30, m, CH₂ N; 1.90, m, CH₂; 0.98, t, CH₃. Mass spectrum m/z 234

for $C_{16}H_{28}N^+$. Silver chloride gravimetric analysis indicated a purity of $100.38 \% \pm 0.31$.

Benzyltributylammonium chloride was available from Fluka as "purum" grade material. It was recrystallised from acetone/ether twice, and dried in a vacuum oven. The melting point was $164-165\text{ }^{\circ}\text{C}$. Silver chloride gravimetric analysis was done with triplicate samples and indicated a purity of $100.38 \% \pm 0.07$.

Benzyltripentylammonium chloride: tripentyl amine (29.2493 g, 129 mmol) was refluxed and stirred with benzylchloride (20.75 g, 164 mmol) at $69\text{ }^{\circ}\text{C}$ for 19h30. The orange solution was dissolved in acetone and reprecipitated twice with anhydrous ether. The resultant white product mass was 11.5453 g, a yield of 25 %. Microanalysis gave C, 74.6; H, 11.7; N, 4.0%, and calculated for $C_{22}H_{40}ClN$: C, 74.6; H, 11.4; N, 4.0 %. ^1H nmr (CDCl_3), δ 7.42, s, aromatic H; 4.88, s, benzyl methylene; 3.35, m, CH_2N ; 1.13-2.00, m, CH_2 ; 0.90, t, CH_3 . The melting point was $140-142\text{ }^{\circ}\text{C}$. Silver chloride gravimetric analysis was done with triplicate samples and indicated a purity of $100.16 \pm 0.07\%$.

2-1-1-2 The nitrate salts

The conversions to other anion salts were carried out using B.D.H. Amberlite IRA-400 (NO_3^-) as an ion-exchange resin, itself converted from the chloride commercially available form by shaking overnight with 2 molar potassium nitrate. The soaking was repeated until chloride concentration still in solution was measured less than 0.005 M, measured using an emf method.

A known amount of the chloride monomer solution was stirred for 1 hour with an excess of nitrate converted resin equivalents. All the filtrates and washings were collected with care, the operation was repeated up to 5 times until the chloride concentration measured

in the solution was less than 3 % of the total amount of monomer first introduced. The solution was completely dried in a vacuum oven at 40-45 °C and weighted.

Benzyltripentylammonium nitrate: this compound was not soluble enough to use the ion-exchange resin conversion method. Instead, it was prepared by precipitation from the chloride solution using potassium nitrate. The precipitate was washed with water and recrystallised twice from acetone/ether.

The purity of the nitrate monomer analogues have been verified by U.V. absorption using the maximum molar absorbancy of the nitrates anions [12] at 262 ± 1 nm, and by emf using an Orion nitrate ion selective electrode, (see part 4-4). The determinations were done in triplicate each time, and the results are summarized in the following table.

Table 2-1: purity of the converted benzyltrialkylammonium nitrate salts

<i>by absorption</i>	methyl	ethyl	propyl	butyl	pentyl
% in NO ₃ ⁻	99.29 ± 0.22	99.54 ± 0.15	99.89 ± 0.14	99.54 ± 0.03	100.11 ± 0.04
<i>by e.m.f.</i>					
% in NO ₃ ⁻	98.54 ± 1.27	97.88 ± 0.65	98.23 ± 1.03	98.32 ± 0.95	97.23 ± 1.35

The results obtained using emf were slightly smaller, with a larger error which often overlapped the absorption values. Both ways were satisfactory to evaluate the purity of our nitrate converted monomer analogues

2-1-2 The linear polymers

The linear polymers have been prepared in two steps [23]. First, chloride salts were synthesised and used as monomers. For the polymerisation, the solvent was a mixture,

water/ethanol (5/1, w/w), into which was introduced the monomers and some free radical initiator. This latter was azobisisobutyronitrile (AIBN).

2-1-2-1 The synthesis of the monomers

Monomers were synthesised from a mixture of trialkylamine and vinylbenzylchloride from a ratio amine/vinylbenzylchloride (1.5-1), input as reactants.

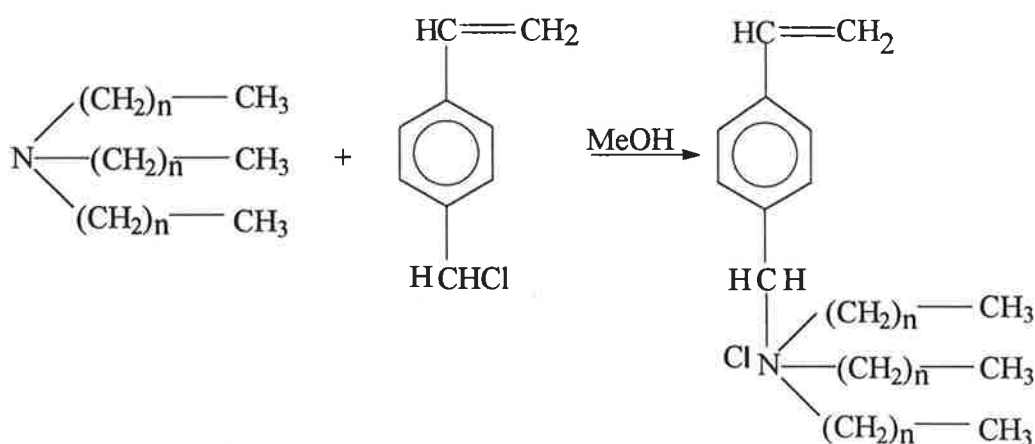


Figure 2-1: synthesis of vinylbenzyltrialkylammonium chloride salts.

Vinylbenzyltrimethylammonium chloride: Aldrich triethylamine 25 % (w/w) (29.98 g, 127 mmol) was diluted in 50 ml of AR grade methanol. Then Kodak vinylbenzylchloride (10.21 g, 67 mmol) was added dropwise and the solution was vigorously stirred at 35 °C. The yellow solution was refluxed for 48 hours. Then the darker solution was washed twice with 50 ml of anhydrous ether, then dissolved in ethanol at 50 °C and recrystallised from anhydrous ether thrice. After drying in a vacuum oven at 50 °C overnight, 11.91 g (56 mmol) of beige product was obtained, a yield of 84 %. Mass spectrometry gave $m/z = 176$ for $(\text{C}_{12}\text{H}_{18}\text{N}^+)$.

Vinylbenzyltriethylammonium chloride: AR grade DBH triethylamine (45.10 g, 446 mmol) was dissolved in 30 ml of AR grade methanol. Vinylbenzylchloride (44.82 g, 294 mmol) was added dropwise and to a vigorously stirred solution and kept at 38 °C. The

dark solution was refluxed for 38 hours and washed thrice with 50 ml of anhydrous ether. The beige compound was dried in a vacuum oven at 45 °C over night, producing 58.02 g (228 mmol) of product, a yield of 77 %. Mass spectrometry gave $m/z = 218$ for $(C_{15}H_{24}N^+)$. ^1H NMR ($CDCl_3$) δ 7.42, m, aromatic H; 5.71, d, $H_2C=C$; 5.31, t, $H_2C=CHAr$; 4.88, s, $ArCH_2N$; 2.0, t, $N(CH_2)_3$; 0.90, s, $N(CCH_3)_3$. ^{13}C nmr ($CDCl_3$) δ 13.0, s, $(CH_3)_3$; 19.0 d, C from ethyl; 52.7, s, C from ethyl; 60.8, s, $ArCN$; 115.6, d, $C=C-Ar$; 116.0, t, $C=C-Ar$; 126.4-139.4, m, aromatic C. Microanalysis for $C_{15}H_{24}NCl \cdot H_2O$, found: C, 66.3; H, 9.6; N, 5.2 and calculated C, 67.2; H, 9.3; N, 5.1 %.

Vinylbenzyltripropylammonium chloride: high purity Fluka tripropylamine (36.56 g, 255 mmol) was dissolved in 40 ml of AR grade methanol vigorously stirred and kept at 40 °C. Vinylbenzylchloride (24.80 g, 163 mmol) was added dropwise. The yellow solution was refluxed for 44 hours, to produce a greasy dark yellow and thick solution which was washed 4 times with 50 ml of anhydrous ether. The resulting light beige compound was vacuum dried at 45 °C overnight, 21.70 g (73 mmol) was obtained, a yield of 45 %. Mass spectrometry gave $m/z = 260$ ($C_{18}H_{30}N^+$).

Vinylbenzyltributylammonium chloride: Aldrich (99% pure) tributylamine (32.51 g, 175 mmol) was dissolved in 22 ml of AR grade methanol. Vinylbenzylchloride (22.48 g, 147 mmol) was added dropwise to a vigorously stirred solution at 30 °C. The yellow solution was refluxed for 48 hours, and washed 3 times with 50 ml of anhydrous ether. The light beige compound was vacuum dried at 45 °C overnight, 15.55 g (46 mmol) was obtained, a yield of 31 %. Mass spectrometry gave $m/z = 302$ for $(C_{21}H_{36}N^+)$. ^1H NMR ($CDCl_3$) δ 7.42, m, aromatic H; 5.76, d, $H_2C=C$; 5.35, t, $H_2C=CHAr$; 4.88, s, $ArCH_2N$; 3.33, t, $N(CH_2)_3$; 1.80, s, $N(CCH_2)_3$; 1.42, s, $N(CC(CH_2))_3$; 0.99, t, $N(CCC(CH_3)_3)$. ^{13}C nmr ($CDCl_3$) δ 13.0, s, $(CH_3)_3$; 19.0 d, C from butyl; 23.7, s, C from butyl; 57.8, s, NC from butyl; 62.0, t, $ArCN$; 115.0, d, $C=C-Ar$; 115.5, t, $C=C-Ar$;

126-139, m, aromatic C. Microanalysis for $C_{21}H_{36}NCl \cdot 2H_2O$, found: C, 67.4; H, 10.8; N, 3.8 and calculated C, 67.9; H, 10.1; N, 3.9 %.

Vinylbenzyltripentylammonium chloride: High purity Fluka triptentylamine (55.13 g, 242 mmol) was dissolved in 35 ml of AR grade methanol. Vinylbenzylchloride (23.92 g, 157 mmol) was added dropwise, vigorously stirred at 30 °C. The yellow solution was refluxed for 60 hours, and washed 3 times with 50 ml of anhydrous ether. The light beige compound was vacuum dried at 45 °C overnight, 40.20 g (106 mmol) was obtained, a yield of 68 %. Mass spectrometer gave $m/z = 344$ for $(C_{24}H_{42}N^+)$. ^1H nmr ($CDCl_3$) δ 7.43, m, aromatic H; 5.77, d, $H_2C=C$; 5.38, t, $H_2C=CHAr$; 4.92, s, $ArCH_2N$; 3.34, t, $N(CH_2)_3$; 1.81, s, $N(CCH_2)_3$; 1.36, s, $N(CC(CH_2)_2)_3$; 0.90, t, $N(CCCC(CH_3)_3)$. ^{13}C nmr ($CDCl_3$) δ 13.2, s, $(CH_3)_3$; 21.6 d, CC from pentyl; 27.7, s, C from pentyl; 58.0, s, NC from pentyl; 62.1, t, $ArCN$; 114.9, d, $C=C-Ar$; 115.5, t, $C=C-Ar$, 126-139, m aromatic C.

2-1-2-2 The linear polymerisation

For all the polymerisations, the solvent was a mixture of water/ethanol (4/1, v/v), the monomers were benzyltrialkylammonium chloride salts, the initiator was AIBN; α, α' -Azobis(isobutyronitrile), $(CH_3)_2C(CN)N:(CN)C(CH_3)_2$, $M_w = 164.21$ g prepared by Tokyo Kasei. Polymer purifications were done at room temperature. The reaction can be illustrated by figure 2-2.

Poly (vinylbenzyltrimethylammonium chloride): trimethylvinylbenzyl chloride (8.52 g, 46 mmol), AIBN (0.0598 g,) were dissolved in 30 ml of solvent and refluxed for 10 hours at 70 °C. The solution was precipitated into 150 ml of acetone and washed twice with acetone. The product was reprecipitated from ethanol/ether and dried in a vacuum oven at 50 °C for 3 hours. The white precipitate weighed 6.55 g, a 77 % yield.

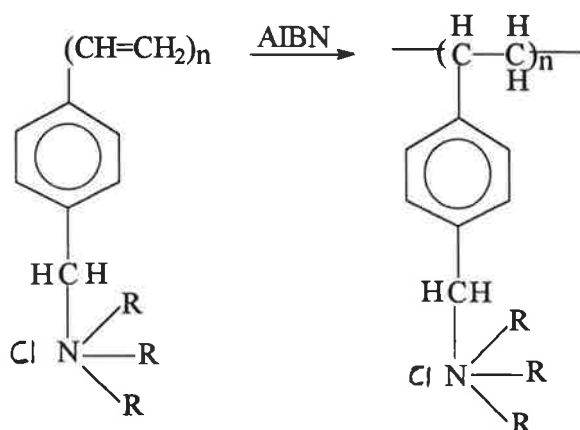


Figure 2-2: synthesis of the linear polymers (R varied from methyl to n-pentyl).

Poly (vinylbenzyltriethylammonium chloride): triethylvinylbenzylammonium chloride (2.0955 g, 5.52 mmol) and AIBN (0.0222 g, 0.14 mmol) were dissolved in water (18 ml) and heated under reflux for 4h30 at 70 °C; the resultant solution was evaporated under vacuum and the solid reprecipitated with heating from acetone/ether to yield 0.46 g (22%) of crude product. The product was further reprecipitated from acetone/ether to obtain a fluffy white solid which was vacuum dried before use.

Poly (vinylbenzyltripropylammonium chloride): tripropylvinylbenzyl chloride (10.21 g, 38 mmol), and initiator (0.1022 g) were dissolved in a water/ethanol (40 ml/8 ml) solution and were refluxed for 9 hours at 70 °C. At room temperature, the solution was precipitated with dry ether and washed with an excess of acetone. This product was reprecipitated from ethanol/ether and dried in a vacuum oven at 50 °C for 6 hours. The snowy white precipitate weighed 7.96 g, a 78 % yield.

Poly (vinylbenzyltributylammonium chloride): tributylvinylbenzylammonium chloride (14.17 g, 42 mmol) and AIBN (0.1288 g) were dissolved in water/methanol (40ml/8ml) and heated under reflux for 13h30 at 60 °C. At room temperature, the resultant solution was precipitated and washed with an excess of acetone. It was

reprecipitated from ethanol/ether and dried in a vacuum oven at 50 °C for 6 hours. The snowy white (very slightly greenish) precipitate weighed 10.02 g, a 71 % yield.

Poly (vinylbenzyltripentylammonium chloride): tripentylvinylbenzyl chloride (13.66 g, 36 mmol), and AIBN (0.1103 g) have been dissolved in 100 ml of solvent and refluxed for 11 hours at 70 °C. The solution was precipitated into 200 ml of acetone, and washed twice with acetone. The product was reprecipitated from ethanol/ether and dried in a vacuum oven at 50 °C for 5 hours. The snowy white precipitate weighed 8.33 g, a 61 % yield.

2-1-3 The cross-linked polymers

The cross-linked polymers were prepared from the vinylbenzyltrialkylammonium chloride monomers. The cross-linker was Aldrich divinylbenzene 55 %; the contained inhibitor had been previously removed using a 10 % sodium hydroxide solution. The solvent was AR methanol, and the free radical initiator azobisisobutyronitrile AIBN was used again. Two sets of each polymers with a different ratio of DVB to monomer were prepared.

2-1-3-1 The synthesis of the high cross-linked polymers

Poly (vinylbenzyltrimethylammonium chloride): trimethylvinylbenzyl chloride (10.2066 g, 48 mmol) and AIBN (0.5012 g, 3 mmol) were dissolved in 80 ml of AR methanol. Divinylbenzene was added (6.5911 g, 28 mmol) and the mixture was stirred at room temperature for 48 hours. The waxy yellow top layer was removed, the white firm bottom layer was washed with methanol and dried in a vacuum oven at 45 °C for 6 h. 10.0548 g of white polymer, water and methanol insoluble, was obtained, a 60 % yield.

Poly (vinylbenzyltriethylammonium chloride): triethylvinylbenzyl chloride (12.7364 g, 50 mmol) and AIBN (0.5091 g, 3 mmol) were dissolved in 120 ml of AR methanol.

Divinylbenzene was added (6.5532 g, 28 mmol) and the mixture was stirred at room temperature for 51 hours. The waxy yellow top layer was removed, the white firm bottom layer was washed with methanol and dried in a vacuum oven at 45 °C for 5 h. 13.3980 g of white polymer, water and methanol insoluble, was obtained, a 69 % yield.

Poly (vinylbenzyltripropylammonium chloride): tripropylvinylbenzyl chloride (9.8154 g, 33 mmol) and AIBN (0.3284 g, 2 mmol) were dissolved in 120 ml of methanol. Divinylbenzene was added (4.3261 g, 18 mmol) and the mixture was stirred at room temperature for 44 hours. The waxy yellow top layer was removed, the white firm bottom layer was washed with methanol and dried in a vacuum oven at 45 °C for 4 h. 6.5487 g of white polymer, water and methanol insoluble, was obtained, a 46 % yield.

Poly (vinylbenzyltributylammonium chloride): tributylvinylbenzyl chloride (10.6308 g, 31 mmol) and AIBN (0.2956 g, 2 mmol) were dissolved in 80 ml of AR methanol. Divinylbenzene was added (4.1004 g, 18 mmol) and the mixture was stirred at room temperature for 48 hours. The waxy yellow top layer was removed, the white firm bottom layer was washed with methanol and dried in a vacuum oven at 45 °C for 4 h. 10.8594 g of white polymer, water and methanol insoluble, was obtained, a 74 % yield.

Poly (vinylbenzyltripentylammonium chloride): tripentylvinylbenzyl chloride (19.0254 g, 50 mmol) and AIBN (0.4926 g, 3 mmol) were dissolved in 150 ml of AR methanol. Divinylbenzene was added (6.4897 g, 27 mmol) and the mixture was stirred at room temperature for 39 hours. The waxy yellow top layer was removed, the white firm bottom layer was washed with methanol and dried in vacuum oven at 45 °C for 4 h. 12.1452 g of white polymer, water and methanol insoluble, was obtained; a 48 % yield.

2-1-3-2 The synthesis of the low cross-linked polymers

A second set of polymers were synthesised with a smaller proportion of the cross-linker, DVB, to obtain a less cross-linked polymer. Except for the amount of DVB, the other reactant proportions and the method were identical.

Poly (vinylbenzyltrimethylammonium chloride): trimethylvinylbenzyl chloride (6.3895 g, 30 mmol), AIBN (0.3033 g, 2 mmol) were dissolved in 95 ml of AR methanol. Divinylbenzene was added (0.7392 g, 6 mmol). The dry polymer weight was 6.3489 g, a 89 % yield.

Poly (vinylbenzyltriethylammonium chloride): triethylvinylbenzyl chloride (8.5844 g, 33 mmol), AIBN (0.2992 g, 2 mmol) were dissolved in 80 ml of AR methanol. Divinylbenzene was added (0.8509 g, 4 mmol). The dry polymer weight was 8.3761 g, a 89 % yield.

Poly (vinylbenzyltripropylammonium chloride): tripropylvinylbenzyl chloride (12.1223 g, 40 mmol), AIBN (0.9542 g, 5 mmol) were dissolved in 80 ml of AR methanol. Divinylbenzene was added (1.0867 g, 3 mmol). The dry polymer weighted 6.20823 g, a 47 % yield.

Poly (vinylbenzyltributylammonium chloride): tributylvinylbenzyl chloride (6.4078 g, 19 mmol), AIBN (0.1921 g, 1 mmol) were dissolved in 75 ml of AR methanol. Divinylbenzene was added (0.4783 g, 3 mmol). The dry polymer weight was 6.20823 g, a 74 % yield.

Poly (vinylbenzyltripentylammonium chloride): tripentylvinylbenzyl chloride (8.8815 g, 23 mmol), AIBN (0.2342 g, 1 mmol) were dissolved in 75 ml of AR methanol.

Divinylbenzene was added (0.5425 g, 8 mmol). The dry polymer weight was 8.3920 g, a 89 % yield.

The yield for the low cross-linked polymers were slightly higher, as if the product was easier to be synthesised.

2-1-3-3 The cross-link determination

When the degree of cross-linking is low (around 0.5 %), the polymer is hardly soluble and called a gel. Usually, above 2 %, the gel becomes hard, a resin. Its porosity is lower, its density higher and a lower order of hydration is observed. The rate of ionic diffusion becomes lower, as well as the ion fixations of high molecular mass. A typical cross-link degree for an ion exchange resin varies from 5 to 12 % with extreme rates for specific uses going from 0.5 % up to 24 % [24^a,25^a]. The cross-linked degree is usually presented as a nominal ratio defined by the mass or mole number of cross-linker, introduced as a reactant for the polymerisation, over the amount of monomer.

This was not satisfactory in our case. Some reactants were lost during the reaction which took place over more than 2 days. When in excess, the cross-linker might not be able to completely react and be lost. This would explain the higher yield obtained for the less cross-linked polymers. The typical smell of DVB has been detected! Cross-linker also could have reacted with itself, without contributing to the structure of the cross-linked polymer. A another possibility is that two terminal reactive sites of DVB could have reacted with the more concentrated monomers, as well as with itself. Yet, a third possibility is that only one site had stayed free. The different possibilities are illustrated in figure 2.3.

How to get the cross-linking degree more accurately? Differential Scanning Calorimetry measurements were tried using a Perkin-Elmer DSC 2 instrument. Unfortunately, no glass transition peaks were detected. An alternative method was developed by Boyd and

Soldano in 1953 [26]. Cross-linking confers rigidity to resins which can not swell much when immersed in a solvent. The mass of water regained by a dried resin when left for few weeks in a moisture controlled atmosphere is related to the degree of cross-linking. Bauman [27] and Pepper [28] have shown that the water retention of a sulphonated styrene-divinylbenzene cation exchange resin varies inversely with the amount of divinylbenzene, the cross-linker.

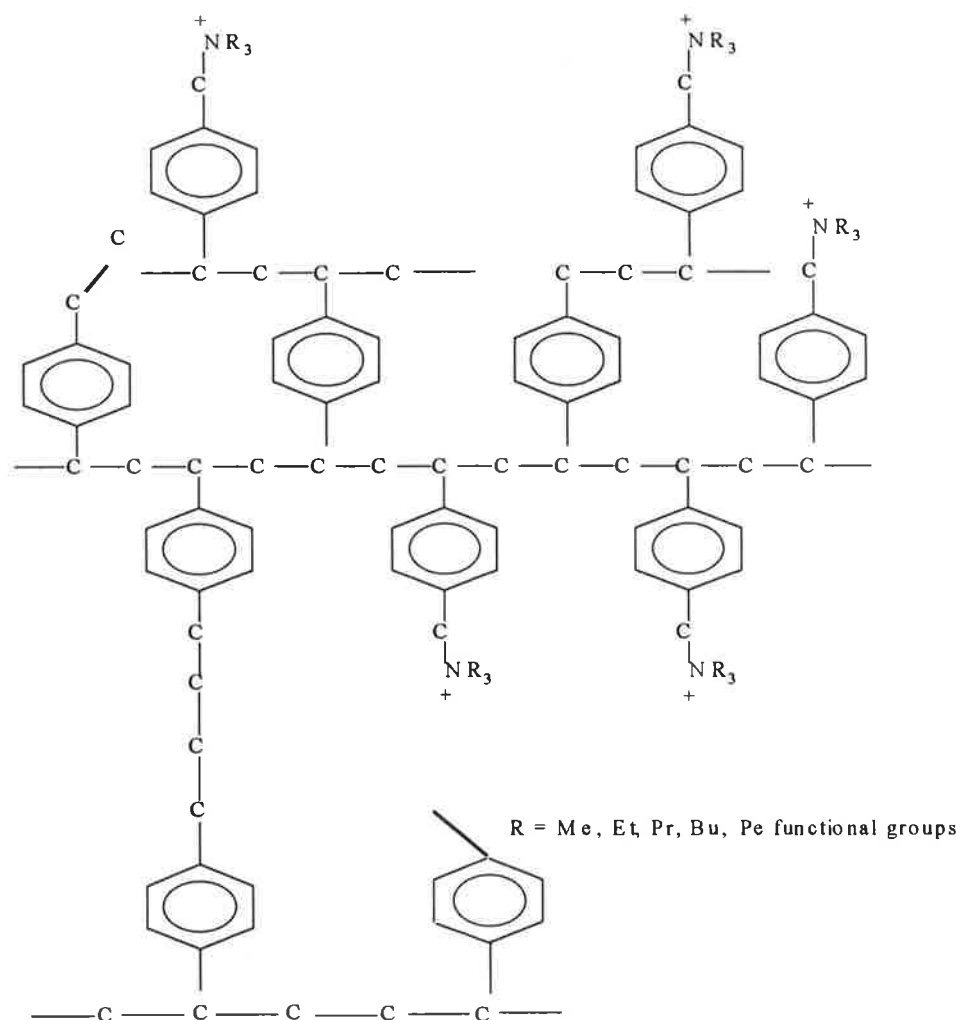


Figure 2.3: Possible structure of the cross-linked polymer

This method was used to determine the relative cross-linking of the polymers synthesised. They were dried overnight in a vacuum oven at 60 °C, until no further mass loss was recorded (M_1). Then, they have been left for 4 weeks in a sealed desiccator

containing a saturated sodium sulphate solution which provide a relative humidity of 93 % at 20 °C. Masses (M_2) have been recorded and the mass of the interstitial water (M_3) was obtained by subtraction of ($M_2 - M_1$).

2-2 PHYSICAL-CHEMISTRY MEASUREMENTS

2-2-1 Density determination

Densities were needed to calculate the relative viscosity (equation 2-19) as well as to convert molality into molarity concentrations. They were measured at 25.00 ± 0.01 °C, using known volume pycnometers. All the solutions were prepared by weight, with Milli-Q water, using a Mettler balance type B6.

2-2-1-1 Method for the soluble materials

Calibration of the pycnometers: five single-stemmed bulb pycnometers were calibrated. Similarly constructed, one of them was filled with water, degassed and sealed; ^{this is} the tare. The mass of the four others pycnometers was recorded when both empty and full of water. The mass difference of the full pycnometer minus tare, was recorded as a function of the height of water from a previously determined scratch mark. Assuming a uniform neck cross-section of the different pycnometers, ^{the} The intercept, M_1 , gave the mass of the pycnometer full minus the mass of the tare. The mass of water to the mark was given by

the intercept plus the mass of the tare and the mass of the empty pycnometer:

$$M_{\text{mark}} = M_1 + M_{\text{tare}} - M_{\text{empty}} \quad (2-1)$$

Dividing by water density, volumes were obtained, the different calibration data were tabulated.

$$V_{\text{mark}} = \frac{M_{\text{mark}}}{\rho_1} \quad (2-2)$$

Table 2-2: calibration of the different pycnometers used for density determinations.

Pycnometers	A	B	C	D
M (tare-empty) (g)	29.93670	31.05071	30.78509	31.52106
radius (cm)	0.0620	0.0618	0.0620	0.0618
M _{water to mark} (g)	30.17857	31.56259	30.41293	31.18270
V _{water to mark} (cm ³)	30.26792	31.74979	30.50298	31.27502

Sample measurements: Pycnometers were cleaned with chromic acid, rinsed with Milli-Q water and dried overnight in an oven before use. Solutions were introduced using a glass syringe and a long stainless-steel capillary, then degassed using a tap vacuum system. The pycnometers were left to equilibrate when changed of environment for 30 minutes at least. The pycnometer masses and the heights of the meniscus from the scratch mark were recorded. The mass of the solution to the mark minus M_2 , the tare minus the pycnometer filled with solution M_1 , were obtained and input in the following formula to get the density from the formula:

$$\rho_{\text{sol}} = \frac{M_2 - M_1}{V_{\text{mark}}} \times \left(1 - \frac{\rho_a}{\rho_b}\right) + \rho_1 \quad (2-3)$$

where $\rho_a = 1.2 \times 10^{-3} \text{ g cm}^{-3}$ and $\rho_b = 8.4 \text{ g cm}^{-3}$ were the air and balance mass densities respectively, and $\rho_1 = 0.997048 \text{ g cm}^{-3}$ was the water (solvent) density.

A density datum was obtained from the average of three heights and two mass measurements. Densities tabulated were the average of three data obtained within $10^{-5} \text{ g cm}^{-3}$. The density difference obtained for the solutions always represented a difference with that of water, used for calibrations.

More theoretical [29] and practical [30] information used for this work is available in the literature.

Using the solution density (ρ), the molarities (C) and molalities (m) of an electrolyte solution are related by the following relations [17^b]:

$$C = \frac{m \times \rho}{1 + 0.001 \times m \times M_w} \quad \text{or} \quad m = \frac{C}{\rho - 0.001 \times C \times M_w} \quad (2-4 \text{ a,b})$$

where M_w is the molecular weight of the solute,

2-2-1-2 Method for cross-linked polymers

Since the capacity of a resin is usually expressed in milliequivalents per volume of polymer in the literature, the density was needed for the capacity conversion.

A 50 ml pycnometer was used. The volume of a known mass of polymer was appraised by comparing the mass of the pycnometer filled with water and filled with water and polymer. The pycnometer volume was kept constant being capped by a stopper. From these densities, the conversion of the capacity of the polymer from equivalent gram to equivalent cm^{-3} was possible.

The mathematical models, concerning the cross-linked polymers, are detailed in the chapter 5 together with the relevant data.

2-2-1-3 Determination of the partial and apparent molal volumes

It is possible to obtain the total solution volume from one n components solution by adding the individual volume contribution of each component:

$$V = \sum_{i=1}^n n_i \bar{V}_i = n_1 \bar{V}_1 + n_2 \bar{V}_2 + \dots \quad (T,P)_{\text{constant}} \quad (2-6)$$

where n_i is the mole number of the component i , $\bar{V}_i$ is the partial molar volume with respect to the concentration at constant temperature, pressure, and mole number of the different components of the solution. The partial molar volume can also be formulated as:

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j, (n_i \neq n_j)} \quad (2-7)$$

For a 2-component system, the apparent molar volume of the solute 2, Φ_2 , is defined from volume of the solution V , and the partial molar volume $V_1 = n_1 \bar{V}_1$ of the solvent 1, by:

$$\Phi_2 = \frac{(V - n_1 \bar{V}_1)}{n_2} \quad (2-8)$$

where Φ_2 is expressed in $\text{cm}^3 \text{mol}^{-1}$ and measures the total change of volume involved in the addition of one mole of solute to a quantity of solvent that will produce a solution of a specified concentration.

As shown by Mulcahy [29], differentiation of equation 2-8, with respect to n_2 , gives at constant temperature and pressure, is:

$$\bar{V}_2 = \Phi_2 + n_2 \frac{\partial \Phi_2}{\partial n_2} \quad (2-9)$$

Handwritten derivation:

$$\bar{V}_2 = \frac{\partial (n_2 \Phi_2)}{\partial n_2} = \Phi_2 + n_2 \frac{\partial \Phi_2}{\partial n_2}$$

At infinite dilution of component 2, the differential term is nil, therefore both apparent and partial molar volumes become equalled:

$$\bar{V}_i^{\circ} = \Phi_i^{\circ} \quad (2-10)$$

A linear regression of the apparent molal volume with concentration, in mole kg⁻¹, gives the partial molal volume, in cm⁻³, at the intercept.

The apparent molal volume Φ_2 of a solute 2, at a known concentration, can be calculated from its solution density ρ_{sol} , in g cm⁻³. For a solvent quantity of 1000 g, the solvent mole number, n_1 , can be expressed in function of the molecular weigh M_1 :

$$n_1 = \frac{1000}{M_1} \quad (2-11)$$

The solute molality m_2 is equal to the number of mole n_2 , and the solution volume V_{sol} is the sum of both solvent and solute volumes:

$$V_{\text{sol}} = \frac{1000 + m_2 \times M_2}{\rho} \quad (2-12)$$

where ρ is the solution density in g cm⁻³.

Substituting equations 2-11 and 2-12 in 2-8, the solute apparent molar volume Φ_2 can be given by:

$$\Phi_2 = \frac{1000(\rho_1 - \rho)}{m\rho_1\rho} + \frac{M_2}{\rho} \quad (2-13)$$

where $\rho_1 = 0.997048$ g cm⁻³ is the density of pure water at 25 °C, ρ density of the solution; M_2 , the molecular weight of the solute in g; m , the solution molality concentration in mol kg⁻¹.

Masson [31] established that the apparent molal volume Φ_2 varied linearly with the squared root of the molarity, $\sqrt{C}$, for dilute solutions:

$$\Phi_2 = \Phi_2^o + S'_v \sqrt{C} \quad (2-14)$$

where Φ_2^o was the apparent molar volume at infinite dilution in $\text{cm}^3\text{mol}^{-1}$, and S'_v was the experimentally determined slope.

The variation of Φ_2 with the square root of the concentration reminded the Debye-Hückel limiting law. S_v should be constant for a given electrolyte charge type. At constant temperature and pressure, for a 1-1 electrolyte in water, the theory predicted a limiting slope of $1.868 \text{ cm}^3 \text{ mol}^{-3/2} \text{ L}^{-1/2}$ [33]. Redlich and Meyer [33] extended the equation 2-14 by adding an extra C term for high concentrations:

$$\Phi_2 = \Phi_2^o + S_v \sqrt{C} + b_v C \quad (2-15)$$

where S_v agrees with the predicted value, b_v was an experimental constant. This equation adequately represented the concentration dependence of many 1:1 and 1:2 electrolytes in dilute solutions.

Root [34], combining the Masson equations (2-15) and the general expression for the apparent molal volume (2-13), found that the solution density can be expressed from the solvent density and the solute concentrations:

$$\rho = \rho_1 + \frac{(M_2 - \rho_1 \Phi_2^o)}{1000} C - \frac{(S_v \rho_1)}{1000} C^{3/2} - \frac{(b_v \rho_1)}{1000} C^2 \quad (2-16)$$

The coefficient S_v and b_v are additive. From equation 2-16, the density of unknown solution can be calculated from their concentrations, using the additivity principle of Φ_2^o and S_v , always valid, [35a,35b].

2-2-2 Viscosity determination

The viscosities of different solutions were measured in order to correct their effect on the relaxation time measurements. Information about sizes of the solutes, and the ion-ion or ion-solvent interactions were deduced from them.

2-2-2-1 Introduction

Viscosity is a transport property dealing with linear momenta, which diffuse down a gradient until uniformity is obtained. Most of the flows, when viscous enough, are said to be Newtonian or in a laminar state flow. Then, the viscosity can be defined as the force per unit area required to maintain an unit difference in velocity between two limit surfaces. It depends on the flux of x-momentum in the z direction:

$$J_z = -\eta \frac{\partial v_x}{\partial z} \quad (2-17)$$

where J_z is the flux along z axis, η the absolute viscosity expressed in poise (P) $1P = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$, and $\frac{\partial v_x}{\partial z}$ is the velocity gradient of the fluid along the x axis.

Poiseuille [36] formulated the viscosity as a rate flow of a fluid through a capillary of radius r as:

$$\eta = \frac{(p_1 - p_2)t\pi r^4}{8Vl} \quad (2-18)$$

where $(p_1 - p_2)$ is the pressure gradient between the two ends of the capillary, l is the length of the tube, V is the volume flowing through the tube in time t and η the absolute viscosity.

2-2-2-2 Viscosity of an electrolyte solution

The charge and size of electrolytes in solution involve interactions with the solvent which tend to create an internal resistance to the solution flow. The relative viscosity is often used and defined:

$$\eta = \frac{\eta}{\eta_1} = \frac{\rho t}{\rho_1 t_1} \quad (2-19)$$

where η and η_1 are the viscosities, ρ and ρ_1 are the densities, t and t_1 are the flow times for the solution and the solvent respectively.

Einstein [37] was the first to treat hydrodynamically the problem of a salt dissolved in solution. He considered the solute to be "rigid spheres suspended in a continuum". The presence of ions should increase in proportion the viscosity. At low concentrations, he found that the total volume of the solute and the viscosity were related:

$$\eta_{rel} = 1 + 2.5\Phi \quad (2-20)$$

where Φ is the volume-fraction occupied of by the solute, then solvated.

Later, Jones-Dole [38] proposed a new equation for electrolyte solutions depending on the concentration for dilute solutions:

$$\eta_{rel} = 1 + A\sqrt{C} + BC \quad (2-21)$$

where C is the molar concentration, in mol dm^{-3} , and $C < 0.1 \text{ M}$; A , a constant depending on the long-range Coulombic forces, previously calculated by Falkenhagen [39], B a parameter related to the size of the ions and their interactions with the solvent. A is small and positive and B is in the order of unity. The last term of the equation becomes predominant when $C \geq 0.002 \text{ M}$. A plot of the function $\frac{(\eta_{rel}-1)}{\sqrt{C}}$ versus $\sqrt{C}$ gives an straight line. The slope A and the intercept B can be determined.

For higher concentration [40], a supplementary term in C^2 was added:

$$\eta_{\text{rel}} = 1 + A\sqrt{C} + BC + DC^2 \quad (2-25)$$

where the new coefficient D is positive which significance is not completely understood but which presence impede that all higher-interactions are absorbed by the B coefficient. A solute-solute interaction contribution has been mentioned [40].

From equations 2-23 and 2-24 and neglecting the small $A\sqrt{C}$ term, the size of the solute is related to the B coefficient:

$$2.5\Phi = BC = 0.0025 VC \quad (2-26)$$

where V is the hydrodynamic volume in $\text{cm}^3 \text{ mol}^{-1}$. For an ideal solvent containing spherical unsolvated solute particles, V should be equal to the solute partial molal volume. B should be a linear function of the solute standard partial molar volume V^0 , with a slope equal to 0.0025 [40].

2-2-2-3 Size determination

From density measurements, it was possible to calculate the apparent molar volume, using equation 2-18. Assuming that the different species were spherical, the radii of the benzytrialkylammonium salts were calculated following the formula:

Interet?

$$r = \frac{3}{4} \pi \sqrt[3]{\Phi_2} \quad (2-27)$$

These radii were compared to those obtained from the limiting conductance data λ_+^0 already measured [23], and computed to the Stokes-Einstein equation which relates

diffusion coefficient D to the effective hydrodynamic radii R_s of the cations:

$$R_s = \frac{kT}{6\pi\eta_0 D} = \frac{eF}{6\pi\eta_0 \lambda_+^0} \quad (3-28)$$

where T is the absolute temperature (K), $k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$ the Boltzmann constant, $\eta_0 = 0.8903 \text{ cP}$, the viscosity of water [32°], and λ_+^0 is the limiting ionic conductivity of the specie in $\text{S m}^2 \text{ equiv}^{-1}$.

The apparent molar volume is almost not sensitive to hydration of the charged species, and sometimes is called the intrinsic volume of the ion. From B coefficients, hydrodynamic volumes were calculated, using the rearranged Einstein equation:

$$V_{\text{hyd}} = 400 \times B \quad (2-29)$$

B coefficients are sensitive to the ion environment, since they modelises the ion solvent interactions.

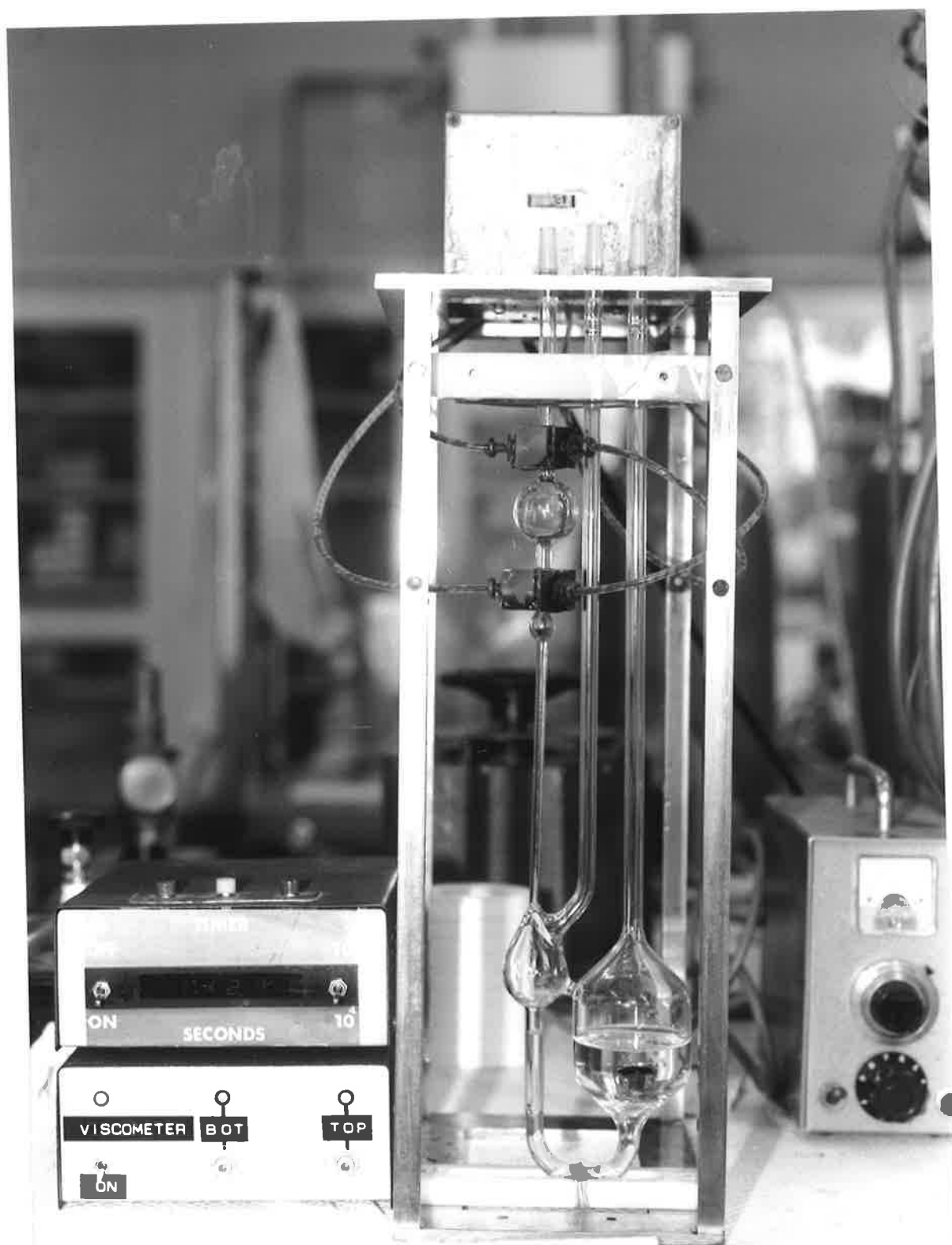
The difference between the partial molar and the hydrodynamic volumes were due to the hydration $V_{\text{H}_2\text{O}}$ of the cations:

$$V_{\text{H}_2\text{O}} = V_{\text{hyd}} - \bar{V}_2 \quad (2-30)$$

From the hydration volumes and the apparent molar volume of one mole of water, it is possible to determine the hydration number for each cation.

2-2-2-4 Method used for viscosity measurements

The measurements were carried out with an Ubbelohde type viscometer which had a capacity of 150 ml, see photo 1. The solution was pushed up past the timing bulb using high purity grade nitrogen. An electronic system was used to record times with an



Photography 1: The Ubbelohde type viscometer used for the experimentations

accuracy of 10^{-2} s. A light source was transmitted by an optical fibre to the capillary, both above and beneath the timing bulb. Opposite the arriving fibres other fibres were located and connected back to the timer. When the solution meniscus passed the top fibres, the narrow beams of light was partially deflected and started the timer. The same phenomena stopped the timer when the liquid passed the bottom fibbers. The viscometer was placed in a thermostated bath at 25.00 ± 0.01 °C. Water flow times t_1 were first measured, around 380 s, then samples were filtered and introduced into the viscometer. A stock solution prepared by weight was first introduced, filtered through a sintered glass funnel, then diluted by addition of known masses of water, covering a concentration range from 0.005 up to 1 molal, depending on the solubility of the sample. The measurements were repeated until three flow times agreed within 0.1 s. The device was carefully cleaned with chromic acid, rinsed with milli-Q water, dried using AR methanol and a tap vacuum between each set of experiments.

The viscosity was measured for both the monomers and the linear polymers.

2-2-2-5 Ion pair influence on viscosity

Davies and Malpass [41] noticed that most of the salts studied underwent extensive ion-pairing. The Jones-Dole equation (2-25) was rearranged to take into account the ion-pair formation and became:

$$(\eta_{rel} - 1) = A'f(I) + BC \quad (2-31)$$

where $f(I) = \frac{\sqrt{I}}{(1+\sqrt{I})} - 0.2I$ is a function of the ionic strength [17^c]. For dissociated binary electrolytes, the B coefficient could be splitted into, B_f and B_{ip} which are respectively the contribution for the free and ion-pair electrolyte.

The equation (2-31) became:

$$(\eta_{rel} - 1) = A' f(I) + B_i \alpha C + B_{ip} (1 - \alpha) C \quad (2-32)$$

where A' is the theoretically calculated value of the Falkenhagen coefficient, and α is the degree of dissociation available from the association constant and extensively discussed [17^d]. The activity coefficients were calculated from the extended Debye-Hückel law [17^c]:

$$\log \gamma_{\pm} = -\frac{0.5115\sqrt{I}}{1 + \sqrt{I}} + 0.2I \quad (2-33)$$

where $I = \frac{1}{2} \sum \alpha m z^2$ is the ionic strength; z being the charge number of the ions.

The influence of ion-pair formation was attempted from the equilibrium constant calculated [12], and the viscosity measured on the potassium nitrate salts solutions

2-3 NMR SPECTROSCOPY

2-3-1 The nuclear magnetic resonance

NMR spectroscopy allowed chemists to study the magnetic properties of atoms. Spin of nuclei, when placed in a magnetic field, are aligned. Depending on their spin numbers I , ($I \neq 0$), nuclei behave like a charged spinning particle and possess a magnetic moment $\vec{\mu}_N$, expressed in terms of the nuclear g -factor g_I and the nuclear magneton β_N :

$$\vec{\mu}_N = \frac{g_I \times \beta_N}{h/2\pi} \vec{I} \quad (2-34)$$

where g_I is a dimensionless constant available in the literature; $\beta_N = \frac{eh}{4\pi m_e}$ in A m²

or JT^{-1} , is the nuclear magneton, e the elementary charge in C and m_e the electron mass in kg; I is the spin vector and $h = 6.626 \times 10^{-34}$ J s is the Planck constant.

The component of the spin vector $\vec{I}$ can take $2I + 1$ orientations corresponding to different energy levels. If a radiation is then pulsed, nuclei can enter into resonance, all their spin are excited, reaching the high energy level states. The energies of the different orientations are:

$$E_I = -\mu_z B_0 \quad (2-35)$$

where $-\mu_z$ is the component along the z axis of the magnetic moment of $\vec{\mu}_N$. These energy can be expressed in term of the Larmor frequency ω_0 : $E_I = -(\frac{1}{2\pi}) \times I \omega_0$, which enter into resonance with the nuclei at a specific value. After the pulse, relaxations occur and which are sensitive to the nuclei environment. These relaxation times can be recorded with a NMR spectrometer.

2-3-1 The relaxation process

In the absence of a magnetic field, atoms share an equal number of α and β orientation nuclear spins, with vectors lying at random angles. The magnetisation M of the sample is nil, fig 2-4a. During a relaxation NMR experiment, the sample is placed in a magnetic field B_0 , along the z -axis. The energies of the two orientations change, the α spins moving to low energy and the β spins to high energy. The spins precess and form two cones, corresponding to the two new energy states, around the z axis. Nuclei absorb radiation, some spins make transitions to their upper α spin states. The number of α and β spins change, with more α than β ones. There is now a net magnetisation in the z direction with a length proportional to the population difference, see figure 2-4b.

If an electromagnetic pulse B_1 is applied, the magnetisation vector rotates into the xy plane. A 90° pulse has been applied, usually in the radio range from few KHz up to 300

MHz and for a duration of few milliseconds. To an external observer, the magnetisation is now rotating in the xy plan. At the end of the pulse, the spin population comes back exponentially to their previous α and β energy states.



Figure 2-4: magnetic moments of a sample: a) in the absence of an external applied field, the α and β spin population is equal; b) in the presence of a field, spins precess around their cones, a slight excess of α spin state involves a net magnetisation along the z axis.

The z component of magnetisation reverts to its equilibrium value with a time called longitudinal relaxation time, T_1 .

$$(n - n_e)_\tau = (n - n_e)_0 e^{(-\frac{\tau}{T_1})} \quad (2-36)$$

where $(n - n_e)_\tau$ is the shift from the equilibrium value at time τ , and $(n - n_e)_0$ at initial time.

A fast relaxation gives a small T_1 .

2-3-3 The longitudinal relaxation times T_1 for nitrate anions

The method used was the inversion recovery technique [50]. A 180° pulse was applied to the sample, (a pulse twice as long as for a 90° one), so that the magnetisation vector

precesses through 180° in the z direction, (fig 2-5). The β spins begin to relax back into α spins, the magnetisation vector shrinking at the same speed. After an interval τ , the 90° pulse is applied and forces the magnetisation vector to rotate into xy plane where a detection coil operates. After the pulse, the magnetisation decreases exponentially, as the interval between the two pulses increases:

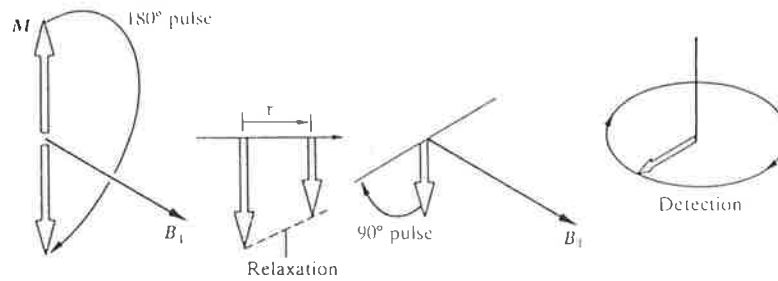


Figure 2-5: effect of a 180° and a subsequent 90° pulse on the magnetisation of a sample [42^a].

T_1 is measured by fitting an exponential curve to the series of spectra obtained at different τ values.

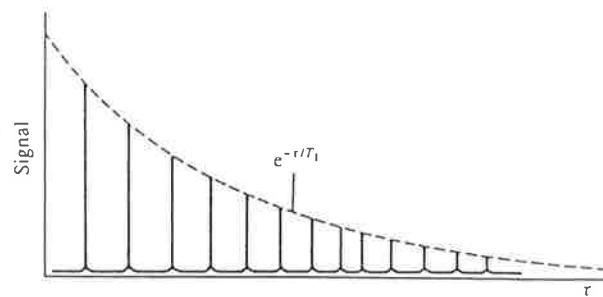


Figure 2-6: fitting of T obtained from the different amplitude of the relaxation, function of the interval between two pulses [42^b].

Under extreme narrowing limit, $2\pi\nu_o\tau_c = \frac{\tau_c}{\omega_o} \ll 1$ where ω_o is the Larmor frequency,

the longitudinal relaxation time T_1 can be related to the correlation time τ_c [43]:

$$\frac{1}{T_1} = \frac{3}{10\pi^2} \times \frac{e^2 q Q}{h} \times \left(\frac{2I+3}{I(2I+1)} \right)^2 \times \frac{1+E^2}{3} \tau_c \quad (2-37)$$

where I is the spin number, τ_c is the correlation time for reorientation of the molecule or the time taken by a molecule to rotate through an angle of 1 rad around the C_3 axis; $(eqQ/h) = 745 \text{ kHz} \pm 2$ [44] is the quadrupole coupling constant and E is the asymmetry factor that represents the distortion of the electric field from axial symmetry. ^{14}N nucleus have even mass and an odd charge numbers which explain a spin number $I = 1$. The nitrate anion has a symmetry (D_{3h} group):

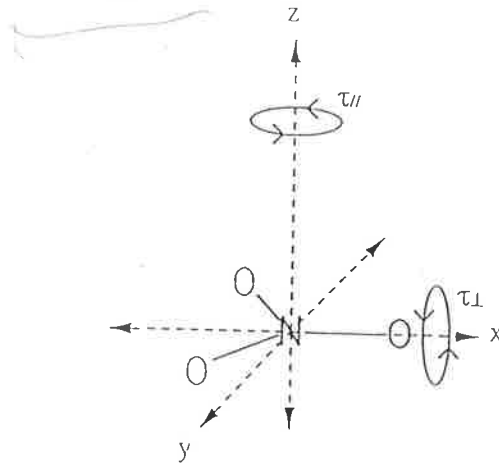


Figure 2-7: Coordinate axis system for the nitrate anion [44].

In the xy plan, the nitrogen nucleus is symmetrically bound to three oxygen atoms and the largest component of the electric field gradient is perpendicular to the ion plane, corresponding to the largest inertial tensor [45]. The symmetrical factor of the equation 2-38 can be ignored [43]:

$$\frac{1}{T_1} = \frac{3}{8\pi^2} (1 + e^{2/3}) \left(\frac{e^2 q Q}{h} \right)^2 \tau_c \quad (2-38)$$

The dependence of T_1 on the viscosity of the solution is given by the Stokes-Einstein-Debye equation which is related to the rotational correlation time τ_c :

$$\tau_c = \tau_o + \frac{V\eta_{rel}}{kT} \quad (2-39)$$

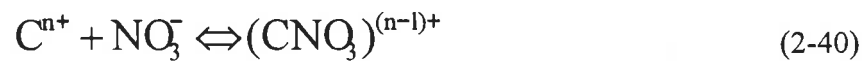
where τ_o is the free molecular rotational correlation time determined by the angular momentum of the molecule and is often negligible [46], $V = 4/3\pi r^3$ is the solute volume, η_{rel} is the relative viscosity of the solution, k the Boltzmann's constant and T the absolute temperature.

Anion-solvent interaction contribution to T_1 was taken into account by the relative viscosity correction term in equation 2-37. Therefore any variation of $\eta_{rel} \times T_1$ with the concentration was attributed to anion-cation association. This was expected to enlarge the correlation time τ_c , and lower correspondingly T_1 .

2-3-4 The ion association from T1 measurements

2-3-4-1 Presentation of the method

In 1987, A. M. de P. Nicholas and R. E. Wasylshen [47] studied the rotational correlation times τ_c around the C_3 axis of nitrate anions when bound to different cations. To do so, they used the relaxation times measured with a nuclear magnetic resonance spectrometer. For a chemical exchange such as:



they found that the spin-lattice relaxation times T_1 depended on four parameters: 1) the nitrate concentration, 2) a free component of T_1 for the unbound nitrates $T_{1,f}$, 3) a bound component of T_1 for the bound nitrates $T_{1,b}$ and 4) the nitrate fraction bound A .

They proposed that a slow rate of chemical exchange for ion pair formation compared to the rates of molecular reorientation (along the C_3 axis) of the nitrate anion, T_1 would obey to:

$$\frac{1}{T_1} = \frac{1}{T_{1,f}} \times (1 - A) + \frac{1}{T_{1,b}} \times A \quad (2-41)$$

For a fast exchange, then T_1 would rather fit to:

$$T_1 = T_{1,f} \times (A - 1) + T_{1,b} \times A \quad (2-42)$$

where A was the mole fraction of the bound nitrate and expressed as:

$$A_f = \frac{(T_1 - T_{1,f})}{(T_{1,b} - T_{1,f})} \text{ or } A_s = \frac{(\frac{1}{T_1} - \frac{1}{T_{1,f}})}{(\frac{1}{T_{1,b}} - \frac{1}{T_{1,f}})} \quad (2-43)$$

for the fast and slow patterns respectively.

$T_{1,f}$ was appraised as 130 ms, obtained from low concentration measurements of non associating salts such as NH_4NO_3 , $T_{1,b} = 9$ ms gave a good fit of our data and has already been cited [47] as an appropriate value.

2-3-4-2 Establishment of the association constant K_a

The amplitude of ion association is usually expressed by a constant K_a called the association constant.

For an equilibrium between cations C^+ and nitrate such as:



The equilibrium constant is given by:

$$K_a = \frac{[\text{CNO}_3]}{[\text{C}^+][\text{NO}_3^-]}$$

no taking explicit (2-45)

where $[\text{CNO}_3]$, $[\text{C}^+]$, $[\text{NO}_3^-]$ are the different bound and free species activities, in molarity. Assuming that:

$$[\text{CNO}_3] = A \times [\text{CNO}_3]_{\text{tot}} \times \gamma_{\text{ip}} \quad (2-46)$$

$$[\text{C}^+] = [\text{NO}_3^-] = (1 - A) \times [\text{CNO}_3]_{\text{tot}} \times \gamma_{\pm} \quad (2-47)$$

where γ_{ip} was the activity coefficient of the bound species and assumed to be equalled to 1, the association constant K_a expression can be expressed as a function of the known initial concentrations of dissolved salt with their activity coefficients:

$$K_a = \frac{A \times [\text{CNO}_3]}{(1-A)^2 \times [\text{CNO}_3]^2 \times \gamma_{\pm}^2} \approx \frac{A}{(1-A)^2 \times [\text{CNO}_3] \times \gamma_{\pm}^2} \quad (2-48)$$

2-3-5 Experimental

The NMR experiments were performed on a Bruker CXP300 spectrometer using a 10-mm probe and an external deuterium lock. All spin-lattice relaxation times were recorded using the inversion recovery pulse sequence [48,49] of the type 180- τ -90-aq-tr. The 90 and 180 refer to 90° and 180° degree pulses, whose width, checked before each set of measurements, was around 80 μs and 160 μs . The waiting period τ varied from 1 to 0.001 second, aq the acquisition time was at least equal to 7 times T_1 usually taken for 1 s, tr a time recovery. Typically a 6000 Hz spectral width and 8K data points were used. The operating frequency for ^{14}N was 21.671 MHz with a magnetic field strength of 7.046 T. $\text{Ca}(\text{NO}_3)_2$ was used to determine the reference frequency. A nitrogen flow

maintained the temperature at 25.0 ± 0.3 °C. For the measurements, the solution were placed in a Wilmad type 513pp 10 mm nmr tube. The scan number varied from 64 up to 1000 depending upon the sample concentration. At least 12 pulse lengths were used to obtain T_1 from the peak intensities, first fitted by the standard Bruker non-linear least squares fit software:

$$I = I(0) \times (1 - 2Ae^{(-\frac{t}{T_1})}) \quad (2-49)$$

where $I(0)$ is the maximum peak intensity, A is the scaling factor close to unity.

T_1 were actually reexamined using an alternative non linear least square fit program [58] on a sun 4/280 computer. The advantage of this new computing step was that it allowed the standard deviations to be determined for each T_1 refitted.

2-4 EMF EXPERIMENTATION

Bolton [13,15] and Clifford [14] determined chloride concentrations by gravimetry titration with AgNO_3 , nitrate concentrations by U.V. spectrometry at 220 nm, sulphate concentrations by turbimetry and checked their results using HPLC chromatography column. We opted for the potentiometric determination of the anions using ion selective electrodes (ISE), now commercially available, which were faster and more convenient to use.

2-4-1 The ion selective electrodes

2-4-1-1 Presentation of the electrodes [88]

The chloride and lead ISE were solid-state electrodes. The sensitive areas of the chloride electrode was made from the insoluble salt AgCl , which was sensitive to the ions

composing the salt or other similar insoluble precipitates such Ag^+ , Cl^- , Br^- , I^- and CN^- . The sensitive area of the ISE is a solid state membrane, containing sulphides of lead and silver bound into an epoxy body [51]. The nitrate ISE is of a liquid ion exchangers. A hydrophobic liquid membrane is used as the sensing element caught between the internal filling solution and the aqueous test solution which can permeate through a "porous lipophilic diaphragm". The selectivity toward ions of interest is due to chelating agents [51,52].

2-4-1-2 Principle of the calibration

Using an I.S.E., the Nernst equation can be simplified. If we consider the chloride electrode, the electrochemical cell can be written as:



where MCl is the chloride solution. At the working electrode, the reaction is



The reference electrode was an $\text{Ag} \mid \text{AgCl}$, double junction electrode. The potential are assumed to be constant, including the reference potential and the junction potentials.

The emf of the cell is:

$$E = E_{\text{Ag/AgCl}} - \frac{RT}{F} \times \log(a_{\text{Cl}^-}) - E_{\text{ref}} - E_j \quad (2-51)$$

where E is the emf value recorded. Once the electrode was calibrated with some known molality solutions, any measured value could then be related to the concentration of any unknown solution.

The activity coefficients can be obtained from emf measurements made from a chloride ion selective electrode.

From 2-51, grouping the 2 fixed potentials:

$$E = E_{\text{Ag/AgCl}} - E_{\text{ref}} - E_j - \frac{RT}{F} \times \log(a_{\text{Cl}^-}) \quad (2-52)$$

and assuming $E' = E_{\text{Ag/AgCl}} - E_{\text{ref}} - E_j$ and $a_{\text{Cl}^-} = \gamma_{\text{Cl}^-} \times m_{\text{Cl}^-}$ where γ_{Cl^-} is the activity coefficient of the chloride at the molality m_{Cl^-} , equation 2-52 becomes:

$$E = E' - \frac{RT}{F} \times \log(\gamma_{\text{Cl}^-} m_{\text{Cl}^-}) \quad (2-53)$$

From this equation, and using a few solutions of known molality which covered the working range of concentrations, it was possible to verify the accuracy of the measuring device. From the recorded e.m.f., plotted against the molality, the slope was calculated and compared to the theoretical value of $k = RT/nF = 59.159/n$ in mV. Having done this, the activity coefficients of the chloride anion were evaluated, and compared to the literature value at a corresponding concentration, following that way:

$$E = E' - k \log(\gamma_{\text{Cl}^-}) - k \log(m_{\text{Cl}^-}) \quad (2-54)$$

The equation (2-54) has two unknowns, E' and γ_{Cl^-} . Rearranging all the measurable terms on the left hand side:

$$E + k \log(m_{\text{Cl}^-}) = E' - k \log(\gamma_{\text{Cl}^-}) \quad (2-55)$$

At very low concentration ($C \approx 0$), the activity coefficient $\gamma_{\pm}$ were 1, and $k \log([\gamma_{\text{Cl}^-}])$ tends to 0, thus $E + k \log(m_{\text{Cl}^-}) \rightarrow E'$. The solutions were diluted enough ($[\text{Cl}^-] < 0.01$ m) to apply the Debye-Hückel limiting law. Plotting $Y = E + k \log([\text{Cl}^-])$ versus $X = \sqrt{c}$, the intercept is E' .

The equation 2-56 becomes:

$$E + k \log(m_{\text{Cl}^-}) - E' = -k \log(\gamma_{\text{Cl}^-}) \quad (2-56)$$

$$\log(\gamma_{\text{Cl}^-}) = (E' - E) / k - \log(m_{\text{Cl}^-}) \quad (2-57)$$

$$\gamma_{\text{Cl}^-} = 10^{(E' - E)/k - \log(m_{\text{Cl}^-})} \quad (2-58)$$

The activity coefficients are always expressed as the geometric mean of both ions present in solution because of the electroneutrality of any electrolyte solution. In this particular case, the activity of the cation is included in the potential of the reference electrode E^0 .

From the equality:

$$\gamma_{\pm} = (\gamma_- \cdot \gamma_+)^{1/2} \quad (2-59)$$

and assuming that $\gamma_{\text{Cl}^-} = \gamma_{\text{K}^+}$, γ_- was compared to $\gamma_{\pm \text{KCl}}$, the activity coefficient given by the other electrodes were tabulated as well, and were a good criteria for checking the validity of the calibrations.

Calculation of the concentration: from equation 2-55, the limiting law expresses $\log \gamma_{\pm}$ to be proportional to $k\sqrt{m}$. The new function $E + k \log(m_{\text{Cl}^-}) = E' - k' \sqrt{m_{\text{Cl}^-}}$ varies only slightly with the concentration m . From an recorded E , a molality was determined roughly using the coefficient from the calibration curves. Root squared, this molality and E' , determined from the calibration, were equalled to the left hand term of the equation. The molality could be extracted again and compared to the previous estimate. This iteration was repeated until no change in concentration was observed. The concentration calculated was then kept for further calculation.

2-4-2 Selectivity survey

During an ionic exchange process, the equilibrium between the different ions in the liquid and solid phase can be expressed by different ways. The main ones are described here for the system:



where the charges A- indicate the dissolved and the over bar $\bar{A}$, the resin phase anions; Z_A is the charge of the ion A.

2-4-2-1 The separation factor

The separation factor α_B^A , is widely used and defined mole as a fraction ratio:

$$\alpha_B^A = \frac{\bar{X}_A \times X_B}{\bar{X}_B \times X_A} \quad (2-61)$$

where X is the ionic equivalent mole fraction and Z_i the charge of the ions:

$$X_i = \frac{z_i \times M_i}{\sum z_i M_i} \quad (2-62)$$

where the overbar signifies again the resin phase, and Z_i is the charge number of the species i. When $\alpha_B^A > 1$, the resins prefer B, even if the factor may be influenced by the ionic strength of the solution.

2-4-2-2 The association constant

For an exchange such as 2-60, the molal thermodynamic equilibrium constant K_B^A is

defined by:

$$K_B^A = \frac{[\bar{A}] \times [B^-]^{z_A}}{[\bar{B}]^{z_A} \times [A^{z_A-}]} \quad (2-63)$$

where $[A^-] = \gamma_A \times m_A$ is the concentration of the dissolved species A, in mol kg⁻¹ of solvent and $[\bar{A}]$ is the concentration of resin phase A, in mol kg⁻¹ of resin.

A resin has an affinity for A if its equilibrium constant K_B^A is above unity.

The mass action law relationships has to be interpreted with great care. About the solution phase, activity coefficients are to be used. When available in the literature, they are usually measured in simple solutions such as a salt dissolved in pure water. The ion exchange equilibrium took place in a richer medium where the ionic strength was not fixed. When it deals with ion exchange resin, the activity coefficients of the bound phase cannot be determined. Instead the fraction of nitrate bound was used. Previously, some authors [53,54] defined this as the concentration of the ion in the resin. Others indicated that there was no satisfactory method available to calculate the activity coefficients of the ions in the resin [24]. Thermodynamically, those ions which are a part of the solid phase, could have an activity equal to unity. The definition of the equilibrium constant K_B^A was therefore vague.

Historically, in 1928, Kerr [55] was the first to prove that the activities of the pure independent solids were not unity, and therefore could not be neglected in an equilibrium appraisal. The equation could be simplified to:

$$K_B^A = \frac{[B^-]^{z_A}}{[A^{z_A-}]} \quad (2-64)$$

where the activity of the resin phase anions were presumed to be equal to the identical ions in solution.

The equilibrium constant was first defined as:

$$K_B^A = \frac{[B^-] \times [\bar{A}]}{[A^-] \times [\bar{B}]} \quad (2-65)$$

where the solid phase concentrations were expressed as moles of bound ions per volume of solution, assuming activity coefficients similar to the liquid phase ions.

Later, Wanselow [56] assumed that the activity of the solid phase was equal to the equivalent mole fraction in the solid:

$$\bar{X}_A = \frac{Z_A \bar{n}_A}{Z_A \bar{n}_A + \bar{n}_B} \quad \text{and} \quad \bar{X}_B = \frac{\bar{n}_B}{Z_A \bar{n}_A + \bar{n}_B} \quad (2-66)$$

where $\bar{n}_A$ is the mole number Z_A the charge of the species A bound and equation (2-65) became:

$$K_B^A = \frac{[B^-] \times \bar{X}_A}{[A^-] \times \bar{X}_B} \quad (2-67)$$

Assuming the activity of the dissolved ions was equivalent to their concentrations, both equilibrium constants (2-65) and (2-67) are identical if the ions have the same valence.

The expression currently used was developed by Guter [18]. The solid phase is expressed in concentrations of bound species per volume or mass of solid material and the equilibrium constant K_B^A given by (2-63) is the one we used.

2-4-2-3 The selectivity coefficient

A quantitative measure of the nitrate/sulfate selectivity (NSS) was defined [15] as:

$$NSS = \log K_S^N - \log \bar{C}_p + 1 \quad (2-69)$$

where $\bar{C}_p$ is the resin capacity (meq/L)

When the selectivity is positive, the affinity goes to the first anion. A strong affinity occurs when the selectivity coefficient approaches 2, [15]. On the same basis, a chloride/sulphate selectivity was established.

2-4-4-4 Equilibrium isotherms

The relative affinity of an ion-exchange resin for some ions can be expressed on a isotherm diagram. The mole fractions of the component in the solid phase are plotted against the mole fraction of the equivalent ion in the solution phase, from measurements done when the aliquots of the co-ion were added. No affinity would be represented by a straight line crossing the graph in diagonal. The closer the curves are plotted by the X or Y edge axis of the square, the stronger is the affinity of the ion for the liquid and solid phase respectively.

2-4-3 Experimental

The experiments were carried out in a thermostated bath, $T = 25.00 \pm 0.01$ °C, where magnetic stirrer and argon bubbling were used constantly. A daily calibration was done, the cell being left for 30 min in the bath to allow thermal equilibrium. The reference electrode used was Orion 90-02 double junction. The inner chamber solution was Orion 900002 solution, a green coloured solution saturated with AgCl salts to provide a constant level of the ion sensed by the reference element, the outer chamber was KNO_3 or $(\text{NH}_4)_2\text{SO}_4$ (depending on the anions measured to avoid any diffusion interference), a low-junction-potential liquid junction with the sample solution which serves as a salt bridge. The working electrodes were Orion 94-17b for the chloride I.S.E., Orion 93-07 for the nitrate I.S.E. and Orion 94-82 for the lead I.S.E. used for an indirect titration of the sulphate. The pH meter was the Orion model 720.

2-4-4 Results

Direct measurements of the free anion concentrations were made using ISE at the same time. Bound concentrations were obtained by subtraction of the free from the total concentrations. Using equations 2-61 and 2-63, separation factors and association constants were calculated as well as selectivity coefficients. From the mole fraction of the bound and free anions, the isotherm were plotted and discussed. The different data and graphs for the linear and cross-linked polymers were included in their respective chapters.

Finally, it is desirable to have rapid exchange. This latest recommendation was examined to avoid us waiting for three months to get a perfect equilibrium as already noticed [13].

***STUDY of the
ANION / MONOMER ASSOCIATION***

3-1 INTRODUCTION

The nitrate/monomer analogue association was assessed using ^{14}N nitrate longitudinal relaxation times, T_1 , measured with an NMR spectrometer. This method studied the rotation of ions in solution, which was affected by its environment as well such as ion-pair formation. Relaxation times could be measured over a wider range of concentration than other techniques, such as Raman spectroscopy or conductance. Concentration varied from near salt saturation to dilute solutions. ^{14}N nitrate ions have a high natural abundance 99.6%, and an average relative sensitivity of 1.01×10^{-3} which makes them attractive for nmr spectroscopy. The signal for this quadrupolar nucleus, had a remarkably narrow linewidth of 25 Hz which allowed good resolution [46]. This was explained by a high degree of electronic symmetry.

Cation/nitrate association was deduced from T_1 . First a simple salt, KNO_3 , was examined, to ascertain whether or not ^{14}N nmr T_1 was appropriate to estimate the association, allowing for the solution viscosity and the relevant activity coefficient. The results obtained were in good agreement with the literature. Then the association of the monomer analogues and vinylbenzylammonium cations with nitrate, were measured and discussed. They were compared to values obtained by conductivity [12].

Densities were measured to allow conversion of convert molalities to molarities, and to correct the measured relative viscosity. Size characteristics such as partial molal volumes and ions radii were calculated from these measurements.

3-2 PHYSICAL-CHEMISTRY PROPERTIES

Salts synthesis, solution preparations and experimental conditions were all detailed in the previous chapter.

3-2-1 Density measurements

Molality concentrations were preferred to molarities because they were calculated from masses of solvent, which were independent of the temperature and could be more accurately determined than volumes. The conversion from one to the other required density measurements.

Our solutions had to contain around 5 % (w/w) of D₂O, which was necessary to lock the NMR spectrometer. Heavy water has a density of 1.10445 [57], 11 % higher than normal water, H₂O. Densities of such blended solutions were not available in the literature and they had to be measured. When compared to the literature values, measured for purely aqueous solutions, a 0.5 % density increasing was expected

Densities were measured using pycnometry. Molarities (C) were calculated from molalities (m) using:

$$C = \frac{\rho \times m}{(1 + 0.001 \times m \times M_2)} \quad (3-1)$$

where C was expressed in mol cm⁻³ (or M), ρ was the solution density in g cm⁻³, m was the molality in mol kg⁻¹, M₂ was the molecular weight of the solute in g.

3-2-1-1 Density of simple salt solution, KNO₃

The working concentration range varied from 0.883 down to 0.007 mol kg⁻¹. Densities were measured for each solution whose nitrate relaxation times had been determined. Data were included in table 3-13 and plotted on graph 3-1. It confirmed that the density

of our solutions, which had D₂O/H₂O mixture as solvent, were slightly higher than the literature ones, from 0.43 to 0.58 %, which were measured in water only, but at the same concentrations. The accuracy of the relaxation time measurements was known to be at the best around 3 %. The contribution to the density of only 0.5 % due to D₂O could, therefore, be ignored.

3-2-1-2 Density of the monomer solutions

Densities were measured of at least 7 different solutions, which fully covered the nitrate T₁ concentration range, were measured. Solutions were prepared from salts and Milli-Q water only. Around 40 ml was needed to fill the pycnometers for each measurement. Much heavy water was therefore saved. From densities, apparent molar volumes of the solute, Φ_2 , were calculated using the equation 3-2; the results were upper in table 3-14:

$$\Phi_2 = \frac{1000 \times (\rho_1 - \rho)}{m\rho_1\rho} + \frac{M_2}{\rho} \quad (3-2)$$

where $\rho_1 = 0.997048 \text{ g cm}^{-3}$ was the water density, ρ the measured solution density, in g cm^{-3} , M_2 the molecular mass of the solute in g, and m the solute molality in mol kg^{-1} . Molarity concentrations (C) and apparent molar volumes were input in the Masson [31] equation:

$$\Phi_2 = \Phi_2^0 + S'_v C \quad (3-3)$$

where Φ_2^0 was the apparent molar volume at infinite dilution expressed in $\text{cm}^3 \text{ mol}^{-1}$ and S'_v was the volumetric virial coefficient characterising the pairwise interaction of solute species in solution, expressed $\text{cm}^3 \text{ mol}^{-2} \text{ kg}^{-1}$ [62]. These coefficients were determined by extrapolation using a non-linear least-squares program [58]. Results were gathered in table 3-14. At infinite dilution, the apparent molar volumes were equivalent to the partial molar volume $\Phi_2^0 = \bar{V}_2^0$, S'_v being an experimental slope.

At 25 °C, the partial molar volumes of chloride and nitrate ions are conventionally taken to be $\bar{V}_{\text{Cl}^-}^0 = 17.83 \text{ cm}^3 \text{ mol}^{-1}$ and $\bar{V}_{\text{NO}_3^-}^0 = 30.30 \text{ cm}^3 \text{ mol}^{-1}$ [32]. The additivity principle between anions and cations was applied and apparent molar volumes of the different cations were calculated, and tabulated table 3-1.

Table 3-1: Coefficients calculated from the Masson relation for aqueous solutions of benzyltrialkylammonium chloride and nitrate salts at 25 °C.

Benzyltrialkylammonium chloride

Alkyl group	Φ_2^0 ($\text{cm}^3 \text{ mol}^{-1}$)	Φ_2^0 [7] ($\text{cm}^3 \text{ mol}^{-1}$)	S'_v ($\text{cm}^3 \text{ mol}^{-2} \text{ kg}^{-1}$)	$\Phi_{2,\text{cation}}^0$ ($\text{cm}^3 \text{ mol}^{-1}$)
methyl	170.5 ± 0.1	171	-3.9 ± 0.1	152.7
ethyl	211.4 ± 0.2	216	-2.1 ± 0.5	193.6
propyl	263.8 ± 0.1		-7.7 ± 0.2	246.0
butyl	308.4 ± 0.1		-5.9 ± 0.1	290.6
pentyl	354.6 ± 0.1		-3.1 ± 0.2	336.8

Benzyltrialkylammonium nitrate

Alkyl group	Φ_2^0 ($\text{cm}^3 \text{ mol}^{-1}$)	S'_v ($\text{cm}^3 \text{ mol}^{-2} \text{ kg}^{-1}$)	$\Phi_{2,\text{cation}}^0$ ($\text{cm}^3 \text{ mol}^{-1}$)
methyl	183.7 ± 0.1	1.0 ± 0.1	154.7
ethyl	226.1 ± 0.05	4.8 ± 0.08	197.1
propyl	277.9 ± 0.1	4.6 ± 0.2	248.9
butyl	318.7 ± 0.04	1.6 ± 0.05	289.7
pentyl	364.5 ± 0.1	1.3 ± 0.9	335.5

The chloride data were measured by G. Owens [59]

The apparent molar volume of the same cation, estimated from the chloride and nitrate salt solutions, were quite similar, within $3 \text{ cm}^3 \text{ mol}^{-1}$. This error was acceptable [58] when obtained from extrapolation of apparent molar volumes calculated from the

Masson equation. The apparent molar volumes of both chloride and nitrate salts increased regularly with the carbon number of the alkyl group. It was expected that a larger functional group would have an impact on the volume of the molecule. Yatome et al. [60] have estimated that for benzyltrimethylammonium chloride, $\Phi_2^0 = 171 \text{ cm}^3 \text{ mol}^{-1}$ with $S'_v = -3.0 \text{ cm}^3 \text{ mol}^{-2} \text{ kg}^{-1}$ and that for benzyltriethylammonium chloride, $\Phi_2^0 = 216 \text{ cm}^3 \text{ mol}^{-1}$. These data were in good agreement with ours.

Negative S'_v values, obtained for the chloride salts, have already been reported for tetraalkylammonium solutions [29-61] and other species [62] and were usually attributed to hydrolysis [35]. For most of the nitrates, S'_v were positive, and of the order of the theoretical value of $1.868 \text{ cm}^3 \text{ mol}^{-3/2} \text{ L}^{-1}$ [33], for a 1:1 electrolyte. The ion-ion interactions lead to an increase in the apparent molar volumes due to any kind of hydration.

The measured densities were fitted to the Root equation [34] using a non-linear least-squares fitting program [58]. For each salt, these fitting parameters were calculated and they were used to get densities at various concentrations. These were required for the molarity conversion or for the calculation of the relative viscosity from the following equation:

$$\rho = \rho_1 + aC - bC^{3/2} - cC^2 \quad (3-4)$$

where ρ_1 was the water density, and C the solution molarity. The resulting coefficient were summarised in table 3-2.

Table 3-2: Coefficients from the Root equation for the monomer analogues.

Benzyltrialkylammonium chloride[59]Benzyltrialkylammonium nitrate				
Alkyl group	a (×100)	b (×100)	a (×100)	b (×100)
methyl	1.56 ± 0.01	-0.39 ± 0.01	4.09 ± 0.02	0.06 ± 0.02
ethyl	1.70 ± 0.02	-2.11 ± 0.01	2.770 ± 0.005	0.186 ± 0.008
propyl	0.69 ± 0.02	-0.76 ± 0.02	1.82 ± 0.01	0.21 ± 0.02
butyl	0.436 ± 0.009	-0.59 ± 0.01	2.237 ± 0.004	0.196 ± 0.005
pentyl	0.04 ± 0.02	-0.31 ± 0.04	1.72 ± 0.01	0.16 ± 0.09

The chloride data were measured by G. Owens [59]

3-2-2 Viscosity measurements

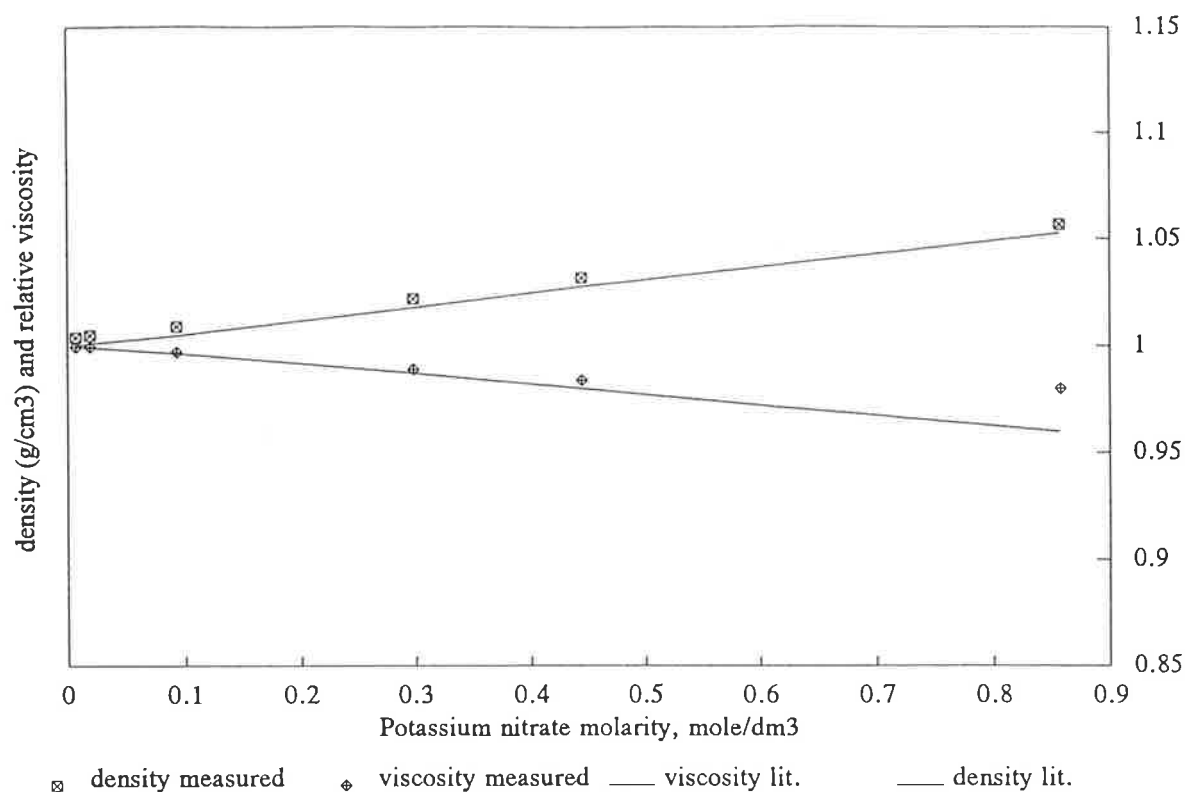
Flow times of nitrate solutions, t , were measured using an Ubbelohde type viscometer, as described in the previous chapter. The flow time, t_1 , of the solvent, Milli-Q purified water, was measured each time and used to ensure the good running of the viscometer device. Relative viscosities, η_{rel} , were calculated from equation 3-5.

$$\eta_{rel} = \frac{\eta}{\eta_1} = \frac{\rho t}{\rho_1 t_1} \quad (3-5)$$

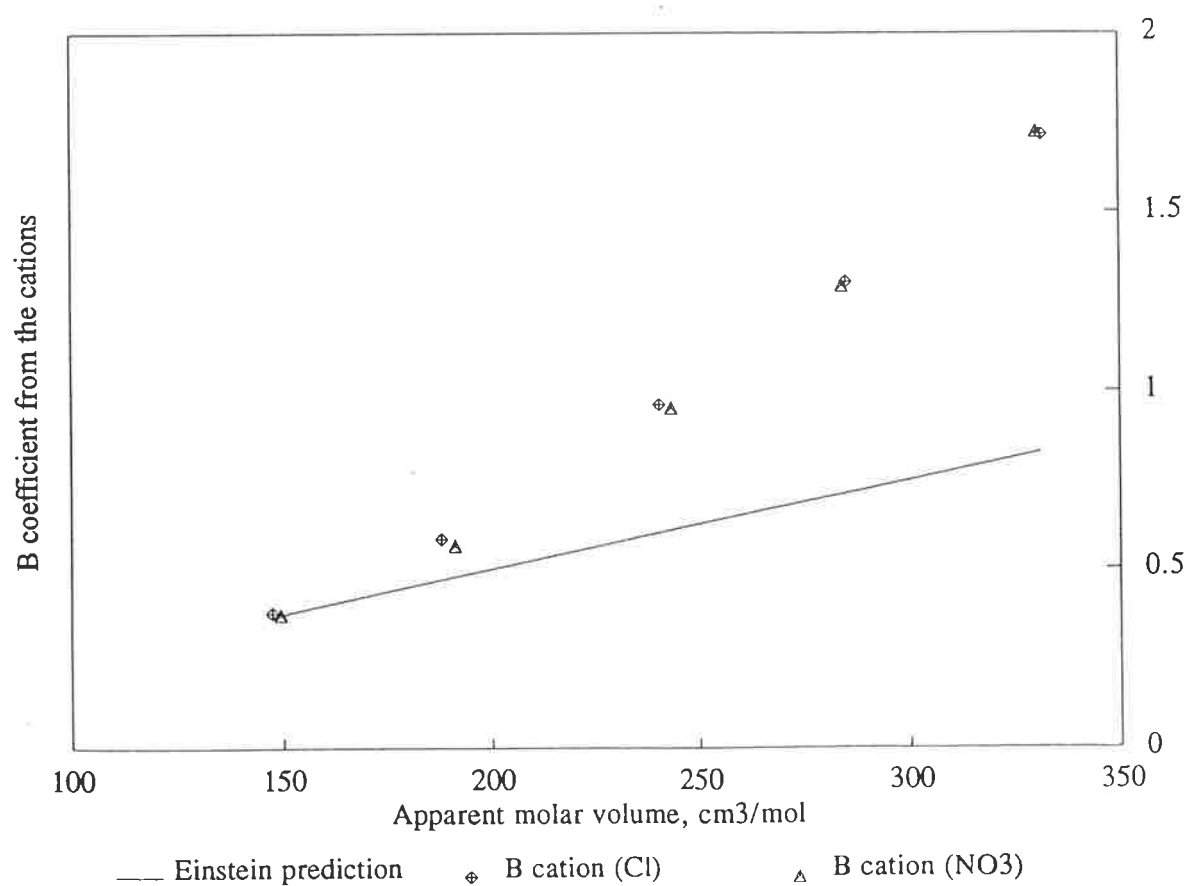
where ρ and ρ_1 were the solution and the water densities in g cm^{-3} .

3-2-2-1 Viscosity of potassium nitrate solutions

The data obtained were included in table 3-13. From graph 3-1, the measured relative viscosities were in good agreement with literature values [34], calculated from the Jones and Talley equation. The presence of 5 % D_2O did not alter the relative viscosity. The monomer analogue viscosities were measured in milli-Q aqueous solutions as solvent.



Graph 3-1: Density and relative viscosity of potassium nitrate solutions.



Graph 3-2: Evolution of the B coefficient with the size of the monomer analogues

3-2-2-2 Viscosity of the monomers

The relative viscosities were calculated using equation 3-5, and were fitted to the Jones and Dole equation [38], when concentrations were strictly below 0.1 M, ($C < 0.1$ M).

The relation was:

$$\eta_{\text{rel}} = 1 + A\sqrt{C} + BC \quad (3-6)$$

where A was the calculated Falkenhagen coefficient [63], and the B coefficients were calculated from a non-linear least-squares fitting program [58]. Results were input in table 3-3.

Table 3-3: Jones and Dole parameters for the monomer analogues.

	Benzyltrialkylammonium chloride [59]			Benzyltrialkylammonium nitrate		
alkyl group	A	B	B _{cation}	A	B	B _{cation}
methyl	0.0071	0.370 ± 0.001	<u>0.377</u>	0.0074	0.338 ± 0.002	0.384
ethyl	0.0075	<u>0.577 ± 0.006</u>	0.584	0.0078	<u>0.52 ± 0.02</u>	0.566
propyl	0.0079	<u>0.954 ± 0.003</u>	0.961	0.0083	<u>0.906 ± 0.005</u>	0.952
butyl	0.0082	1.30 ± 0.01	<u>1.30₇</u>	0.0086	1.25 ± 0.01	1.29 ₆
pentyl	0.0084	1.71 ± 0.02	1.71 ₇	0.0089	1.68 ± 0.05	1.72 ₆

The chloride data were measured by G. Owens [59].

At least 7 data were fitted. B coefficients were in the expected order, increasing with the size of the salts. They were in agreement with the two B coefficients published for benzyltrimethylammonium and benzyltriethylammonium chloride, 0.413 and 0.623 respectively [64]. The trends in B coefficients were similar for both chloride and nitrate.

The division of B coefficients into individual ionic values has been justified by Stokes and Mills [39] from an equality of the mobility of each ion in simple salts such as KCl. The values of $B_{\text{Cl}} = -0.007$ and $B_{\text{NO}_3} = -0.0467$ from KCl and KNO_3 , are in good agreement

with both thermodynamic calculations and published results. Assuming the additivity principle, B coefficient for the cations were calculated from both nitrate and chloride salts and a comparison of the values obtained salts was very satisfying.

3-2-3 Size appraisal of the different salts

3-2-3-1 The apparent and partial molar volumes

B coefficient from the Jones and Dole equation quantified the ion-solvent interactions, in which the size is a major factor. A plot of B versus the partial molar volumes, graph 3-2, displayed an curves whose positive slope was higher than the expected one predicted by the Einstein [37] formula which had assumed ions to be spherical:

$$B = 0.0025 \times V \quad (3-7)$$

where V was the total volume occupied by the solute (s).

For nitrate salts, B coefficients were found to be close to those predicted by the Einstein equation when the short alkyl groups such as methyl and ethyl, but as the size of the alkyl groups increased so did the difference. This was due to the net structural effect of the solute on the solvent. A negative difference signified that the salt was classified as structure breaker while a positive one corresponded to the structure maker property. The assumption of spherical molecules done by Einstein's relation might not suit the larger benzyltrialkylammonium halide salts. Tuan and Fuoss [65] found that tetraalkylammonium salts obeyed Einstein's law in nonaqueous solutions. In water, only "iceberg" formation or hydrophobic hydration around the cation, which is essentially organic in nature, could explain the departure from Einstein's predictions. Frank and Wen [66] noticed a large excess of the heat capacity for aqueous tetrabutylammonium bromide solutions that they attributed to the melting of icelike patches formed around the cations. It would be this ice-like character which was observed for the B coefficients through an irregular raising of their magnitude.

From density measurements and the Masson equation, it was possible to calculate the apparent molar volumes, which may be considered a measure of the intrinsic volume of the ions. The intrinsic volume is less sensitive to hydration of the charged species. From B coefficients, hydrodynamic volumes were calculated, using the rearranged Einstein equation:

$$V_{\text{hyd}} = 400 \times B \quad (3-8)$$

B coefficients were sensitive to the ion environment, since it modelled the ion solvent interactions. The difference between the apparent molar and the hydrodynamic volumes was due to the hydrophobic hydration of the cations, equation 3-9:

$$V_{\text{H}_2\text{O}} = V_{\text{hyd}} - \Phi_2^\circ \quad (3-9)$$

The volume of 1 mole of water was deduced from its density. At 25 °C, 997.048 g of water occupies 1 dm³ [57]. When divided by its molecular mass, $M_{\text{H}_2\text{O}} = 18.015 \text{ g}$ [57], the water volumes per mole was $V_{\text{H}_2\text{O}} = 18.068 \text{ cm}^3$. The molecular volume obtained was $\bar{V}_{\text{H}_2\text{O}} = 30.0036 \times 10^{-30} \text{ m}^3$, similar to Robinson and Stokes data [17^e]. The water mole numbers per mole of equivalent monomers were calculated from equation 3-10 and results were included in the table 3-4.

$$n_{\text{H}_2\text{O}} = \frac{V_{\text{H}_2\text{O}}}{\bar{V}_{\text{H}_2\text{O}}} \quad (3-10)$$

Table 3-4: Apparent molar and hydrodynamic volume, hydrophobic hydration of the monomer analogues:

Benzyltrialkylammonium chloride salts					
Alkyl group	B_{cation}	V_{hyd} (cm ³ mol ⁻¹)	Φ_2° (cm ³ mol ⁻¹)	$V_{\text{H}_2\text{O}}$ (cm ³ mol ⁻¹)	$n_{\text{H}_2\text{O}}$
methyl	0.377	150.8	147.3	3.5	0
ethyl	0.584	233.6	188.2	45.4	2.5
propyl	0.961	384.4	240.6	143.8	8
butyl	1.307	522.8	285.2	237.6	13
pentyl	1.717	686.8	331.4	355.4	20

Benzyltrialkylammonium nitrate

Alkyl group	B_{cation}	$V_{\text{hyd.}}$ ($\text{cm}^3 \text{ mol}^{-1}$)	Φ_2° ($\text{cm}^3 \text{ mol}^{-1}$)	$V_{\text{H}_2\text{O}}$ ($\text{cm}^3 \text{ mol}^{-1}$)	$n_{\text{H}_2\text{O}}$
methyl	0.384	149.6	149.3	0.3	0
ethyl	0.566	226.4	191.7	34.7	2
propyl	0.952	380.8	243.5	137.3	8
butyl	1.296	518.4	284.3	234.1	13
pentyl	1.726	690.4	330.1	360.3	20

The chloride data were measured by G. Owens [59].

The hydrophobic hydration number increased with the size of the cation as already suggested [32,40] and it was independent of the co-anion. T. Kurucsev [61] found similar hydration numbers for metal complexes, where the hydration number increased with the size of inorganic complexes. Hydration started to raise with the ethyl monomers, $n_{\text{H}_2\text{O}} = 2$, and was 10 times as much for the pentyl. It corresponded to the deviation noticed from the B cation when fitted to the Einstein equation and illustrated by graph 3-4. It probably corresponded to an increase of the structure maker character of the cation with the increasing size of the alkyl group among the different monomer analogues.

Even if the apparent molar volume at infinite dilution Φ_2° is often considered as the intrinsic volume of the solute in solution, one can have quandaries about the certitude that this results does not include any water molecule bound by one way or the other. Should we comment about the hydration numbers calculated as relative hydration numbers? An ideal way to realise what was the extent of the hydrophobic hydration would have been to compare the apparent molar volumes obtained at infinite dilution Φ_2° with the volume obtained from the density of the solid phase of the salt, which would have been completely water free. Unfortunately, these values were not available from the literature, and we did not succeed to get any crystals whose structure would have clarified the real size of the cation. However, one density of benzyltrimethylammonium

chloride was found in the Sigma sale-book and was equal to 0.92 g cm^{-3} , which readily gave a molar volume of $201.70 \text{ cm}^3 \text{ mol}^{-1}$, 18.3 % higher than the volume found from the solution densities. Obviously, this density was the one of the powder compound as it was sold. *At* this stage, we had admitted that the results obtained were maybe relative, but the trend of the hydrophobic hydration was real.

3-2-3-2 Determination of the radius

Assuming that the solute species were spherical, the hydrodynamic radii of the benzytrialkylammonium cations were calculated from the contribution of these cations to the apparent molar volumes $\Phi_{2,\text{cation}}^{\circ}$, using the formula:

$$r = \frac{3}{4} \pi \sqrt[3]{\Phi_{2,\text{cation}}^{\circ}} \quad (3-11)$$

They were compared to those obtained from limiting conductance data λ_+° [12], and fitted to the Stokes-Einstein equation which relates the diffusion coefficient D to the effective hydrodynamic radii R_s of spherical particles:

$$R_s = \frac{kT}{6\pi\eta D} = \frac{eF}{6\pi\eta\lambda_+^{\circ}} \quad (3-12)$$

where T is the absolute temperature (K), $k = 1.38066 \times 10^{-23} \text{ JK}^{-1}$ is the Boltzmann constant, $\eta = 0.8903 \text{ cP}$ is the viscosity of water [17^f], e is the elementary charge $1.6023 \times 10^{-19} \text{ C}$, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$) and λ_+° is the limiting ionic conductivity of the specie in $\text{S m}^2 \text{ equiv}^{-1}$.

The Stokes-Einstein law was not applicable for particles smaller than 500 pm [17^g]. A correction factor was added under the form of a tabulated constant c [17]. The modified

Stokes' law was given by:

$$R_s = \frac{82.0 \times |z|}{\lambda \eta} \times c \quad (3-13)$$

where R_s was expressed in pm. The different results were presented in table 3-5.

Table 3-5: Radii of benzyltrialkylammonium cations calculated from different equations.

Alkyl group	Benzyltrialkylammonium chloride				Benzyltrialkylammonium nitrate			
	$R_s^{(a)}$ (pm)	$R_s^{(b)}$ (pm)	$R_s^{(c)}$ (pm)	$R_s^{(d)}$ (pm)	$R_s^{(a)}$ (pm)	$R_s^{(b)}$ (pm)	$R_s^{(c)}$ (pm)	$R_s^{(d)}$ (pm)
methyl	284	403	391	388	284	403	390	390
ethyl	341	430	452	421	340	430	448	424
propyl	412	461	534	457	412	461	532	459
butyl	469	491	592	484	469	491	590	483
pentyl	511	519	649	508	511	519	649	508

$R_s^{(a)}$ radius calculated from Stokes-Einstein equation 3-12 and conductance data [12].

$R_s^{(b)}$ radius calculated from the modified Stokes Einstein equation 3-13.

$R_s^{(c)}$ radius calculated from the viscosity B coefficient.

$R_s^{(d)}$ hydrodynamic radius from partial molar volumes, using equation 3-7.

The Stokes radii are usually smaller than other radii calculated by a different way [58], since the Stokes law is restricted to ions having a radius greater than 500 pm .

The radii calculated were quite similar, only the radii obtained from viscosity were larger, probably due to the hydrophobic hydration. Again, the disagreement between radii obtained by density, and the corresponding radii obtained from viscosity B coefficients, was due to hydration. No X-ray data were available in the literature, and the crystals obtained were not stable enough to be run with an X-ray machine.

3-2-3-3 Association from the viscosity

In order to estimate the influence of the ion-pair formation on the viscosity, B coefficients were fitted following the equation proposed first by Davies and Malpass [41] and simplified for a 1:1 electrolyte solution:

$$(\eta_{\text{rel}} - 1) - AI = B_i \alpha m + B_{ip} (1 - \alpha) m \quad (3-14)$$

where I was the ionic strength, α the degree of dissociation were deduced from the association constants calculated from conductivity experiments [12], B_i and B_{ip} the B coefficient for the ions and ion pair respectively. After fitting, the results were tabulated:

Table 3-6: B coefficient for the free and ion-paired species:

Alkyl group	Benzyltrialkylammonium chloride			Benzyltrialkylammonium nitrate		
	B	B_i	B_{ip}	B	B_i	B_{ip}
methyl	0.370	0.394 ± 0.003	0.15 ± 0.04	0.331	0.328 ± 0.005	0.42 ± 0.04
ethyl	0.630	0.540 ± 0.003	1.03 ± 0.03	0.522	0.38 ± 0.03	1.8 ± 0.3
propyl	0.953	0.927 ± 0.005	1.28 ± 0.05	0.810	0.89 ± 0.01	1.04 ± 0.06
butyl	1.30	1.22 ± 0.03	2.0 ± 0.3	1.23	1.11 ± 0.02	2.0 ± 0.1
pentyl	1.75	1.91 ± 0.04	-4.0 ± 0.5	1.69	2.2 ± 0.1	-3 ± 1

The value of B_i and B_{ip} increased regularly from the methyl to the butyl group. But the fitting resulting from this new model was not better than the classic Jones-Dole equation. However, it showed that the non associated ions, fixed as the dominating species by the high degree of disassociation, were responsible for most of the viscosity effect, since B_i values were close to B. The negative result for both pentyl salts may be unreliable because being, less soluble, they were obtained from few data only. The comparison of B_i also showed that the free chlorides had a higher influence on the total B than nitrates, this results was certainly due to the higher dissociation of the chloride salt [12].

However, the trend of B_{ip} values was erratic and this model could not be satisfactory to fit the viscosity behaviour of our potassium nitrate solutions, probably because the association was not large enough to be analysed [41].

3-2-3 Conclusion

Density and viscosity of potassium nitrate solutions covering a concentration range from 0.007 M up to 0.888 M were measured. They were necessary to correct the longitudinal relaxation times discussed in the second part of this chapter. The agreement of our data was good when compared to the literature. Used as control, the validity of our measurements was shown.

The same measurements were carried out on the monomer solutions. The apparent molar volumes and B coefficients were calculated from densities and viscosities respectively, and were found to be in good agreement with similar salts such as the tetralkylammonium halides. Hydrophobic hydration numbers were appraised from a comparison of apparent molar and hydrated volumes, obtained from density and the Einstein relation for viscosity B coefficients. They showed that the structure maker character of the cation increased with the size of the alkyl group. The cation radii were computed using four different models.

3-3 SPIN LATTICE RELAXATION TIMES T_1

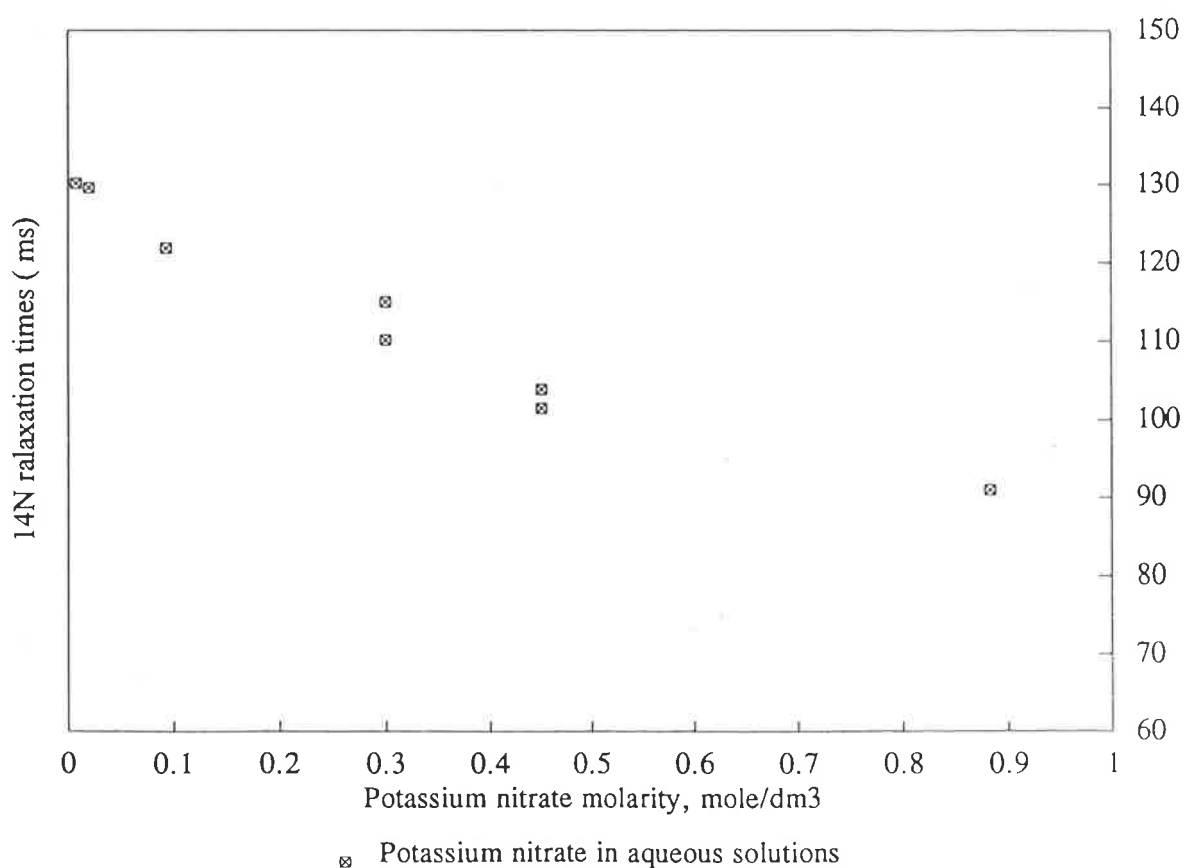
3-3-1 Potassium nitrate relaxation times

Solution preparation and method used were all described in the former chapter. The solution molalities were converted to molarities, using densities calculated from Root

equation coefficients. Viscosities were measured and used to correct the T_1 data. The association of nitrate potassium was appraised using relaxation times and compared to the literature values.

The recovery intensities were refitted versus the different recovery times τ using a non-linear least-squares program [58]. From at least 10 τ , refitted T_1 values were obtained together with the standard deviations, previously not obtainable with the standard Bruker software.

The relaxation times decreased when the concentrations increased, showing that association increased with higher concentrations. Data were gathered in table 3-13 and plotted on graph 3-3. Our relaxation times were slightly lower than Nicholas et al. [47] (1 M, $T_1 = 89.7 \pm 2.7$ ms and for 0.1 M; $T_1 = 119.4 \pm 8.3$ ms) but in good agreement with Nakahara's [67] (1 M, $T_1 = 84.8 \pm 1.7$ ms and for 0.1 M; $T_1 = 111.4 \pm 2.2$ ms). Especially, since the authors [47,67] did not mention any viscosity corrections.



Graph 3-3: ¹⁴N Nitrate relaxation times for potassium nitrate solutions.

Relaxation times T_1 were related to the molecular reorientation correlation times τ_c by

$$\frac{1}{T_1} = \frac{3}{8\pi^2} (1 + e^{\frac{2}{3}}) \left(\frac{e^2 q Q}{h} \right)^2 \tau_c \quad (3-15)$$

where $(eqQ/h) = 745 \pm 2$ kHz is the quadrupole coupling constant [44] and E is the asymmetry factor that represents the distortion of the electric field from axial symmetry. For example relaxation times of 119.4 ms and 89.7 ms corresponded to correlation times of 1.02 and 1.36 ps respectively.

3-3-1-1 Appraisal of the association from relaxation times

The viscosity corrected T_1 were fitted to equations taking into account both the free and bound species. The mole fraction bound was found and the equilibrium constant calculated.

The nitrate fraction bound A was fitted to the equation 3-16 a and b . the best fit disclosed whether the rate of ion-pair chemical exchange was slow or fast relative to the rate of molecular reorientation along the C_3 axis of the nitrate anion:

$$A_{\text{fast}} = \frac{(T_1 - T_{1,f})}{(T_{1,b} - T_{1,f})} \quad A_{\text{slow}} = \frac{(\frac{1}{T_1} - \frac{1}{T_{1,f}})}{(\frac{1}{T_{1,b}} - \frac{1}{T_{1,f}})} \quad (3-16 \text{ a\&b})$$

T_1 measured was the refitted value which was corrected for the viscosity. $T_{1,f}$ and $T_{1,b}$ were the free and bound relaxation times, assumed to be respectively 130 ms and 9 ms [12]. The calculated fractions bound were input in table 3-7.

Table 3-7: Fraction bound for potassium nitrate solution at 25 °C.

KNO ₃ (mol kg ⁻¹)	A _{slow}	A _{fast}
0.88311	0.034 ± 0.004	0.337 ± 0.04
0.45058	0.020 ± 0.003	0.230 ± 0.04
0.45058	0.022 ± 0.006	0.249 ± 0.07
0.30076	0.014 ± 0.007	0.135 ± 0.08
0.30076	0.011 ± 0.005	0.175 ± 0.07
0.09311	0.005 ± 0.006	0.070 ± 0.08
0.01948	0.001 ± 0.004	0.004 ± 0.07
0.00722	-0.000 ± 0.007	-0.00 ± 0.11

The fraction bound was smaller using the slow fitting models decreasing from 0.034 to nil at low concentration. According to the fast pattern, up to 25 % of the nitrate was still forming an ion-pair at a concentration of 0.45 M, percentage which decreased for lower concentrations. The errors were around 10 % and corresponded to the general accuracy of the relaxation time measurements. It was not possible to choose between the slow and fast pattern at this stage.

The association constant was calculated from the fraction bound and the concentration and compared to the literature value. The equilibrium for a 1:1 electrolyte may be represented by the equation 3-17:

$$K_a = \frac{Ay}{([KNO_3]_{tot} \times (1-A)^2 \times y_{\pm}^2)} \quad (3-17)$$

where y was the activity coefficient of the ion-pair species taken to be unity, and $y_{\pm}$ was the molal activity coefficient for the dissociated species, calculated for the different molalities from literature data [68,69] using a data regression $\gamma_{\pm}$ versus $\sqrt{C}$. They were converted to the molar activity coefficient $y_{\pm}$ using [57]:

$$\gamma_{\pm} = \frac{Cy_{\pm}}{m\rho_1} \quad (3-18)$$

where ρ_1 is the solvent density, and C and m were the molarity and molality concentrations of the solute.

The data obtained were summarised in table 3-8.

Table 3-8 The activity corrected equilibrium association constant.

[KNO ₃] (mole dm ⁻³)	K _a , slow	K _a , fast	K _a [2]
0.8568	0.1949 ± 0.11	4.790 ± 2.75	
0.4447	0.1369 ± 0.09	5.659 ± 3.83	
0.4447	0.1525 ± 0.17	6.452 ± 7.42	
0.2983	0.0889 ± 0.21	4.922 ± 12.23	(0.100M, 0.467)
0.2983	0.1198 ± 0.18	6928 ± 10.85	(0.020M, 0.637)
0.0931	0.0988 ± 0.39	16.41 ± 66.32	(0.005M, 0.704)
0.0195	0.0200 ± 1.02	14.83 ± 759	
0.0072	-0.013 ± 3.78	-26.11 ± 7261	

The slow pattern gave closer K_a's to the association constants derived from conductivity measurements as well as a more consistent trend. The data were more homogeneous and the standard deviation smaller.

Some fittings were done using values less than 9 ms for T_{1, bound}. The final association constants were not affected although the standard deviation tended to increase for such substitutions.

It was important to have an association constant which took into account all the available data. An extrapolated association constant was calculated using a non-linear, least-squares program [58] including the activity coefficients. Both weighted and not weighted variations were tried.

Table 3-9: Association constant extrapolated.

Variations		Slow pattern	Fast pattern
	number of data	8	8
no weighting	K _a activity corrected	0.139 ± 0.014	2.48 ± 0.33
weighting	K _a	0.046 ± 0.001	2.92 ± 0.39
weighting	K _a activity corrected	0.152 ± 0.011	2.84 ± 0.30

There were 6 different molalities covering a range from 0.007 up to 0.857 mol kg⁻¹.

Robinson & Stokes had found an association constant of 0.508 [17 e] from conductivity measurements of Shedlovsky [72]. The activity corrected data gave an association constant in the range of Robinson & Stokes's when fitted to the slow pattern. The slow pattern has already been preferred by other workers for similar nitrate salts [47].

3-1-2 Appraisal of the association from conductivity

Some previously published conductivity data were refitted, using a derived form by Lee and Wheaton equation for 1:1 electrolyte salt. Data from Robinson & Stokes [17], others from Harned and Owen [35], Justice et al. [70], Mc Kenzie and Fuoss [71], or Shedlovsky [72] were all reprocessed.

The association constants obtained were tabulated in table 3-10.

Table 3-10: The association constant for KNO_3 from conductivity measurements.

	data	literature	LW00(a)	LW01(b)	LW02(c)
Harned & Owen	7	1.4	0.79 ± 0.07	0.79 ± 0.07	1.02 ± 0.06
J.C. Justice et al.	11	0.73 ± 0.02	1.10 ± 0.01	0.71 ± 0.02	n.a.(d)
Mc K. & Fuoss	31	1.64	0.73 ± 0.01	0.73 ± 0.01	n.a.(d)
Robins. & Stokes	6	0.508	0.69 ± 0.02	0.69 ± 0.02	n.a.(d)
T. Shedlovsky	11	(e)	1.4 ± 0.4	1.4 ± 0.3	1.7 ± 0.3

(a,b,c) LW was the Lee-Wheaton derived program [73], to fit the conductance data versus the concentration, the equivalent conductance at infinite dilution, the association constant and a size parameter. The keys 00, 01, 02 qualified different version known as new model(a), series form(b) and primitive(c) respectively which mainly depended on the definition of the size parameter. The Lee-Wheaton model was considered reliable since already tested and more up to date [12].

(d) n.a. was written when no convergence was found after 501 iterations.

(e) Shedlovsky used his conductivity data to get the limiting equivalent conductivity at infinite dilution only. The literature corresponded to the result found in the original paper, with the fitting equations available at that time. Justice et al used the fitting program "Fuoss-Onsager".

The association constants varied from 0.508 up to 1.4 depending on the set of data or on the fitting model chosen. This discrepancy was reasonable because the association was small and therefore difficult to measure. Our final result $K_a = 0.152$ was sensible as well, since it was not that far from the value estimated by Robinson & Stokes [17] and compared with the range of values already calculated.

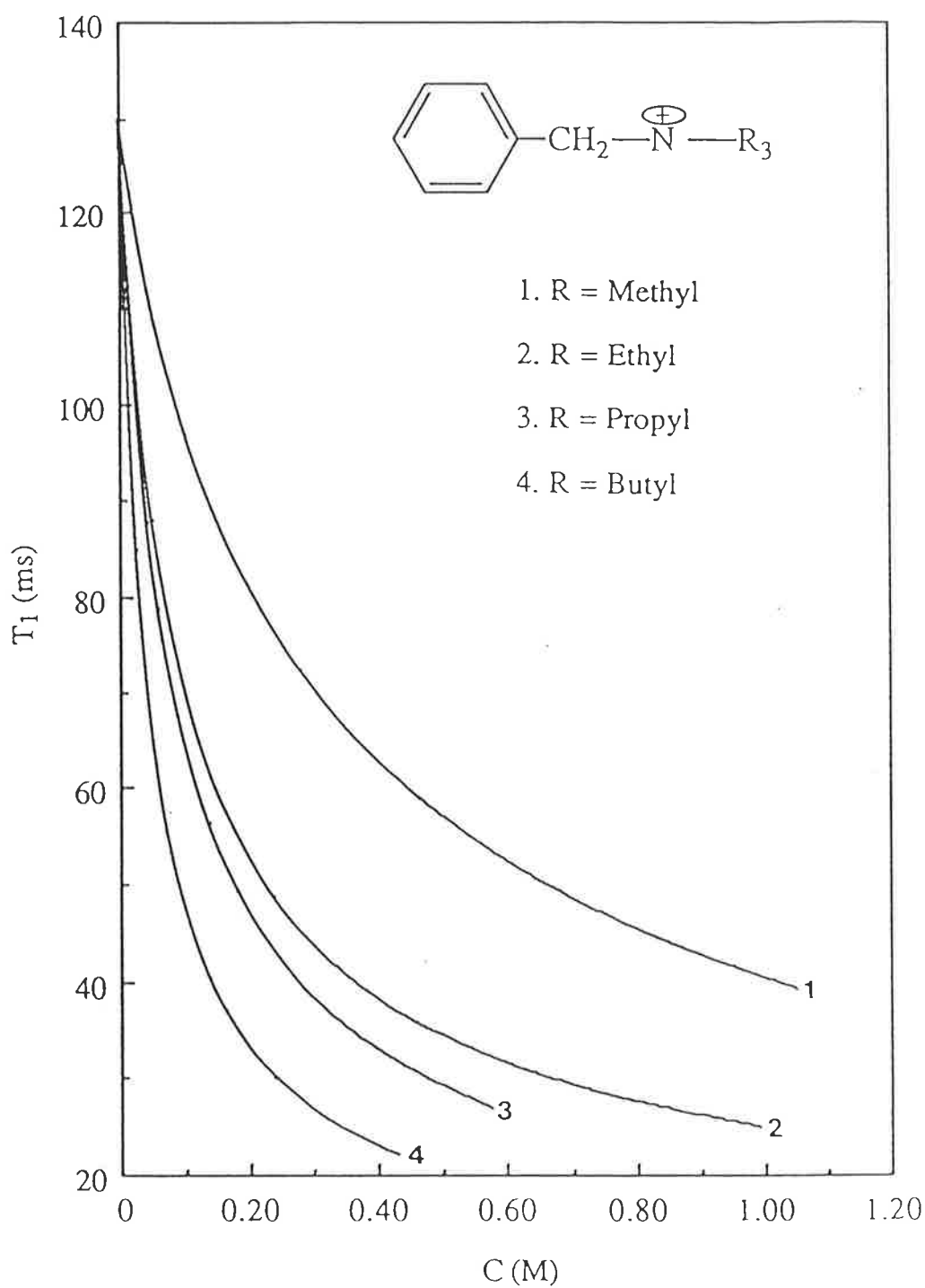
3-3-1-3 Conclusion

T_1 measurements agreed with the literature [12]. From them, association constants for potassium nitrate solutions were calculated and found in agreement with K_a 's obtained by other methods. Our association constant was 0.15, comparable to the Robinson and Stokes results [17] ($K_a = 0.508$) found using conductivity data by the same salt. Other published association constants were higher, the fitting equation chosen can partly explain this discrepancy. We showed that the rate of chemical exchange responsible for the ion-pair formation was slow compared to the rates of molecular reorientation of the nitrate anion and the ion-pair bound.

3-3-2 Relaxation times on monomers solutions

The same method was used as for potassium nitrate solutions although the working concentration range was more limited. High concentrations were limited by the salt solubility, especially for long alkyl functional groups. Low concentrations were limited by the minimum amount of nitrate necessary to obtain a nmr signal of reasonable signal to noise ratio, around $0.005 \text{ mole dm}^{-3}$. Densities and viscosities were calculated from predetermined coefficients for both Root and Jones-Dole equations.

The T_1 data were refitted from the different recovery times using non-linear least squares [58] program and viscosity corrected. The results were gathered in table 3-14, graph 3-4 illustrated the concentration dependence of longitudinal relaxation times for the nitrate monomers. The trend of the T_1 values was similar for the different monomers analogues.



Graph 3-4: Refitted ^{14}N longitudinal relaxation times for benzyltrialkylammonium nitrate in aqueous solution at 25 °C

T_1 were longer for the shorter alkyl groups such as methyl, and increased rapidly when the nitrate concentration decreased as the alkyl length increased. Applying equation 3-15, correlation times were calculated and were between 1 and 5 ps which corresponded to $T_1 = 121$ ms and $T_1 = 24.3$ ms. Association constants, K_a , were estimated using a similar method as for the simple salts, where the dependence of concentration was studied versus the relaxation times.

Using the relation 3-16, the fractions bound were calculated and from these, the association constants. Results, for the slow pattern, were included in the table 3-14. Both association constants, K_a , for slow and fast patterns were calculated and compared to results previously obtained by conductance [12] in table 3-11.

Table 3-11: Association constants for benzyltrialkylammonium nitrate salts in water

slow pattern fitting				
Alkyl group	b'(a)	K _a	SS (b)	conductance
methyl activity (c)	0.045	0.41 ± 0.01	1042	2.02
		0.24 ± 0.01	1083	
ethyl activity (c)	0.03	1.08 ± 0.12	1296	2.45
		0.70 ± 0.09	1723	
propyl activity (c)	0.125	1.30 ± 0.03	51	3.28
		0.91 ± 0.02	50	
butyl activity (c)	0.21	2.29 ± 0.14	408	3.80
		1.9 ± 0.1	375	
fast pattern fitting				
Alkyl group	b'(a)	K _a	SS (b)	conductance
methyl activity (c)	0.235	8.5 ± 0.5	1046	2.02
		7.9 ± 0.6	1578	
ethyl activity (c)	0.31	25.7 ± 2.9	681	2.45
		28.7 ± 2.9	1747	
propyl activity (c)	0.54	33.0 ± 1.9	107	3.28
		45.1 ± 6.0	559	
butyl activity (c)	0.79	67.2 ± 8.0	733	3.80
		118.4 ± 20.2	1567	

(a) b' is the coefficient in the Debye-Hückel equation to calculate the activity coefficient

- (b) SS is the sums of squares calculated from the least squares fit.
 (c) activity meant that the association constant were activity corrected, and the values located underneath were not.

From table 3-11, it was clear that the slow pattern gave associations much closer to the conductivity than the fast pattern. The errors and the sums of the squares were smaller. The activity coefficients improved the fitting. The activity corrected slow pattern was chosen as the best model for our data. The general trend of higher benzyltrialkylammonium nitrate association with longer alkyl chain length was supported. From the association constants measured from conductance and from relaxation times, extrapolated association constants K_a° were calculated using lotus data regression and least-square fit programs. Results were gathered in table 3-12.

Table 3-12: Extrapolated association constant K_a° .

Alkyl	slow pattern		fast pattern		conductance
	$K_a^\circ(a)$	$K_a^\circ(b)$	$K_a^\circ(a)$	$K_a^\circ(b)$	
methyl	0.43	0.41 ± 0.01	7.73	8.5 ± 0.5	2.02
	0.29	0.24 ± 0.01	3.95	7.9 ± 0.6	
ethyl	0.98	1.08 ± 0.12	20.85	25.7 ± 2.9	2.45
	0.72	0.70 ± 0.09	10.75	28.7 ± 4.9	
propyl	1.28	1.30 ± 0.03	27.61	33.0 ± 1.9	3.28
	0.90	0.91 ± 0.02	13.49	45.1 ± 6.0	
butyl	2.06	2.29 ± 0.14	50.07	67.2 ± 8.0	3.80
	1.45	1.9 ± 0.1	23.75	118.4 ± 20.2	

(a) from Lotus linear data regression.

(b) from the least-square fit program.

As expected, the slow pattern gave K_a° closer to the conductivity estimates. It was significant that datafit and extrapolation results were in good agreement with the slow pattern to favour it against fast one.

3-3-3 Conclusion

The association between different cations and nitrate anions was measured using longitudinal relaxation times in aqueous solutions. This method allowed us to work in a wide range of concentration nearly up to saturation. Association constants were estimated and were found to be small for both potassium and all benzyltriaklylammonium nitrate salts. They were in good agreement with association constant already measured. The nitrate /monomer analogue association increased with the length of the alkyl group. By fitting relaxation time data, it was clear that the chemical exchange of the ion pair formation was slow compared to the relaxation times for all of the salts tested. This seemed to be a sensible conclusion since the reorientation times had been around a few picoseconds, and a faster phenomena would have had to have been in the range of electron transfer velocity rather than ion-pair formation.

Table 3-13:

Density, viscosity, T_1 and association of the
potassium nitrate salts solutions with 5 % D_2O

KNO_3 (mole kg^{-1})	density (gcm^{-3})	KNO_3 (mole cm^{-3})	relative viscosity	Relaxation times (a) (ms)	activity coefficient
0.88311	1.05685	0.85681	0.9801	91.00 ± 5.6	0.467
0.45058	1.03181	0.44466	0.9840	103.80 ± 4.6	0.589
0.45058				101.43 ± 8.5	
0.30076	1.02187	0.29827	0.9889	114.94 ± 22.9	0.645
0.30076				110.07 ± 7.7	
0.09311	1.00932	0.09311	0.9974	121.81 ± 10.4	0.756
0.01948	1.00544	0.01955	1.0001	129.52 ± 8.8	0.832
0.00722	1.00456	0.00724	1.0002	130.10 ± 10.5	0.858

(a) The relaxation times were given with the standard errors, (a 10 % error is usually expected on relaxation time measurements).

Table 3-14

Density and viscosity of the aqueous
benzyltrialkylammonium nitrate solutions at 25 °C

benzyltrimethylammonium nitrate solution				
concentration M (mole dm ⁻³)	density ρ (g dm ⁻³)	P.M.V. (a) $\bar{V}$ (cm ³)	concentration M (mole dm ⁻³)	viscosity η_{rel}
0.005062	0.997265	169.88	0.002894	1.001158
0.010832	0.997511	170.01	0.006925	1.002568
0.020715	0.997920	170.66	0.012585	1.004112
0.035829	0.998503	172.15	0.023487	1.008733
0.040574	0.998721	171.52	0.038494	1.014112
0.055884	0.999360	172.38	0.061059	1.022051
0.064185	0.999655	171.14	0.078849	1.028188
0.073938	1.000084	172.70	0.098845	1.035153
0.144506	1.002905	172.23	0.110097	1.053105
0.249505	1.007109	172.44	0.144507	1.052736
0.933282	1.034695	172.42	0.173609	1.064378
			0.193861	1.071820
			0.213161	1.082529
			0.249498	1.094170
			0.293895	1.110988
			0.333447	1.127541

benzyltriethylammonium nitrate solution

concentration M (mole dm ⁻³)	density ρ (g dm ⁻³)	P.M.V. (a) $\bar{V}$ (cm ³)	concentration M (mole dm ⁻³)	viscosity η_{rel}
0.064185	0.999655	227.96	0.001688	0.999624
0.073938	1.000084	228.07	0.003254	1.000337
0.129836	1.000549	228.02	0.006497	1.001382
0.144506	1.002905	228.06	0.012549	1.005958
0.215264	1.002823	227.98	0.013616	1.006658
0.249505	1.007109	228.12	0.018050	1.009319
0.429233	1.008383	228.53	0.025959	1.013032
0.560657	1.011762	228.70	0.051874	1.027696
			0.081599	1.046761
			0.121953	1.067157
			0.259154	1.124920
			0.315807	1.149814
			0.468322	1.220738
			0.609747	1.283577
			0.830126	1.384046

(a) P.M.V. was the partial molar volume of the solute in cm³.

Table 3-14 (continued):

Density and viscosity of the aqueous
benzyltrialkylammonium nitrate solutions at 25 °C

benzyltripropylammonium nitrate solution

concentration M (mole dm ⁻³)	density ρ (g dm ⁻³)	P.M.V. (a) $\bar{V}$ (cm ³)	concentration M (mole dm ⁻³)	viscosity η_{rel}
0.007458	0.997181	279.35	0.003112	1.002699
0.011053	0.997243	279.54	0.007189	1.006277
0.018716	0.997377	279.65	0.013978	1.013458
0.031920	0.997608	279.60	0.027438	1.026078
0.069147	0.998251	279.80	0.048702	1.045657
0.154389	0.999745	279.72	0.069876	1.065444
0.235788	1.001079	280.05	0.082867	1.077372
0.361994	1.003195	280.38	0.092494	1.086378
0.433269	1.004275	280.05	0.100237	1.093820
			0.139310	1.108419
			0.171937	1.135822
			0.220687	1.176944
			0.292778	1.243731
			0.358755	1.310373
			0.401635	1.356090

benzyltributylammonium nitrate solutions

concentration M (mole dm ⁻³)	density ρ (g dm ⁻³)	P.M.V. (a) $\bar{V}$ (cm ³)	concentration M (mole dm ⁻³)	viscosity η_{rel}
0.008254	0.997232	317.13	0.001785	1.002951
0.011093	0.997293	317.33	0.003556	1.003560
0.021405	0.997517	317.51	0.004550	1.005158
0.039575	0.997911	317.61	0.007853	1.008046
0.078401	0.998744	317.79	0.030052	1.036713
0.179246	1.000904	317.91	0.043733	1.054430
0.349445	1.004467	319.19	0.060933	1.077300
0.563218	1.008822	318.52	0.083228	1.106355
0.805628	1.013445	319.09	0.099653	1.129450
			0.174813	1.239538
			0.217293	1.306513
			0.287998	1.429776
			0.358557	1.566864
			0.477292	1.843321

(a) P.M.V. was the partial molar volume of the solute in cm³.

Table 3-14 (continued):

Density and viscosity of the aqueous
benzyltrialkylammonium nitrate solutions at 25 °C

benzyltripentylammonium nitrate solution

concentration M (mole dm ⁻³)	density ρ (g dm ⁻³)	P.M.V. (a) $\bar{V}$ (cm ³)	concentration M (mole dm ⁻³)	viscosity η_{rel}
0.007125	0.997166	365.07	0.000731	1.005926
0.009857	0.997216	364.61	0.002387	1.006999
0.012641	0.997265	364.47	0.004797	1.010860
0.032360	0.997592	361.05	0.008434	1.018065
0.039386	0.997714	364.73	0.012641	1.025594
			0.032359	1.056247
			0.039386	1.065707

(a) P.M.V. was the partial molar volume of the solute in cm³.

Table 3-15:

Spin-lattice time, T_1 , for benzyltrialkylammonium nitrate
aqueous solution at 25 °C.

Benzyltrimethylammonium nitrate (a)				
$b'=0.045$				
concentration M (mole dm ⁻³)	density (b) ρ (g dm ⁻³)	viscosity (b) η_{rel}	molar activity coefficient (c)	relaxation times(d) (ms)
0.0511	0.99857	1.01851	0.839	104.5 ± 2.9
0.1006	1.00002	1.03606	0.807	101.0 ± 2.5
0.1216	1.00063	1.04362	0.799	104.2 ± 1.3
0.1495	1.00144	1.05378	0.790	84.6 ± 1.6
0.1960	1.00288	1.07108	0.779	72.4 ± 3.1
0.2778	1.00511	1.10258	0.766	75.9 ± 2.9
0.2778	1.00511	1.10258	0.766	70.8 ± 1.3
0.3769	1.00790	1.14267	0.758	58.7 ± 2.3
0.4611	1.01024	1.17843	0.754	63.8 ± 3.9
0.4611	1.01020	1.17843	0.754	60.5 ± 3.4
0.6047	1.01420	1.24304	0.752	52.8 ± 3.5
0.6806	1.01636	1.27904	0.752	46.7 ± 6.4
0.7811	1.01898	1.32871	0.753	42.8 ± 8.3
0.8714	1.02140	1.37527	0.755	45.4 ± 7.2
1.0506	1.02616	1.47311	0.760	46.7 ± 10.5

Benzyltriethylammonium nitrate				
$b'=0.03$				
concentration M (mole dm ⁻³)	density (b) ρ (g dm ⁻³)	viscosity (b) η_{rel}	molar activity coefficient (c)	relaxation times(d) (ms)
0.0254	0.99774	1.01332	0.879	91.4 ± 1.2
0.0483	0.99836	1.02464	0.853	85.7 ± 6.6
0.1609	1.00137	1.07899	0.807	77.8 ± 2.2
0.2351	1.00333	1.11413	0.795	53.4 ± 1.2
0.3083	1.00525	1.14838	0.787	46.5 ± 2.4
0.4570	1.00904	1.21588	0.780	35.1 ± 2.5
0.6960	1.01520	1.32387	0.777	29.1 ± 1.9
0.7912	1.01760	1.36552	0.778	25.1 ± 1.8
0.8653	1.01946	1.39756	0.779	29.5 ± 1.6
0.9910	1.02260	1.45116	0.781	23.2 ± 1.6
0.9910	1.02260	1.45116	0.781	23.6 ± 0.7

(a) Data from G. Owens [50]

(b) Both density and relative viscosity were calculated using formula 3-4 and 3-6, which coefficients were calculated from a fit of experimental data.

(c) Activity coefficients calculated from the extended Debye-Hückel law, using b' recorded on the top of each table.

(d) Standard errors given by the non-linear least-square fitting program.

Table 3-15: (continued)

Benzyltripropylammonium nitrate (a)

b'=0.125				
concentration M (mole dm ⁻³)	density (b) ρ (g dm ⁻³)	viscosity (b) η_{rel}	molar activity coefficient (c)	relaxation times(d) (ms)
0.0396	0.99775	1.03001	0.863	93.2 ± 6.8
0.0566	0.99805	1.04292	0.850	74.3 ± 9.8
0.1350	0.99940	1.10517	0.825	56.3 ± 3.8
0.1793	1.00015	1.14251	0.821	48.2 ± 3.1
0.3178	1.00246	1.26963	0.825	38.3 ± 1.9
0.3965	1.00374	1.34897	0.833	32.6 ± 1.8
0.4752	1.00501	1.43350	0.843	28.1 ± 2.4
0.5762	1.00656	1.54530	0.858	27.7 ± 1.4

Benzyltributylammonium nitrate

b'=0.21				
concentration M (mole dm ⁻³)	density (b) ρ (g dm ⁻³)	viscosity (b) η_{rel}	molar activity coefficient (c)	relaxation times(d) (ms)
0.0234	0.99756	1.02760	0.894	85.4 ± 5.5
0.0378	0.99787	1.04488	0.881	85.4 ± 2.8
0.0796	0.99878	1.09799	0.868	50.3 ± 3.4
0.0796	0.99878	1.09799	0.868	49.8 ± 5.4
0.1362	1.00000	1.17737	0.870	36.3 ± 1.7
0.1603	1.00051	1.21365	0.873	34.3 ± 2.5
0.2380	1.00214	1.34168	0.890	29.5 ± 0.7
0.3200	1.00385	1.49466	0.914	23.0 ± 1.2
0.4001	1.00550	1.66185	0.941	21.3 ± 1.4
0.4001	1.00550	1.66185	0.941	21.5 ± 1.2
0.4285	1.00608	1.72534	0.952	23.6 ± 0.4

Benzyltripentylammonium nitrate

b'=0.00				
concentration M (mole dm ⁻³)	density (b) ρ (g dm ⁻³)	viscosity (b) η_{rel}	molar activity coefficient (c)	relaxation times(d) (ms)
0.0139	0.99731	1.02444	0.903	83.9 ± 5.1
0.0209	0.99740	1.03652	0.889	74.7 ± 4.2

(a) Data from G. Owens [50]

(b) Both density and relative viscosity were calculated using formula 3-4 and 3-6, which coefficients were calculated from a fit of experimental data.

(c) Activity coefficient calculated from the extended Debye-Hückel law, using b' recored on the top of each table.

(d) Standard errors given by the non-linear least-square fitting program.

STUDY of the ANION / LINEAR POLYMER ASSOCIATION

The different linear polymers were synthesised from vinylbenzyltrialkylammonium chloride monomers using a free radical initiator AIBN. Soluble in water, they were mixed with a potassium nitrate solution to measure the ^{14}N nitrate longitudinal relaxation times, T_1 . Density and relative viscosity of the same solutions were measured. For higher mole ratio of polymer/anion, emf was used to study the polymer anion association.

The solutions were prepared by weight. The base molality of the linear polymer solutions were upper limited at 10^{-2} eq.mol dm^{-3} because of the noise they were causing to the relaxation time signal. On the other hand, the nitrate concentrations were kept constant around 5×10^{-2} mole dm^{-3} in order to enable the detection of the T_1 signals in presence of the polymer. Milli-Q purified water was added to obtain a total volume around 60 ml, which was needed to fill the Ubbelohde viscometer. All the solutions contained around 5% D_2O necessary to lock the spectrometer.

4-1 PHYSICAL-CHEMISTRY MEASUREMENTS

Polyelectrolytes possess many ionisable groups which are responsible for their solubilities and other interesting properties, such as interaction with other charged ions or neutral molecules and drastic changes in the fluidity of solutions when they are dissolved. [76]. Density and viscosity measurements were necessary for the concentration conversion and to appraise the solvent-solute interactions respectively. They were carried out following the procedure previously detailed in the materials and methods chapter .

4-1-1 Density measurements

The density was used for the conversion of molality to molarity. Results were included in table 4-5. Density results varied from 1.006 to 1.008 g cm⁻³. They were higher than the densities recorded for the monomer solutions at an equivalent molality. This could be explained by the fact that linear polymer solutions also contained D₂O whose density was higher than normal water, $\rho_{D_2O}^0 = 1.10445 \text{ g cm}^{-3}$ [57] and KNO₃ as a co-ion. Because of these other contributing components, density variations were not fully dependent on the polymer concentration.

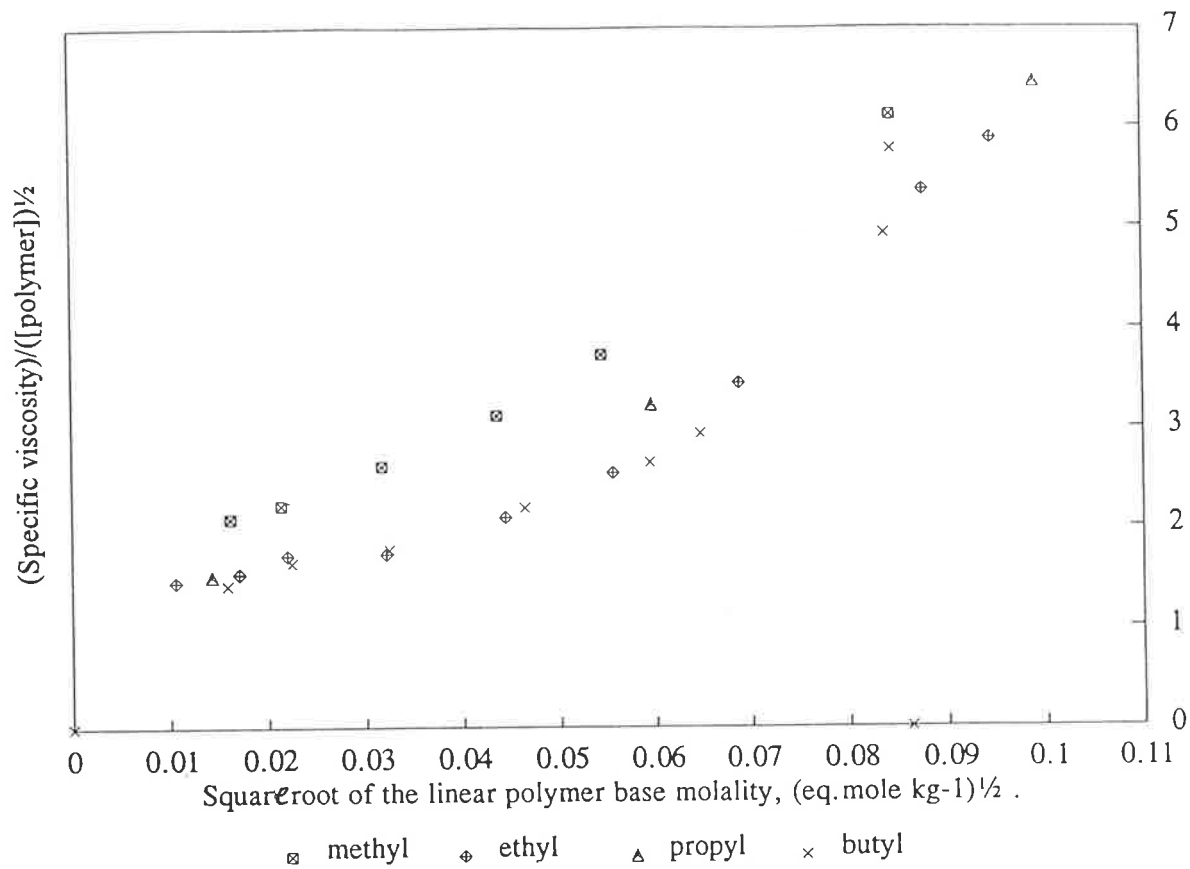
4-1-2 Viscosity measurements

The viscosity was used to correct the T_1 measurements. They were recorded in table 4-5 and plotted on graph 4-1. The specific viscosity divided by the square root of the molality, $(\eta-1)/\sqrt{m}$, increased rapidly with the square root of concentration. This expanded scale illustrated the strong effect of the polyelectrolyte on the viscosities. Polymethyl was a bit more viscous than the other polymers and the regular increasing in viscosity was hardly affected by the size of the alkyl group except for the polymethyl.

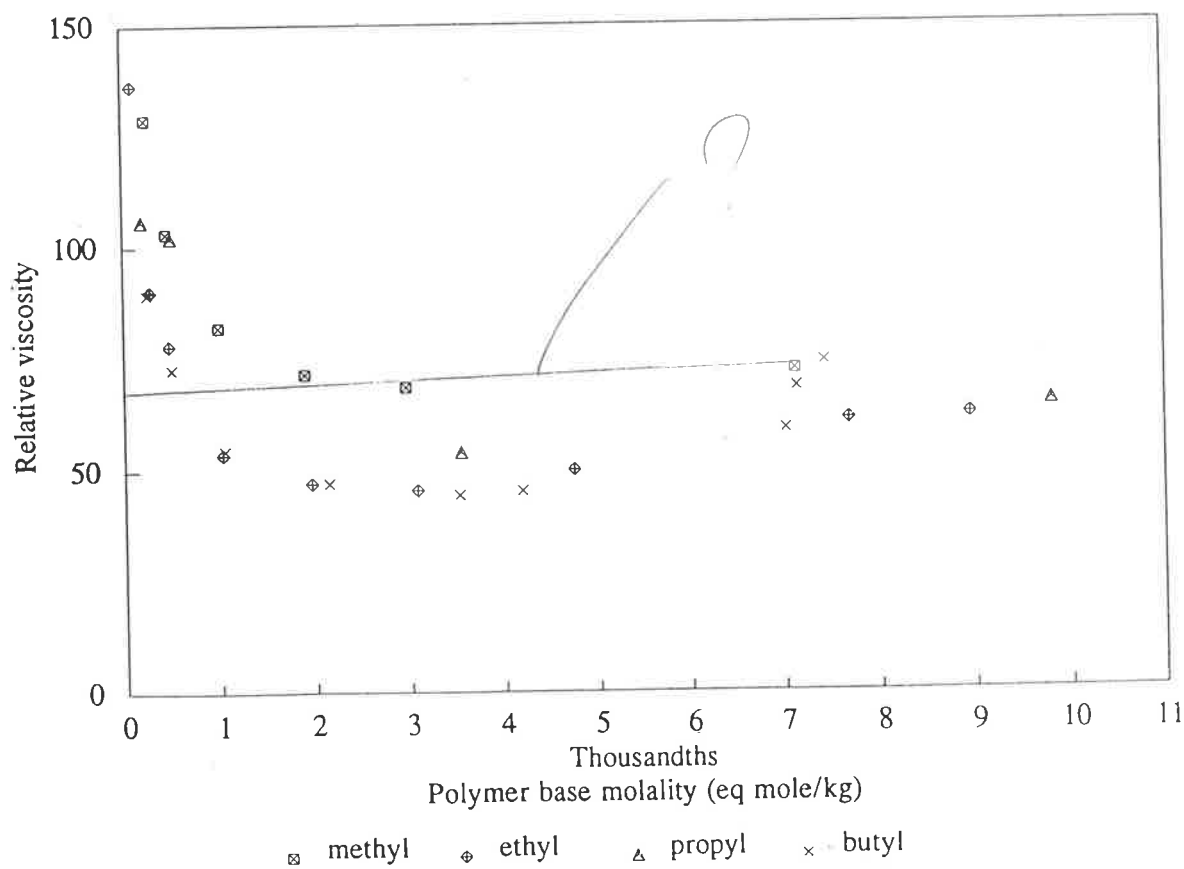
The degree of polymerisation has an effect on the viscosity. In 1942, Huggins proposed a relationship between the intrinsic viscosity $[\eta]$, also known as the limiting viscosity number, and the mass concentration of the polymer ρ_p [74-88]:

$$[\eta] \equiv \lim_{\rho_p \rightarrow 0} \left(\frac{\eta_{rel} - 1}{\rho_p} \right) \quad (\text{when } \rho \rightarrow 0) \quad (4-1)$$

where $\eta_{rel} = \eta / \eta_1$ was the relative viscosity and $\rho_p = m_p/V$ was the concentration of the polymer; the equivalent base molality (in mole/kg) was used in our calibration. Later,



Graph 4-1: Viscosity of the linear polymers in water at 25 °C



Graph 4-2: Intrinsic viscosity of the linear polymers in water at 25 °C

Mark-Howink linked the intrinsic viscosity with average molar mass of the polymer M_p [74]:

$$[\eta] = K \times (M_p)^a \quad (4-2)$$

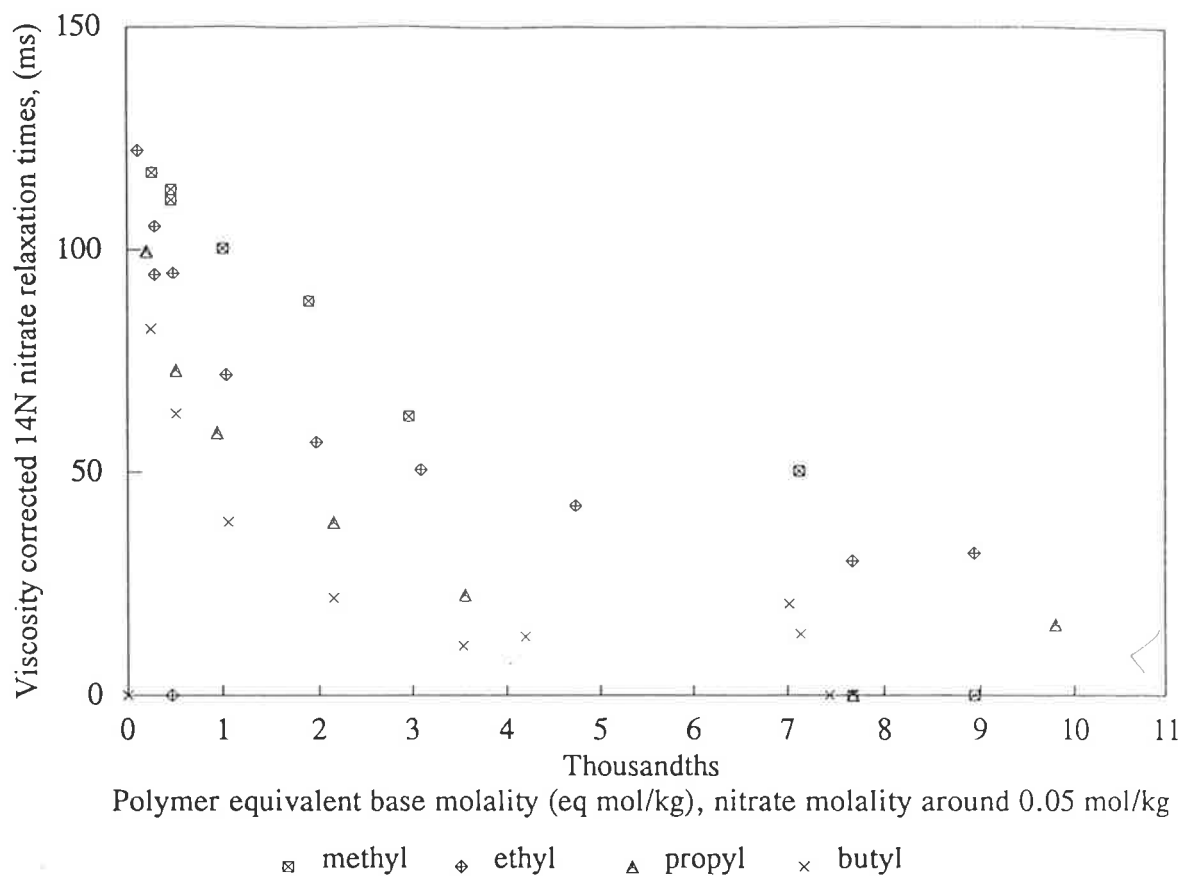
where K and a were empirical constants.

From the literature [75], the 2 coefficients of the Huggin's relation could be calculated for the poly(vinylbenzyltrimethylammonium chloride) taking into account the presence of KNO_3 , in the reference, the salt added was $NaCl$ instead of KNO_3 here. The coefficients were $1.2638 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$ and 0.7833 for " K " and " a " respectively. The intrinsic viscosity was 69.24, calculated from the more concentrated viscosity data, see graph 4-2, which corresponded to the literature concentration range [75]. The ratio $([\eta]/K) = 547\,871$ from which the average molar mass for the polymer was deduced and was equal to $22 \times 10^6 \text{ g}$. It corresponded to an average of 10^5 monomer units per chain. Assuming that both coefficient K and a were constant for our polymers, the size of the other samples would be of the same order since their viscosities were similar.

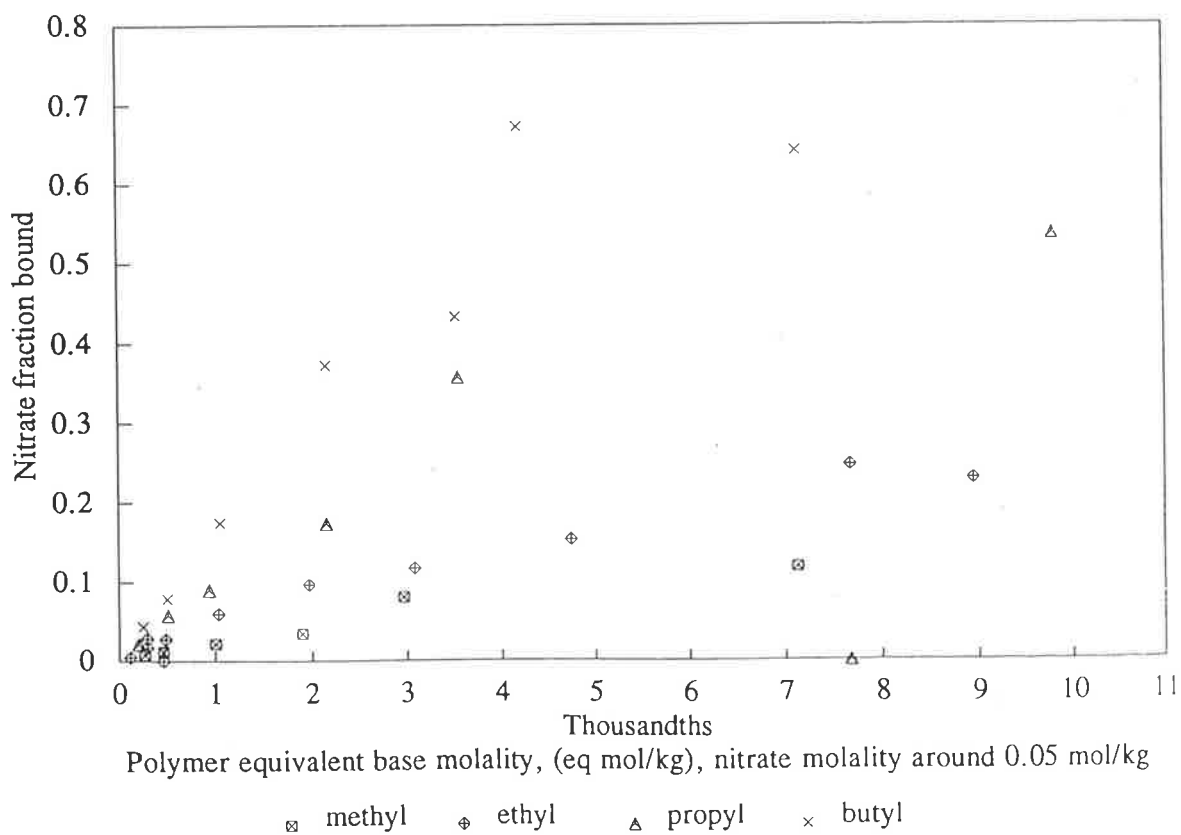
In a good solvent such as water, solute/solvent interactions are strong and polyelectrolytes tend to expand their conformation. The increasing of η_{sp}/m with decreasing concentration seemed of first peculiar but has already been observed for many polyelectrolytes. It was attributed to polyion or ionised polyelectrolyte expansion, combined with increasing interactions between the expanding polyions [77 a, 77].

4-2 NMR SPECTROSCOPY

The spin lattice relaxation times were measured and summarised in table 4-5. A plot of T_1 versus polymer concentration was included in graph 4-3. When the concentration of the polymer was too high, the noise level recorded during the experimentation was also too high. The upper concentration limit for our samples was around $0.01 \text{ mole equivalent kg}^{-1}$.



Graph 4-3: ^{14}N nitrate relaxation times in aqueous solution with linear polymers



Graph 4-4: Nitrate fraction bound to the linear polymers

The variation of relaxation times with molality, for all the polymers studied here, shared a common trend. Relaxation times decreased quickly from 100 to 115 ms from low polymer concentrations, to between 15 and 50 ms for the more concentrated polybutyl and polymethyl samples respectively. As for the monomer, long alkyl substituent on the quaternary ammonium group of the (poly)cations decreased the measured ^{14}N nitrate relaxation times.

The cation anion interaction model, used to quantify the association of the monomer analogues with nitrates, was not valid for polyelectrolytes. Following the slow pattern, chosen from the monomer study, the nitrate bound mole fractions were calculated and plotted versus the anion cation mole ratios, data in table 4-5 and on graph 4-4. The fractions of nitrate bound were high and represented an excess of anion associated. When input into the equilibrium constant formula for the nitrate association (equation 2-48), the excess of nitrate bound involved not enough free nitrates which were at the origin of negative equilibrium constants. On graph 4-4, the fraction bound increased with nitrate concentration and with length of the alkyl group. However, there were more anions measured bound than binding sites available on the polymer chain. The different monomers of a polyelectrolyte constituted a charged chain which were not independent any more and were acting like a polyion. The dissolved polyelectrolytes formed a strong cationic atmosphere which were able to attract an excess of nitrates. It is very likely that some bound measured nitrates were only "trapped" by some specific electrostatic conformations due to the cationic atmosphere surrounding the polyelectrolytes. The addition of a simple salt to a polyelectrolyte solution shields, or neutralises, the cation charge and therefore reduces the expansion of the polymer [76 c]. The polyelectrolyte shrank and formed a coil in which stronger interactions with nitrates were possible as shown on figure 4-1. No theories have been able to explain the complexity of a polyelectrolyte expansion in a polar solvent and the effect of an electrolyte addition [76c].

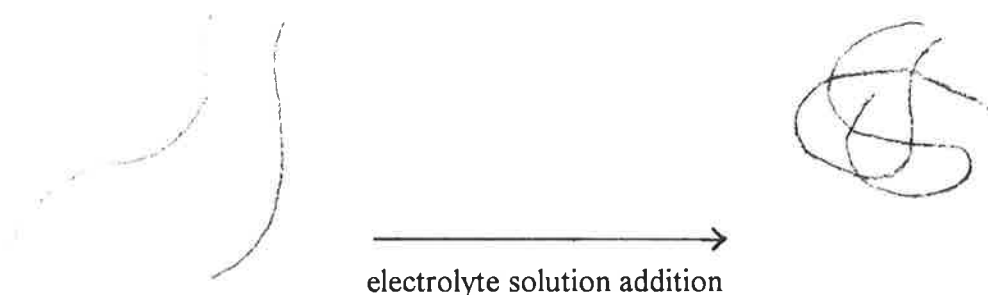


Figure 4-1: Effect of a salt added on the degree of expansion of polyelectrolytes [76 c].

Another interesting phenomena occurs when a critical polyelectrolyte concentration in solution is reached. The solution becomes saturated or "entangled" having drastic new dynamic properties. This state is marked by a strong augmentation in the viscosity with the polymer concentration [89], augmentation that we did not meet, see graph 4-1.

Measured relaxation times showed that an abnormally high fraction of nitrate bound to the polyelectrolyte was measured. Nevertheless, the trend of a long group, fixed on quaternary ammonium favouring a higher association, was confirmed. However, the nitrate polyelectrolyte concentration ratios were too high in favour of nitrates to be of interest for our purpose. High nitrate concentrations were necessary to get an observable signal from the nitrate, and low polyelectrolyte concentrations were required to reduce the noise level. This high nitrate ratio probably favoured the binding of that many nitrates. Another experiment was designed to study the same interactions with a ratio nitrate polymer less than unity.

4-3 EMF EXPERIMENTATION

The idea was to measure the association between the linear cationic polyelectrolytes and other anions such as chlorides, nitrates and sulphates at low mole ratio anion/polymer, closer to the concentration range occurring in an ion-exchange process. The emf technique

was used to measure the concentrations. The polymer base molality was kept around $0.01 \text{ eq.mol dm}^{-3}$ while the counter anion concentrations were adjusted to cover a range ratio starting at 0.01. The theory and the experimental procedure were described in chapter 2.

Release of chloride was first studied, then chloride/nitrate, sulphate/chloride and sulphate/nitrate associations. Only the chloride and nitrate I. S. E. were used for these experiments.

4-3-1 Calibration of the electrodes

Both chloride and nitrate electrodes were calibrated with four solutions of known molality, covering the total working range concentration. The calibration was accomplished by calculating the slope of the function $E = E^\circ - k \log(a_{\text{Cl}^-})$. The Orion electrode manual gave a tolerance of $56 \pm 2 \text{ mV}$. Following the pattern described in chapter 2, the activity coefficients were also calculated and compared with the literature. A typical set of data were included in table 4-6.

4-3-2 Dilution effect on the chloride polymer association

A preliminary experiment studied the behaviour of chloride linear polymers association when diluted with water. A polymer solution of known concentration was placed first into the cell and water was added by weight. The free chloride concentration was measured, and the bound concentration deduced by subtraction from the total chlorides themselves calculated from the amount of polyelectrolyte input at the beginning of the experiment. Data were gathered on table 4-7. The fractions of chloride bound were plotted versus the polymer base molality, graph 4-5, which varied from 0.1 down to $0.05 \text{ eq mole kg}^{-1}$. The chloride binding increased slightly with the polymer concentration, and with the size of the alkyl group, ranked from methyl around 0.72-0.70 to pentyl 0.83-0.80. A 20 fold dilution had little effect on the chloride/polymer association.

In the range of concentrations studied, chloride/linear polymer association was high, around 70-80 % of bound chloride. This result agreed with a high association expected from

polyelectrolyte with their ions when dissolved in aqueous solution. If the polymer association was compared to the chloride/monomer analogue association already studied [12], the same increase with the size of the alkyl group was observed.

4-3-3 The chloride nitrate selectivity

The release of chloride was then studied when a nitrate solution was added. Around 15 g of polymer solution (base molality of 0.10 mol kg^{-1}) were introduced into the cell, and aliquots of nitrate solution, 0.6 mol kg^{-1} , were added until the nitrate concentration was higher than the initial chloride concentration.

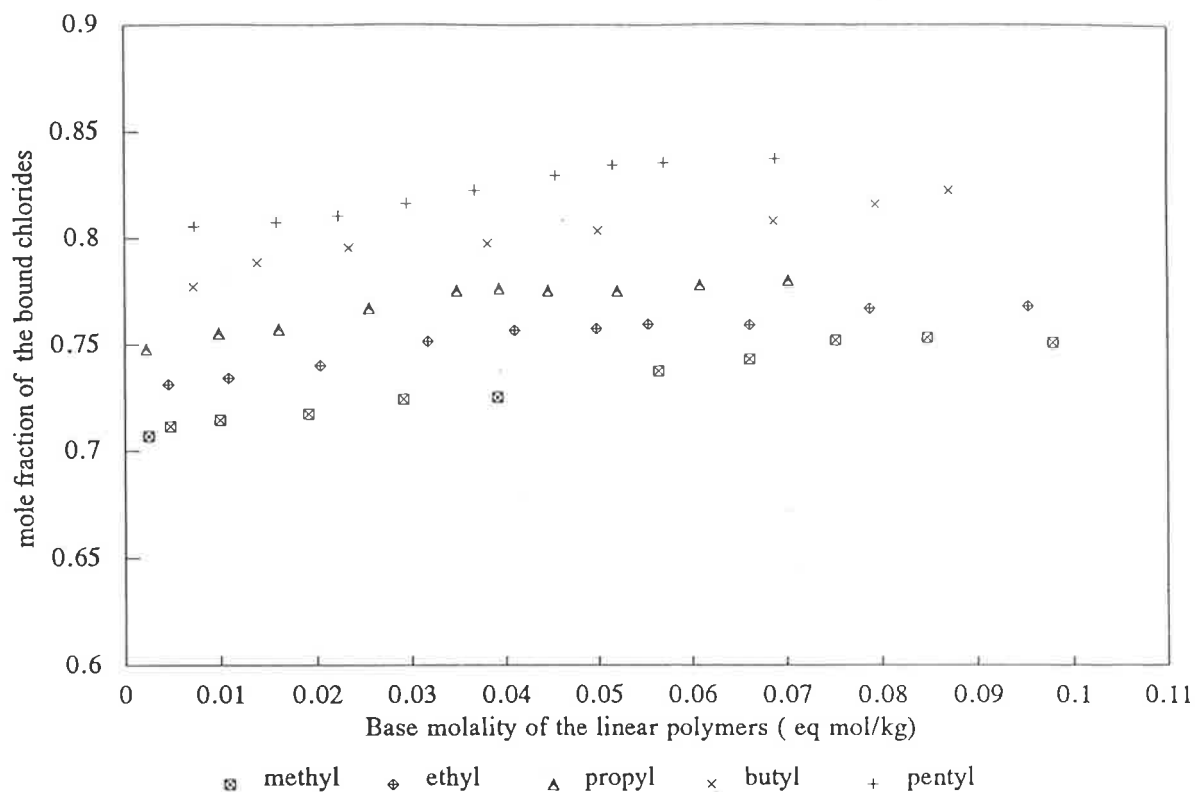
Both chloride and nitrate I. S. E. were used to measure the free anion concentrations. From the total mass input, bound concentration were calculated and plotted versus the nitrate molality on graphs 4-6. When no nitrate was added, the fraction of bound chloride were measured and compared to the results from the dilution experiment (section 3-2) in table 4-1.

Table 4-1: ratio of chloride bound in aqueous solution at a constant polymer base molality of 0.1 mol dm^{-3}

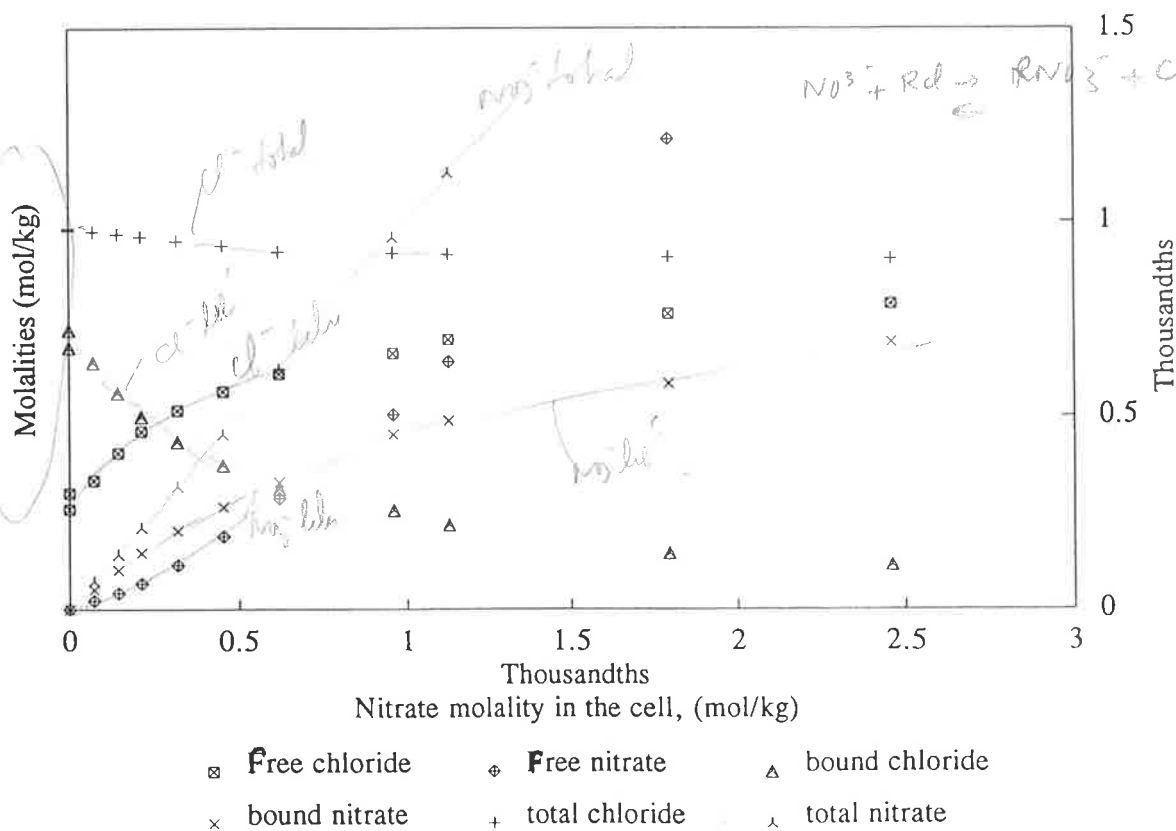
	methyl	ethyl	propyl	butyl	pentyl
Dilution	0.708	0.733	0.752	0.779	0.798
Nitrate	0.695	0.735	0.758	0.779	0.802

Both fractions bound were similar.

When nitrates were introduced (graph 4-6), the free chloride concentration increased until the majority of the ions were almost free (80 % free for methyl up to 95 % to pentyl). The fraction of nitrate bound to the polymer correspondingly increased with the amount of nitrate solution added to reach 80 % bound for methyl up to 95 % for pentyl polymers. At equiconcentration of anion, from 40 to 55 % of the nitrates were bound. An exchange stability was reached when total nitrates were twice the chloride concentrations.

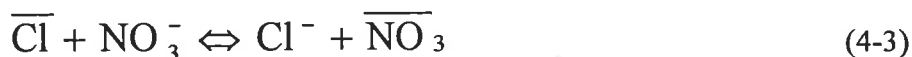


Graph 4-5: Chloride binding to the linear polymers in aqueous solution.



Graph 4-6: Chloride and nitrate association to linear polyethyl.

There was good correlation between the amount of chlorides freed and nitrates bound measured. For the five polymers considered, the free chloride ratios increased with the length of the alkyl group. The fraction of nitrate bound increased with the length of the alkyl group. An attempt to quantify the extent of the equilibrium exchange was made. For the equilibrium:



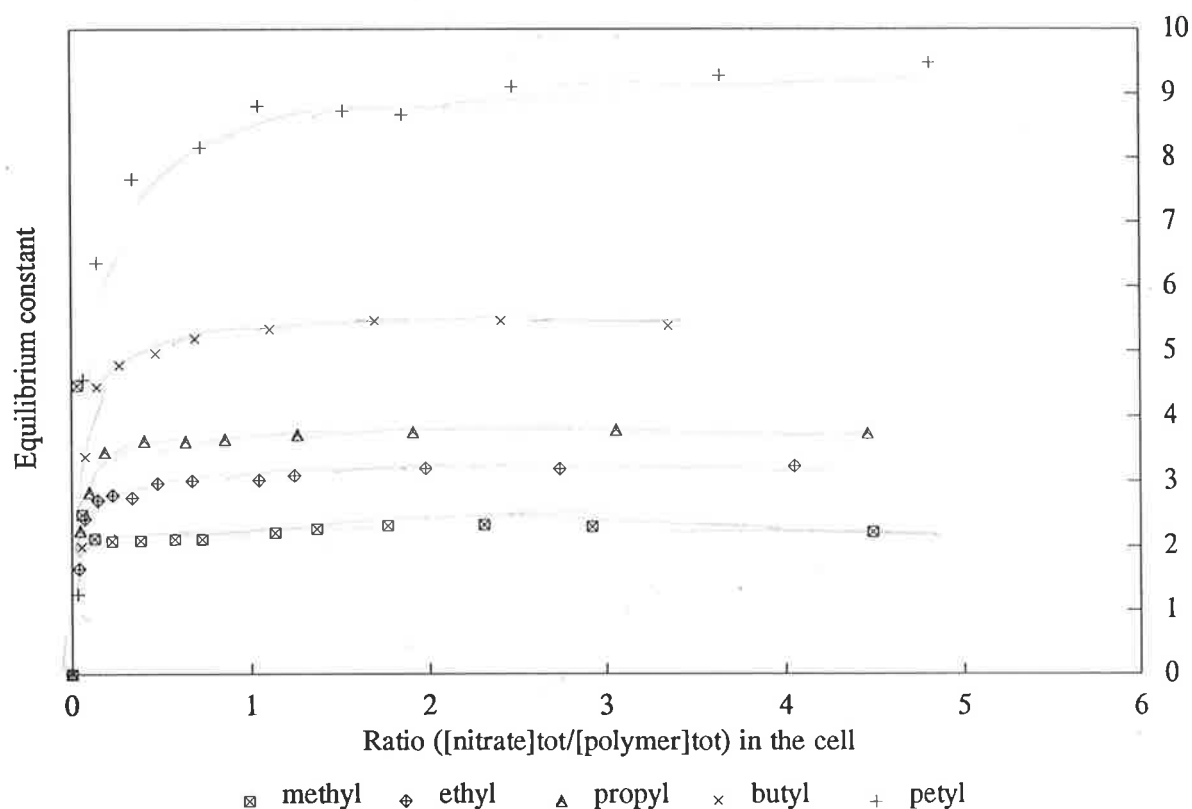
where the Cl or NO₃ overbarred referred to anions in the resin phase, and the charged species corresponded to the free anions. The equilibrium constant was:

$$K_{\text{Cl}}^{\text{NO}_3} = \frac{a_{\text{Cl}^-} \times \overline{X}_{\text{NO}_3}}{a_{\text{NO}_3^-} \times \overline{X}_{\text{Cl}}} \quad (4-4)$$

where a_{Cl^-} was the activity of the chloride anion, and $\overline{X}_{\text{NO}_3}$ was the mole fraction of bound nitrate. The activity coefficients were ignored, since for KNO₃ and KCl, they were similar and would have cancelled in the above formula. The equilibrium constants obtained, table 4-2 and graph 4-9, were not as constant as expected, especially at the low nitrate concentration. It could be due to the low of sensitivity of the I.S.E at such concentrations. The arithmetic mean of the equilibrium constants were calculated and they indicated a small degree of nitrate selectivity of all the linear polymers. This selectivity increased with the size of the alkyl group.

Table 4-2: Chloride/nitrate equilibrium constant calculated from emf.

Chloride/nitrate	methyl	ethyl	propyl	butyl	pentyl
Equilibrium constant	2.3 ± 0.6	3.0 ± 0.2	3.4 ± 0.4	4 ± 1	8 ± 2
Number of data	13	12	10	10	11

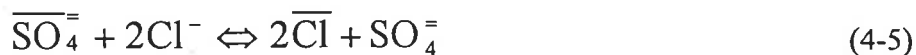


Graph 4-9 : Nitrate chloride equilibrium constants versus the ratio nitrate/linear polymer concentration.

4-4-4 The sulphate chloride selectivity

Chloride linear polymers were converted to the sulphate form using Amberlite IRA-400 (SO_4) exchanger. The release of sulphate was studied upon addition of a known chloride to the polymer in the sulphate form. The same initial amount of polymer was introduced, (25 g of a 0.10 base molality solution) as for the chloride nitrate survey. Aliquots of two different sodium chloride solutions were added to cover a chloride concentration from zero up to 0.05 mol kg^{-1} . The latter concentration was five times the sulphate concentration, but did

not increase much the cell solution volume. The equilibrium for the chemical exchange could be simplified to:



where overbarred anion were in the resin phase and the charged anions in solution.

The chloride I.S.E. was used to measure the free ion concentration. The sulphate concentration was calculated assuming:

$$n_{\text{SO}_4, \text{ free}} = 2 \times n_{\text{Cl bound}} \quad (4-6)$$

where n_{SO_4} and n_{Cl} represented the mole number of sulphate and chloride.

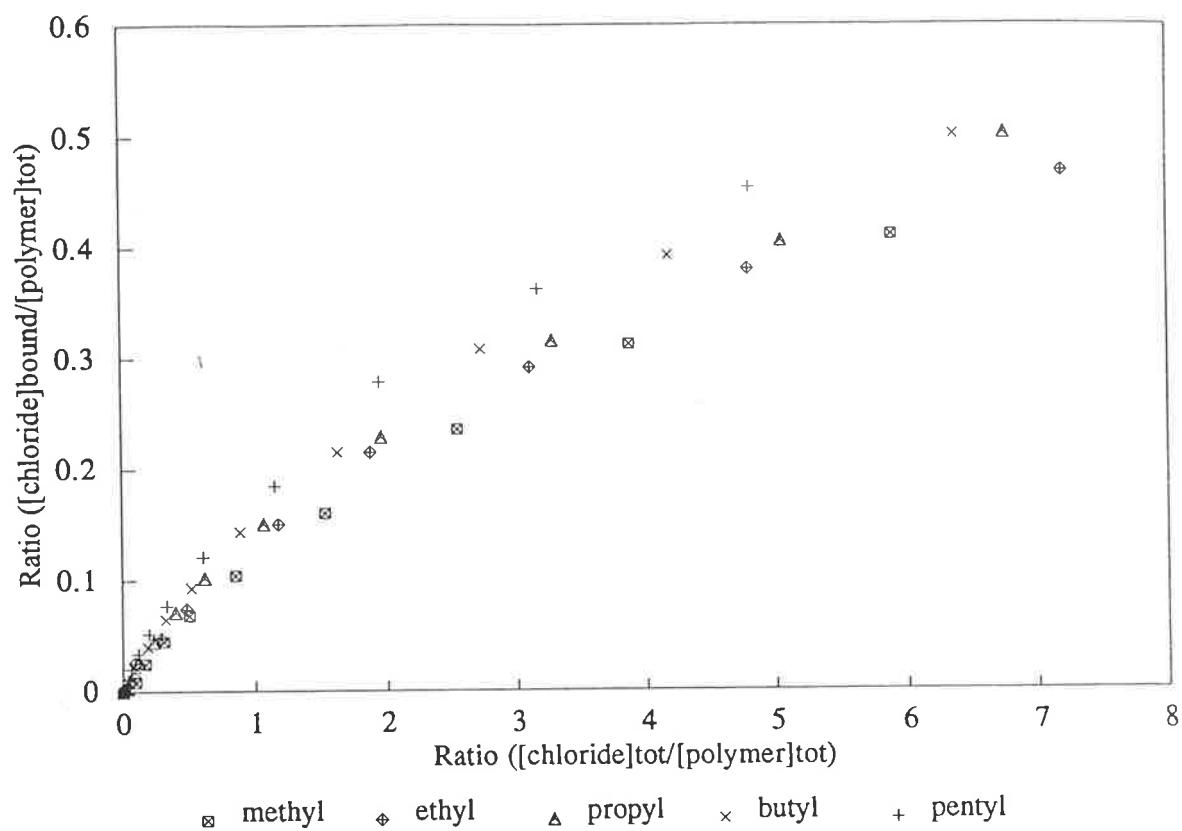
This assumption was justified by the good agreement found between the chloride release and nitrate bound observed in the chloride/nitrate association study. The fraction bound of chloride was small, but increased with the length of the alkyl groups attached to the quaternary ammonium group, around 45 % were bound for methyl up to 55 % for pentyl. Bound chlorides level levelled out when the total chloride concentration was six times that of the sulphate. The equilibrium constants $K_{\text{SO}_4}^{\text{Cl}^-}$ were calculated from a derivative of the formula 2-63:

$$K_{\text{SO}_4}^{\text{Cl}^-} = \frac{(a_{\text{SO}_4}) \times \overline{X}_{\text{Cl}}^2}{a_{\text{Cl}^-}^2 \times (\overline{X}_{\text{SO}_4})} = \frac{(m_{\text{SO}_4} \times \gamma_{\text{SO}_4}) \times n_{\text{Cl}}^2}{(m_{\text{Cl}^-} \times \gamma_{\text{Cl}^-})^2 \times n_{\text{SO}_4} \times (n_{\text{SO}_4} + n_{\text{Cl}})} \quad (4-7)$$

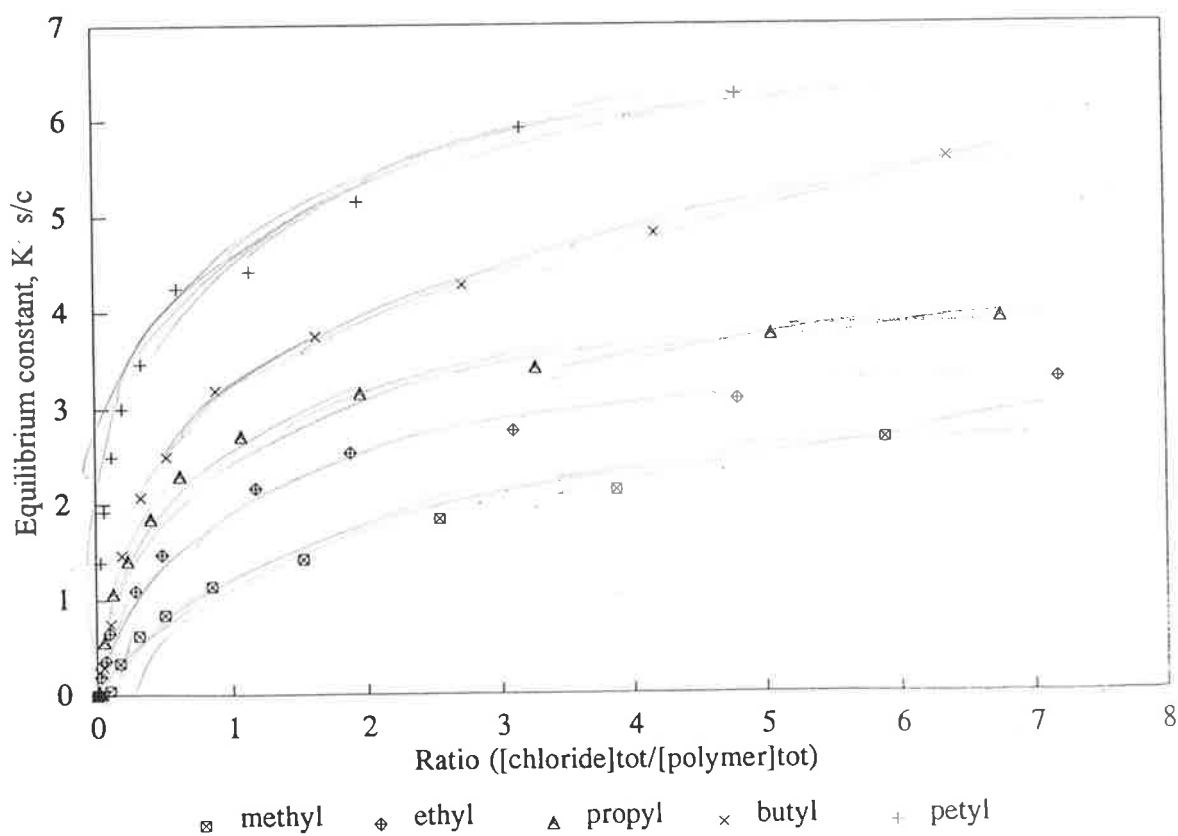
where $a_{\text{Cl}^-} = (m_{\text{Cl}^-} \times \gamma_{\text{Cl}^-})$ was the activity of the dissolved chloride species, and $\overline{X}_{\text{Cl}} = \frac{n_{\text{Cl}}}{\sum_A n_A}$

was the mole fraction of the chlorides in the resin phase.

Equilibrium constants were tabulated, table 4-9, plotted versus the chloride molality on graph 4-11; the arithmetic mean were in table 5-3.



Graph 4-10: Chloride binding to the linear polymers with sulphate.



Graph 4-11: Chloride sulphate equilibrium constant.

Table 4-3: Sulphate/chloride equilibrium constant from emf measurements:

Sulphate/chloride	methyl	ethyl	propyl	butyl	pentyl
Equilibrium constant	1.0 ± 0.3	1.3 ± 0.9	2 ± 1	2 ± 1	3 ± 1
Number of data	10	9	10	10	10

For the 2-1 electrolyte system, the equilibrium constants calculated were more erratic than for the chloride/nitrate system, especially at low concentrations. This can be attributed to limitation in electrode reproducibility in the low concentration and also to the assumptions made in the calculation of the activity coefficient using the Debye-Hückel limiting law [17 c]. Even activity corrected, the equilibrium constants showed a chloride selectivity which increased with the size of the alkyl groups.

4-3-5 The sulphate nitrate selectivity

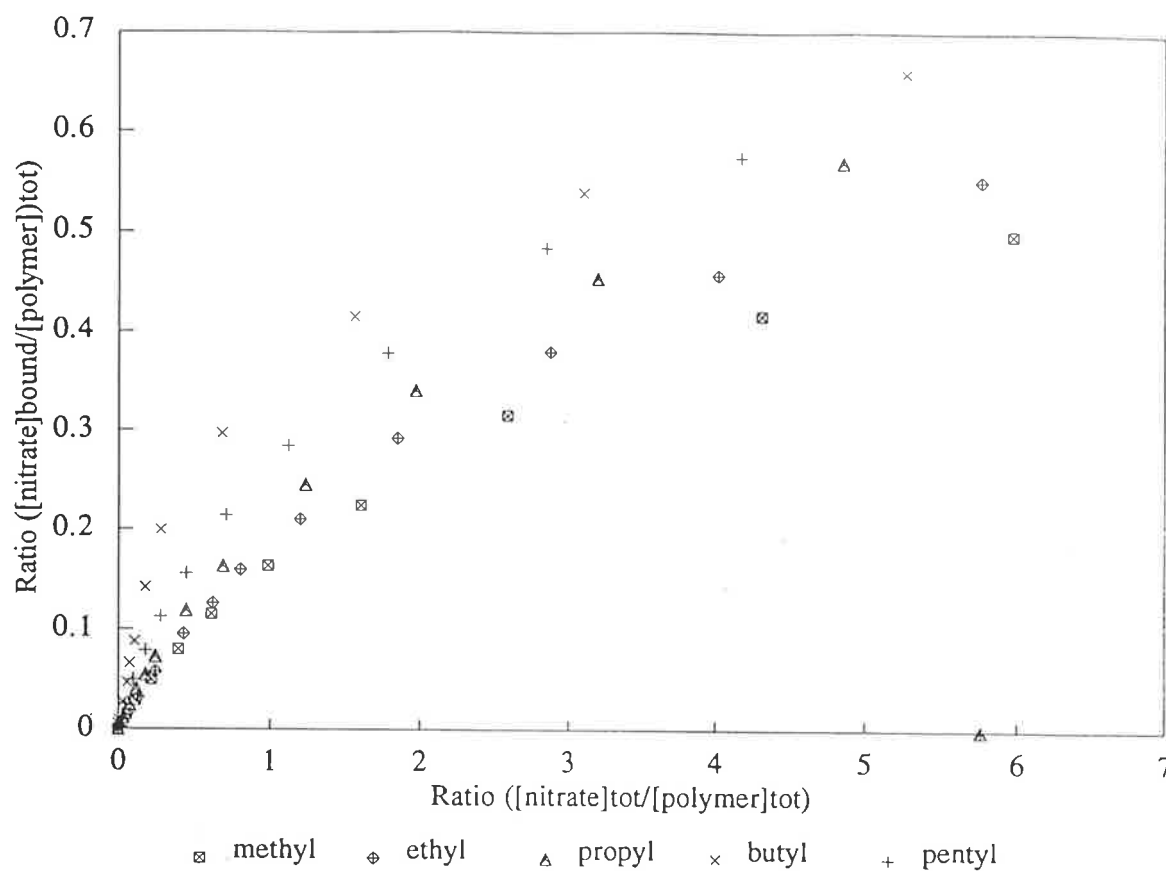
A nitrate solution of known concentration was added to polymers converted in the sulphate forms, and the sulphate nitrate association was studied. The same initial amount of polymer was used, (25 g of a 0.10 base molality solution) as for the chloride nitrate survey. Aliquots of two different potassium nitrate concentration solutions were added to cover a nitrate concentration from nil up to 0.05 mol/kg. The nitrate concentration was five times the sulphate one, without increasing the total volume very much.

The free nitrate concentrations were obtained using nitrate I.S.E.. The sulphate concentrations were calculated using the assumption:

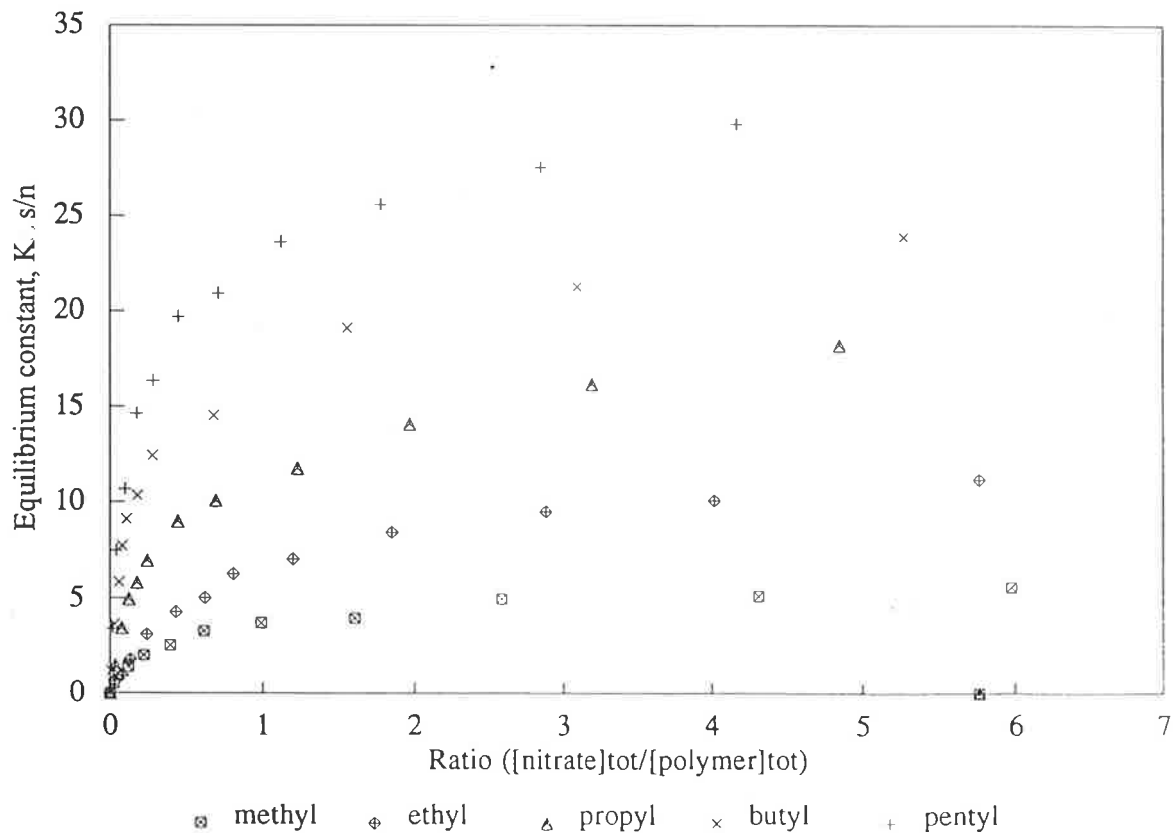
$$n_{\text{SO}_4, \text{ free}} = 2 \times n_{\text{NO}_3 \text{ bound}} \quad (4-8)$$

where n_{SO_4} and n_{NO_3} represented the mole number of sulphate and nitrate.

The equilibrium was very similar to (4-6), where nitrates have been replaced by chlorides.



Graph 4-12: Nitrate binding to the linear polymers with sulphates.



Graph 4-13: Nitrate sulphate equilibrium constant.

The different fractions of anions free and bound, gathered in table 4-10, were plotted versus the total nitrate molality on graph 4-12. The nitrates bound were higher than the chlorides bound, and the association was enhanced by longer alkyl groups on the quaternary ammonium group. The nitrate fraction bound increased from 45 % for methyl to 65 % for pentyl respectively and did not evolved further when nitrate concentrations were six times the sulphate equivalent concentrations.

The data were in table 4-10 and the equilibrium constants were plotted versus the total nitrate molality on graph 4-13; the arithmetic mean of the data were gathered in table 4-4:

Table 4-4: Sulphate/nitrate equilibrium constants from emf measurements:

Sulphate/nitrate	methyl	ethyl	propyl	butyl	pentyl
Equilibrium constant	3 ± 1	6 ± 3	9 ± 5	12 ± 6	20 ± 6
Number of data	10	11	10	10	10

The assumption of one sulphate released for two nitrates bound was made to enable the calculation of the sulphates free. Using the activity coefficients calculated from the Debye-Hückel limiting law, the equilibrium constants for the sulphate/nitrate association were calculated. They were found not as stable as expected probably due to limitation in measuring low concentrations with ISE. However, some trends were observed, such as an increase in nitrate selectivity with an increase in size of the alkyl group, and also that the association constants did not change when the nitrate concentration was three times that of the sulphate.

4-3-6 Conclusion

From the viscosity measurements and applying the Mark-Houwling equation, it was possible to estimate the average size of the linear polymer chain. This was around 90 000 monomer units long.

^{14}N nitrate relaxation times showed that when nitrates were in excess compare to the polymer base molality, the association was very high. It was found that chemical exchange of the association was slow compared to the reorientation time, τ_c , of the nitrate ion. To attempt to explain the excess of nitrate bound recorded, two main types of association were thought to occur. An ion-pair formation based on electrostatic attraction and a strong interaction between trapped nitrate ions whose reorientations were hindered by the polymer coil formation.

Emf was used to study the same phenomena when the ratio of nitrate/polymer was below or near unity. The activity of the chloride and nitrate ions in solution was estimated with accuracy using both chloride and nitrate I.S.E. Equilibrium constants were calculated for three binary systems involving chlorides, nitrates and sulphates. The results indicated a small affinity for the nitrate from the five polymers and to lesser extent for chloride. The nitrate affinity increased with the size of the alkyl group attached to the quaternary ammonium nitrogen of the binding site.

Table 4-5:

Density, viscosity, longitudinal relaxation time, T₁,
and nitrate fraction bound A_S, for linear polymer aqueous solutions at 25 °C

Poly(benzyltrimethylammonium chloride), potassium nitrate

Polymer conc. ^a (mol dm ⁻³)	Nitrate conc. (mol dm ⁻³)	mole ratio ^b	density ρ (g cm ⁻³)	relative viscosity η _{rel}	Relaxation times ^e (ms)	Fraction bound A _{slow} (×10 ⁻³)
0.00026 ^c	0.04696	180.2	1.00691	1.03373	113.4 ± 11.2	8.1 ± 0.1
0.00046 ^d	0.04826	105.6	1.01042	1.04740	108.4 ± 2.4	10.8 ± 0.2
0.00046 ^d	0.04826	105.6	1.01042	1.04740	106.1 ± 2.2	12.6 ± 0.3
0.00100 ^d	0.05049	50.5	1.01113	1.08254	92.7 ± 3.0	22.0 ± 0.7
0.00190 ^d	0.05176	27.3	1.01110	1.13591	77.7 ± 1.3	35.2 ± 0.6
0.00297 ^c	0.04972	16.8	1.00652	1.20318	51.9 ± 6.1	80 ± 9
0.00713 ^c	0.04657	6.6	1.00666	1.51561	33.2 ± 1.9	118 ± 7

Poly(benzyltriethylammonium) chloride, potassium nitrate,

Polymer conc. ^a (mol dm ⁻³)	Nitrate conc. (mol dm ⁻³)	mole ratio ^b	density ρ (g cm ⁻³)	relative viscosity η _{rel}	Relaxation times ^e (ms)	Fraction bound A _{slow} (×10 ⁻³)
0.00011 ^c	0.055483	494.8	1.00688	1.01541	120.3 ± 9.7	4.8 ± 0.4
0.00029 ^c	0.05107	176.5	1.00602	1.02620	102.5 ± 4.8	17.5 ± 0.8
0.00029 ^c	0.05107	176.5	1.00602	1.02620	91.9 ± 5.9	28 ± 2
0.00048 ^d	0.04965	103.1	1.01083	1.03777	91.1 ± 1.7	27.9 ± 0.5
0.00104 ^d	0.04933	47.8	1.01079	1.05558	67.9 ± 2.1	61 ± 2
0.00197 ^d	0.04885	24.8	1.01087	1.09296	51.8 ± 1.2	96 ± 2
0.00309 ^c	0.05184	19.9	1.00717	1.14066	44.3 ± 2.8	117 ± 7
0.00474 ^c	0.04810	10.2	1.00676	1.23658	34.4 ± 4.8	153 ± 21
0.00767 ^c	0.05068	6.6	1.00700	1.46992	20.5 ± 3.7	247 ± 44
0.00894 ^c	0.05077	5.6	1.00629	1.55485	20.5 ± 4.0	229 ± 45

Table 4-5: (continued)

Poly(benzyltripropylammonium chloride), potassium nitrate,

Polymer conc. ^a (mol dm ⁻³)	Nitrate conc. (mol dm ⁻³)	mole ratio ^b	density ρ (g cm ⁻³)	relative viscosity η_{rel}	Relaxation times ^e (ms)	Fraction bound A_{slow} ($\times 10^{-3}$)
0.00020 ^c	0.04793	238.0	1.00693	1.02155	97.7 $\pm$ 8.3	23 $\pm$ 2
0.00051 ^d	0.04743	93.4	1.01034	1.05218	69.1 $\pm$ 2.4	59 $\pm$ 2
0.00094 ^d	0.04814	51.3	1.01047	1.11095	52.9 $\pm$ 1.1	90 $\pm$ 2
0.00216 ^d	0.04811	22.3	1.01048	1.24382	31.3 $\pm$ 0.9	174 $\pm$ 5
0.00355 ^c	0.04490	12.7	1.00698	1.19218	18.8 $\pm$ 2.1	357 $\pm$ 40
0.00979 ^c	0.04449	4.6	1.00777	1.63686	9.7 $\pm$ 0.7	535 $\pm$ 39

Poly(benzyltributylammonium chloride), potassium nitrate,

Polymer conc. ^a (mol dm ⁻³)	Nitrate conc. (mol dm ⁻³)	mole ratio ^b	density ρ (g cm ⁻³)	relative viscosity η_{rel}	Relaxation times ^e (ms)	Fraction bound A_{slow} ($\times 10^{-3}$)
0.00025 ^c	0.04533	180.9	1.00680	1.02256	80.1 $\pm$ 6.7	44 $\pm$ 4
0.00051 ^d	0.04898	97.0	1.01074	1.03693	60.7 $\pm$ 3.7	79 $\pm$ 5
0.00106 ^d	0.04804	45.7	1.01050	1.05756	36.7 $\pm$ 2.0	175 $\pm$ 10
0.00216 ^d	0.04705	21.9	1.01084	1.10151	19.7 $\pm$ 1.3	371 $\pm$ 24
0.00353 ^c	0.04988	14.2	1.00655	1.15687	9.5 $\pm$ 1.0	805 $\pm$ 85
0.00420 ^c	0.05272	12.6	1.00662	1.18962	10.9 $\pm$ 1.1	671 $\pm$ 68
0.00702 ^c	0.04881	8.3	1.00723	1.41317	9.1 $\pm$ 3.0	640 $\pm$ 211
0.00714 ^c	0.05377	7.6	1.00651	1.48734	14.5 $\pm$ 1.3	398 $\pm$ 36

a the polymer concentration was expressed in monomer equivalent mole per mass of solvent, mole dm⁻³.

b the ratio was the mole ratio of nitrate to polymer.

c this work.

d data from G. Owens [10].

e the T_1 error was the standard deviation given by the least-square program.

Table 4-6:

Emf data for the calibration of the chloride I.S.E.

$[Cl^-]$ mol kg ⁻¹	$\sqrt{[Cl^-]}$ mol ^{1/2} kg ^{-1/2}	$\log([Cl^-])$	emf (mV)	$E+k\log[Cl^-]$	$\log \gamma_{Cl^-}$ calcul.	$\log \gamma_{Cl^-}$ literature
0.116540	0.341380	-0.9335	71.9	0.0167	0.729	0.719
0.027058	0.164493	-1.5677	105.8	0.0131	0.840	0.860
0.003631	0.060254	-2.4400	154.6	0.0102	0.937	0.943
0.000734	0.027095	-3.1342	194.2	0.0088	0.992	0.999

Data regression results:

i) $emf = a \times [Cl^-] + b$
 $a = 19.30 \pm 0.85,$
 $b = 55.64 \pm 0.51$

ii) $Emf + k \times \log([Cl^-]) = a \times \sqrt{[Cl^-]} + b$
 $a = 0.0086 \pm 0.0005$
 $b = 0.024 \pm 0.002$

Emf data for the calibration of the nitrate I.S.E.

$[NO_3^-]$ mol kg ⁻¹	$\sqrt{[NO_3^-]}$ mol ^{1/2} kg ^{-1/2}	$\log[NO_3^-]$	emf (mV)	$E+k\log$ ([NO ₃ ⁻])	$\log \gamma_{NO_3^-}$ calcul.	$\log \gamma_{NO_3^-}$ literature
0.049694	0.222922	-1.3037	71.9	0.0167	0.729	0.719
0.004723	0.068726	-2.3258	105.8	0.0131	0.840	0.860
0.000591	0.024311	-3.2284	154.6	0.0102	0.937	0.943
0.000071	0.008454	-4.1459	194.2	0.0088	0.992	0.999

Data regression results:

i) $emf = a \times [Cl^-] + b$
 $a = 19.30 \pm 0.85,$
 $b = 55.64 \pm 0.51$

ii) $Emf + k \times \log([Cl^-]) = a \times \sqrt{[Cl^-]} + b$
 $a = 0.0086 \pm 0.0005$
 $b = 0.024 \pm 0.002$

Table 4-7:

BINDING of
POLY(VINYLBENZYLTRIALKYLAMMONIUM CHLORIDE)
in an AQUEOUS SOLUTION

Methyl		Ethyl		Propyl	
base molality ^a	fraction bound	base molality ^a	fraction bound	base molality ^a	fraction bound
0.0025	0.707	0.0046	0.731	0.0023	0.748
0.0048	0.711	0.0109	0.734	0.0099	0.755
0.0100	0.714	0.0204	0.740	0.0161	0.757
0.0192	0.717	0.0317	0.751	0.0255	0.767
0.0292	0.724	0.0409	0.756	0.0348	0.775
0.0391	0.725	0.0498	0.757	0.393	0.776
0.0565	0.737	0.0553	0.759	0.0445	0.775
0.0662	0.743	0.0662	0.759	0.0520	0.775
0.0752	0.752	0.0788	0.767	0.0609	0.778
0.0848	0.753	0.0953	0.768	0.0702	0.780
0.0979	0.751				

Butyl		Pentyl	
base molality ^a	fraction bound	base molality ^a	fraction bound
0.0072	0.777	0.0074	0.805
0.0139	0.788	0.159	0.807
0.0234	0.795	0.0223	0.810
0.0381	0.797	0.0295	0.816
0.0500	0.803	0.0367	0.822
0.0687	0.808	0.0454	0.829
0.0794	0.816	0.0516	0.834
0.0871	0.822	0.0571	0.835
		0.0689	0.837

^a linear polymer concentrations were expressed in equivalent mole per kilogram of solvent.

Table 4-8: BINDING of
POLY(VINYLBENZYLTRIALKYLAMMONIUM CHLORIDE)
in a POTASSIUM NITRATE AQUEOUS SOLUTION

Poly(vinylbenzyltrimethylammonium chloride)						
Polymer molality (eqmol kg ⁻¹)	Nitrate molality (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	mole fraction of bound chloride	mole fraction of bound nitrate	Equilibrium constant K _{Cl} ^{NO₃}
0.00119		0.00036	0.00001			
0.00119	0.00004	0.00039	0.00000	0.960	0.040	4.48
0.00118	0.00007	0.00044	0.00001	0.925	0.075	2.49
0.00117	0.00015	0.00049	0.00004	0.858	0.142	2.15
0.00116	0.00026	0.00055	0.00008	0.769	0.231	2.08
0.00114	0.00044	0.00059	0.00015	0.656	0.344	2.09
0.00111	0.00064	0.00066	0.00026	0.547	0.453	2.11
0.00111	0.00081	0.00071	0.00037	0.477	0.523	2.11
0.00111	0.00126	0.00081	0.00069	0.345	0.655	2.21
0.00110	0.00150	0.00084	0.00087	0.298	0.702	2.27
0.00110	0.00194	0.00088	0.00123	0.236	0.764	2.32
0.00109	0.00251	0.00090	0.00167	0.188	0.812	2.33
0.00109	0.00318	0.00092	0.00224	0.151	0.849	2.30
0.00107	0.00480	0.00096	0.00284	0.101	0.899	2.20

Poly(vinylbenzyltriethylammonium chloride)						
Polymer molality (eqmol kg ⁻¹)	Nitrate molality (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	mole fraction of bound chloride	mole fraction of bound nitrate	Equilibrium constant K _{Cl} ^{NO₃}
0.00098		0.00026	0.00001			-
0.00098	0.00004	0.00032	0.00000	0.957	0.043	2.15
0.00097	0.00007	0.00035	0.00001	0.911	0.089	2.93
0.00097	0.00014	0.00039	0.00003	0.831	0.169	3.01
0.00096	0.00022	0.00044	0.00005	0.756	0.244	2.99
0.00095	0.00032	0.00051	0.00009	0.659	0.341	2.95
0.00094	0.00045	0.00056	0.00015	0.553	0.447	2.97
0.00092	0.00062	0.00060	0.00024	0.456	0.544	3.01
0.00092	0.00096	0.00067	0.00046	0.328	0.672	3.02
0.00091	0.00113	0.00070	0.00057	0.282	0.718	3.09
0.00091	0.00180	0.00075	0.00108	0.179	0.821	3.20
0.00090	0.00246	0.00079	0.00167	0.129	0.871	3.19
0.00089	0.00360	0.00082	0.00277	0.084	0.916	3.23

Table 4-8: (continued)

Poly(vinylbenzyltripropylammonium chloride)

Polymer molality	Nitrate molality	Free chloride	Free nitrate	mole fraction of bound chloride	mole fraction of bound nitrate	Equilibrium constant $K_{Cl}^{NO_3}$
(eqmol kg ⁻¹)	(mol kg ⁻¹)	(mol kg ⁻¹)	(mol kg ⁻¹)			
0.00103		0.00023	0.00000			-
0.00103	0.00005	0.00026	0.00001	0.950	0.050	2.25
0.00102	0.00010	0.00031	0.00002	0.888	0.112	2.84
0.00102	0.00019	0.00036	0.00004	0.782	0.218	3.46
0.00099	0.00022	0.00048	0.00012	0.582	0.418	3.63
0.00097	0.00062	0.00060	0.00022	0.448	0.552	3.62
0.00097	0.00083	0.00065	0.00034	0.358	0.642	3.65
0.00096	0.00121	0.00070	0.00058	0.256	0.744	3.72
0.00096	0.00183	0.00080	0.00105	0.168	0.832	3.76
0.00095	0.00290	0.00085	0.00203	0.099	0.901	3.79
0.00093	0.00414	0.00087	0.00325	0.067	0.933	3.74

Poly(vinylbenzyltributylammonium chloride)

Polymer molality	Nitrate molality	Free chloride	Free nitrate	mole fraction of bound chloride	mole fraction of bound nitrate	Equilibrium constant $K_{Cl}^{NO_3}$
(eqmol kg ⁻¹)	(mol kg ⁻¹)	(mol kg ⁻¹)	(mol kg ⁻¹)			
0.00131		0.00029	0.00000			-
0.00130	0.00007	0.00040	0.00001	0.938	0.062	1.99
0.00129	0.00010	0.00048	0.00002	0.905	0.095	3.38
0.00128	0.00018	0.00056	0.00003	0.824	0.176	4.45
0.00126	0.00034	0.00069	0.00007	0.676	0.324	4.79
0.00123	0.00058	0.00076	0.00014	0.516	0.484	4.97
0.00123	0.00085	0.00086	0.00027	0.384	0.616	5.19
0.00122	0.00135	0.00095	0.00053	0.250	0.750	5.33
0.00121	0.00205	0.00103	0.00105	0.152	0.848	5.46
0.00120	0.00288	0.00108	0.00179	0.100	0.900	5.56
0.00119	0.00399	0.00110	0.00285	0.067	0.933	5.38

Table 4-8: (continued)**Poly(vinylbenzyltripentylammonium chloride)**

Polymer molality (eqmol kg ⁻¹)	Nitrate molality (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	mole fraction of bound chloride	mole fraction of bound nitrate	Equilibrium constant K _{Cl} ^{NO₃}
0.00120		0.00024	0.00001			-
0.00120	0.00004	0.00028	0.00001	0.968	0.032	1.25
0.00119	0.00008	0.00033	0.00001	0.913	0.087	4.56
0.00118	0.00017	0.00042	0.00002	0.801	0.199	7.36
0.00116	0.00040	0.00051	0.00006	0.565	0.435	8.66
0.00111	0.00081	0.00066	0.00021	0.315	0.685	8.65
0.00110	0.00115	0.00073	0.00039	0.208	0.792	8.80
0.00109	0.00166	0.00079	0.00071	0.133	0.867	8.72
0.00109	0.00200	0.00082	0.00099	0.102	0.898	8.66
0.00108	0.00267	0.00084	0.00163	0.064	0.936	9.09
0.00107	0.00390	0.00089	0.00284	0.038	0.962	9.26
0.00106	0.00510	0.00090	0.00405	0.026	0.974	9.46

Table 4-9:

**BINDING of POLY(VINYLBENZYLTRIALKYLAMMONIUM SULPHATE) with
SODIUM CHLORIDE in AQUEOUS SOLUTION**

Poly(vinylbenzyltrimethylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality NaCl total (mol dm ⁻³)	molality free Cl ⁻ (mol dm ⁻³)	mole fraction chloride bound $\bar{X}_{Cl}$	Equilibrium constant $K_{SO_4}^{Cl}$
0.00112	-	0.00036	1.013	-
0.00112	0.00002	0.00038	0.994	0.07
0.00112	0.00005	0.00040	0.965	0.31
0.00111	0.00011	0.00040	0.905	0.60
0.00110	0.00019	0.00045	0.833	0.76
0.00108	0.00034	0.00048	0.732	0.91
0.00108	0.00055	0.00054	0.638	0.99
0.00107	0.00091	0.00060	0.573	1.05
0.00106	0.00167	0.00068	0.447	1.15
0.00105	0.00267	0.00073	0.391	1.25
0.00104	0.00403	0.00078	0.318	1.33
0.00102	0.00601	0.00082	0.253	1.42

Poly(vinylbenzyltriethylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality NaCl total (mol dm ⁻³)	molality free Cl ⁻ (mol dm ⁻³)	mole fraction chloride bound $\bar{X}_{Cl}$	Equilibrium constant $K_{SO_4}^{Cl}$
0.00106	-	0.00001	-0.012	-
0.00106	0.00003	0.00002	0.005	0.19
0.00105	0.00007	0.00005	0.013	0.36
0.00104	0.00015	0.00012	0.026	0.65
0.00102	0.00029	0.00024	0.045	1.09
0.00102	0.00048	0.00040	0.074	1.47
0.00102	0.00128	0.00101	0.150	1.52
0.00101	0.00194	0.00170	0.215	2.53
0.00100	0.00310	0.00276	0.291	2.76
0.00098	0.00473	0.00427	0.380	3.08
0.00096	0.00686	0.00628	0.468	3.28

Table 4-9: (continued)

Poly(vinylbenzyltripropylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality NaCl total (mol dm ⁻³)	molality free Cl ⁻ (mol dm ⁻³)	mole fraction chloride bound $\bar{X}_{Cl}$	Equilibrium constant $K_{SO_4}^{Cl}$
0.00106	0.00000	0.00001	-0.01	-
0.00106	0.00002	0.00002	0.003	0.04
0.00106	0.00006	0.00004	0.012	0.57
0.00105	0.00013	0.00010	0.027	1.07
0.00103	0.00024	0.00019	0.045	1.42
0.00101	0.00041	0.00033	0.072	1.86
0.00101	0.00063	0.00052	0.102	2.29
0.00100	0.00107	0.00091	0.151	2.70
0.00099	0.00194	0.00168	0.229	3.15
0.00098	0.00321	0.00284	0.315	3.41
0.00096	0.00485	0.00436	0.934	3.76
0.00094	0.00635	0.00659	0.502	3.93

Poly(vinylbenzyltributylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality NaCl total (mol dm ⁻³)	molality free Cl ⁻ (mol dm ⁻³)	mole fraction chloride bound $\bar{X}_{Cl}$	Equilibrium constant $K_{SO_4}^{Cl}$
0.00106	0.00000	0.00001	0.000	-
0.00106	0.00002	0.00001	0.004	0.20
0.00106	0.00005	0.00004	0.009	0.29
0.00105	0.00011	0.00009	0.021	0.74
0.00104	0.00020	0.00016	0.040	1.46
0.00102	0.00034	0.00028	0.065	2.07
0.00101	0.00053	0.00043	0.093	2.49
0.00101	0.00090	0.00074	0.143	3.18
0.00100	0.00263	0.00139	0.215	3.74
0.00099	0.00270	0.00234	0.307	4.27
0.00098	0.00410	0.00362	0.393	4.81
0.00096	0.00612	0.00548	0.500	5.59

Table 4-9:(continued)

Poly(vinylbenzyltripentylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality NaCl total (mol dm ⁻³)	molality free Cl ⁻ (mol dm ⁻³)	mole fraction chloride bound $\bar{X}_{Cl}$	Equilibrium constant $K_{SO_4}^{Cl}$
0.00112	-	0.00001	-0.008	-
0.00112	0.00001	0.00001	0.002	0.02
0.00111	0.00004	0.00002	0.011	1.39
0.00111	0.00007	0.00005	0.020	1.92
0.00110	0.00013	0.00009	0.034	2.49
0.00109	0.00022	0.00017	0.052	3.00
0.00108	0.00037	0.00028	0.077	3.47
0.00108	0.00066	0.00052	0.121	4.25
0.00107	0.00123	0.00102	0.184	4.42
0.00107	0.00209	0.00174	0.278	5.15
0.00105	0.00333	0.00287	0.362	5.92
0.00103	0.00495	0.00435	0.453	6.25

Table 4-10:

**BINDING of POLY(VINYLBENZYLTRIALKYLAMMONIUM SULPHATE)
with POTASSIUM NITRATE in AQUOUS SOLUTION**

Poly(vinylbenzyltrimethylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality KNO ₃ total (mol dm ⁻³)	molality free NO ₃ ⁻ (mol dm ⁻³)	mole fraction nitrate bound $\bar{X}_{\text{NO}_3^-}$	Association constant $K_{\text{SO}_4}^{\text{NO}_3}$
0.00121	-	0.00001	0.001	-
0.00121	0.00003	0.00002	0.006	0.51
0.00120	0.00007	0.00005	0.015	0.99
0.00119	0.00014	0.00011	0.029	1.40
0.00118	0.00026	0.00020	0.050	1.98
0.00116	0.00046	0.00036	0.080	2.54
0.00115	0.00071	0.00057	0.115	3.25
0.00115	0.00114	0.00093	0.163	3.70
0.00114	0.00183	0.00154	0.224	3.94
0.00113	0.00292	0.00250	0.315	4.99
0.00111	0.00479	0.00420	0.417	5.14
0.00109	0.00651	0.00579	0.498	5.60

Poly(vinylbenzyltriethylammonium sulphate)

molality polymer (eqmol dm ⁻³)	molality KNO ₃ total (mol dm ⁻³)	molality free NO ₃ ⁻ (mol dm ⁻³)	mole fraction nitrate bound $\bar{X}_{\text{NO}_3^-}$	Association constant $K_{\text{SO}_4}^{\text{NO}_3}$
0.00106	-	0.00001	-0.012	-
0.00106	0.00003	0.00002	0.005	0.64
0.00105	0.00008	0.00006	0.013	0.91
0.00105	0.00014	0.00010	0.026	1.75
0.00103	0.00025	0.00019	0.045	3.09
0.00101	0.00044	0.00034	0.074	4.27
0.00101	0.00063	0.00050	0.150	5.04
0.00101	0.00082	0.00065	0.215	6.26
0.00101	0.00121	0.00097	0.286	7.01
0.00100	0.00185	0.00151	0.380	8.43
0.00099	0.00285	0.00239	0.468	9.50
0.00098	0.00394	0.00336	0.468	10.11
0.00096	0.00553	0.00479	0.468	11.20

table 4-10 (continued):

Poly(vinylbenzyltripropylammonium sulphate)

molality polymer (eqmol dm^{-3})	molality KNO_3 total (mol dm^{-3})	molality free NO_3^- (mol dm^{-3})	mole fraction nitrate bound $\bar{X}_{\text{NO}_3^-}$	Association constant $K_{\text{SO}_4}^{\text{NO}_3}$
0.00108	-	0.00001	-0.006	-
0.00108	0.00004	0.00002	0.012	1.44
0.00107	0.00008	0.00005	0.026	3.44
0.00107	0.00013	0.00009	0.041	4.96
0.00106	0.00019	0.00013	0.055	5.83
0.00106	0.00026	0.00018	0.073	6.97
0.00105	0.00047	0.00034	0.119	9.02
0.00105	0.00073	0.00054	0.163	10.11
0.00104	0.00128	0.00099	0.245	11.79
0.00104	0.00205	0.00163	0.340	14.06
0.00102	0.00326	0.00265	0.454	16.18
0.00101	0.00490	0.00409	0.569	18.23

Poly(vinylbenzyltributylammonium sulphate)

molality polymer (eqmol dm^{-3})	molality KNO_3 total (mol dm^{-3})	molality free NO_3^- (mol dm^{-3})	mole fraction nitrate bound $\bar{X}_{\text{NO}_3^-}$	Association constant $K_{\text{SO}_4}^{\text{NO}_3}$
0.00103	0.00000	0.00000	0.000	-
0.00103	0.00001	0.00002	0.006	1.16
0.00102	0.00003	0.00006	0.009	3.63
0.00101	0.00006	0.00010	0.016	5.83
0.00101	0.00008	0.00014	0.031	7.70
0.00100	0.00011	0.00021	0.050	9.11
0.00100	0.00018	0.00041	0.070	10.34
0.00099	0.00028	0.00066	0.080	12.44
0.00099	0.00068	0.00121	0.189	14.50
0.00098	0.00153	0.00199	0.308	19.11
0.00096	0.00298	0.00324	0.478	21.24
0.00094	0.00495	0.00503	0.598	23.89

Table 4-10 (continued):

Poly(vinylbenzyltripentylammonium sulphate)

molality polymer (eq mol dm ⁻³)	molality KNO ₃ total (mol dm ⁻³)	molality free NO ₃ ⁻ (mol dm ⁻³)	mole fraction nitrate bound $\bar{X}_{\text{NO}_3^-}$	Association constant $K_{\text{SO}_4}^{\text{NO}_3}$
0.00112		0.00001	0.005	
0.00112	0.00002	0.00001	0.008	3.39
0.00112	0.00005	0.00003	0.020	7.48
0.00111	0.00011	0.00006	0.041	10.67
0.00110	0.00020	0.00012	0.070	14.61
0.00109	0.00031	0.00020	0.101	16.33
0.00109	0.00049	0.00032	0.144	19.71
0.00109	0.00078	0.00053	0.200	20.90
0.00108	0.00121	0.00086	0.274	23.60
0.00107	0.00191	0.00143	0.370	25.60
0.00106	0.00302	0.00235	0.484	27.56
0.00105	0.00438	0.00351	0.588	29.82

STUDY of the ANION / CROSS-LINKED POLYMER ASSOCIATION

5-1 PRESENTATION

The association between some common anions found in water, namely chlorides, nitrates and sulphates, and some monomer analogues and their linear polymerised forms had been studied. The survey showed a certain affinity of these different cations towards nitrates.

The same study was carried out with the cross-linked polymer forms, the usual structure of an ion exchange resin. The synthesis part was detailed in paragraph 1-3 of "Materials and methods" chapter. It is known that polymerisation tends to enhance the properties observed in the monomer species. The selectivity of an ion exchange resin relies on the ion pair formation phenomena of the different ions in solution. We want to compare the binding of the cross-linked polymers with the anions and with results already discussed with monomers and linear polymers. An understanding of the structural effects on the nitrate selectivity was the aim of this work. Specifically, two sets of polymers were tested, one highly and the other less cross-linked respectively 9.0 and 22.1 % (mole/mole) divinylbenzene, (DVB).

Some chemical and physical properties were discussed such as the basicity, the capacity, the cross-linking degree.

5-2 PROPERTIES OF THE CROSS-LINKED POLYMERS

5-2-1 Chemical property

The determination of the nature (basicity or acidity) of the exchange group is of considerable importance for the use or the regeneration of the resin [25]. A titration of the resin is usually enough to clarify. In our case, the knowledge of the exchange group, phenolic quaternary ammonium, indicates a weak basic resin [53], and a working limit temperature around 60 °C [25 b]

Butler insufficient

5-2-2 The capacity

The capacity is a characteristic parameter of a resin which appraises the amount of exchangeable ions in milliequivalents per ml. It can be deduced from the inflection point of a titration curve [24], or simply be calculated from the number of groups capable of entering into an ion exchange reaction [25]. It has also been determined [13,15] by elution of a chloride form resin with 1 M NaNO₃ solution and analysis for chloride.

We calculated the capacity from the amount of chloride freed when co-ions were added in the cell, while an affinity measurement was done. A limit for level of free chloride was reached. This amount corresponded to the exchange capacity of the polymer. The most stable dissociated chloride values were averaged, then divided by the mass of resin input and by the density of the polymer to get an exchange capacity expressed in meq ml⁻¹; the results obtained were in table 5-1.

Table 5-1: Capacity of the resin in meq/ml of the different polymers.

	methyl	ethyl	propyl	butyl	pentyl
Low cross-link	2.30	2.35	2.34	2.30	2.34
High cross-link	1.82	1.76	1.66	1.55	1.52

The capacities of each set of polymers were similar. The nature of the alkyl groups and the different cross-linking degree had a little effect on the capacities, which decreased slightly for the high-cross-linked polymers. They were in the range or slightly higher than the usual values found in the literature [14,15]. The Amberlite IRA 400-Cl capacity given by the producer was 1.4 meq ml⁻¹.

5-2-3 The density

At first, the polymer capacities were expressed in meq g⁻¹ of resin. Densities were measured to convert the exchange capacity to meq ml⁻¹, the usual units. They were calculated from the mass change of pycnometers when filled with water plus a known mass of solid material.

A 50 ml pycnometer was cleaned using chromic acid, rinsed with Milli-Q water and tared, M_{tare} , then filled with water only and weighed M_{pycno} . A mass of polymer was placed in a pycnometer, ($M'_{poly} = M_{poly} + M_{tare}$), which was filled up with water and weighted, M'_{pycno} . The pycnometer volume was constant being capped by a stopper. The resins input had previously been rinsed with water, tap vacuum dried in a sintered funnel for 30 min. The polymer density was calculated from the volume of water displaced by the polymer when introduced. This volume was obtained from the mass of water displaced by the polymer $M_{water\ displ.}$, mass obtained by comparing the two masses of the pycnometer M_{pycno} and M'_{pycno} when filled with water or with polymer and water:

$$M_{pycno} = M_{water} + M_{tare} \quad (5-1)$$

$$M'_{pycno} = M_{poly} + M'_{water} + M_{tare} \quad (5-2)$$

The mass and the volume of the polymer can be deduced the mass and the water density:

$$M_{water\ displ} = M_{water} - M'_{water} \quad (5-3)$$

$$M_{water\ displ} = M_{pycno} - (M'_{pycno} + M'_{poly}) \quad (5-4)$$

$$V_{\text{poly}} = \frac{M_{\text{water displ}}}{\rho_{\text{water}}} \quad (5-5)$$

where $\rho_{\text{water}} = 0.997048 \text{ g cm}^{-3}$ and the polymer density is readily available:

$$\rho_{\text{poly}} = \frac{M_{\text{poly}}}{V_{\text{poly}}} \quad (5-6)$$

From the densities, the conversion of the capacity of the polymer from eq g^{-1} to eq ml^{-1} was possible.

Table 5-2: density of cross-linked poly(vinyl-benzyltrialkylammonium chloride)

Low cross-linked

9.0 % DVB	methyl	ethyl	propyl	butyl	pentyl
M_{tare}	29.83417	29.83425	29.83407	29.83422	28.83413
M'_{poly}	30.65843	30.75097	30.47549	30.62141	30.74183
M_{pycno}	79.51048	79.51080	79.51064	79.51036	79.51084
M'_{pycno}	79.54211	79.54627	79.53549	79.54147	79.54724
M_{poly}	0.82426	0.91672	0.64142	0.78719	0.90770
Density	1.03684	1.03718	1.03723	1.03807	1.03870

High crossed-linked

21.4% DVB	methyl	ethyl	propyl	butyl	pentyl
M_{tare}	29.78722	29.78728	29.78751	29.78707	28.78110
M'_{poly}	30.27118	31.48465	30.01019	30.66017	29.63950
M_{pycno}	79.66003	79.71355	79.64674	79.68172	79.67575
M'_{pycno}	79.63741	79.63751	79.63720	79.63731	79.63734
M_{poly}	0.48396	1.69737	0.22268	0.87310	0.85840
Density	1.04593	1.04381	1.04168	1.05048	1.04375

At similar cross-link degree, the density were around 1.037 ± 0.001 and 1.044 ± 0.003 for respectively the low and high cross-link polymers. A higher cross-link degree had a small effect on the density of the polymer.

5-2-4 The cross-linking degree

Cross-linking provides anchoring points for the chains which form a three-dimensional network and maintain the position of the chain. It brings structure and some rigidity proportional to the cross-linking degree. Free spaces formed by the structure, can be filled with ions depending on their size, and their charge. The amount of cross-linking determines the size of these free spaces. It is therefore an important selectivity factor. For example, a 2 % DVB cross-linked resin will be able to separate some polypeptides, and while a 24 % will not retain ions bigger than 0.4 nm wide. Therefore, selectivity increases with the cross-linking degree [24^c,25^a].

The proportion of DVB added can vary from 1 % to 20 %. An average figure is about 8 % [53]. High nominal levels of cross-linking up to 25 % have been mentioned [13]. They refer to the amount of cross linker compare to monomer input in the original mixture before polymerisation [53,25^d]. Two questions remain in that method, how can one be sure that none of the reactant have been lost, and how to appraise if the cross-linker has reacted with the monomer or with itself? Several methods were tried and appraised.

5-2-4-1 The glass transition T_g

The glass transition T_g could provide an answer. When a solid polymer is heated up, dramatic reversible changes in the physical properties, such as hardness and elasticity, occurs. In the initial glass-like transition, the chains of the amorphous state are frozen, as a solid, with a random structure. Above T_g , in the rubber-like state, chains are in relatively loose motion [79^a]. T_g is a second order transformation which enthalpy can be detected using a Perkin-Helmer type 2 DSC machine. Unfortunately, no signals were

detected with our sample. It was thought that T_g was too high and was concealed by the much bigger melting signal.

5-2-4-2 Microanalysis

Microanalysis was used to determine C, H, N for five samples methyl, ethyl and pentyl in Melbourne [81]. Dried in vacuum oven and kept in a desiccator, the analysis was requested in dry atmosphere and in duplicate, and results were tabulated. Chloride proportions were calculated, assuming an equal ratio of chloride to nitrogen, because of the charge balance.

Knowing the mass percentage of nitrogen in the monomers and assuming that 1 g of sample contained (1-x) g of monomer and x g of DVB, the cross-link ratio was established from the microanalysis results and expressed in mole fraction of DVB, X_{DVB} .

Table 5-3: DVB proportion from microanalysis.

	methyl	ethyl		pentyl	
cross-linking	high	low	high	low	high
% C	60.16	62.62	65.69	68.29	72.83
% H	8.76	9.94	10.24	10.31	10.39
% N	5.27	5.00	4.34	3.36	2.84
% Cl	13.36	12.68	11.00	8.52	7.21
total	87.55	90.24	91.27	81.48	93.27
X_{DVB}	0.203	0.092	0.212	0.088	0.228

The four elements, C, H, N and Cl, represented around 90 % of the constituent of the polymers, which was a reasonable value for polymer microanalysis. Moisture contamination might be responsible of the missing 10 %, especially oxygen. The DVB mole fraction calculated was around 0.090 for the low cross-link, and 0.214 for the high ones. Those results were quite similar and could be compared to the initial reactant proportion, around 0.10 and 0.55 %. Half of the cross-linker was not used for the

polymerisation of the high cross link and 10 % for the other one. Maybe a mole fraction of 0.21 could represent an upper limit for a cross-linking degree.

Five samples out of ten were sent for microanalysis, and the amount of DVB was needed to be confirmed for the others. Microanalysis gave the proportion of cross-linker in the polymer, without specifying how DVB was attached to the rest of the whole polymer, or how much of it was used as cross-linker?

5-2-4-3 Water retention

Water retention or water regain method allowed the measurement of the cross-linking degree. It is based on the inverse proportionality between the water retained by a resin and its cross-linking factor. When in contact with a solvent, a polymer swells. The augmentation of the size is inversely proportional to the cross-linking. Mc Laren and Rowen [82], Boyd and Soldano [83] were among the first to study the variation of the mass of water in polymers depending on their different cross-linking in a different moisturised atmosphere. Inspired by their work, a known mass of the samples were placed in watch glasses previously tared. They were left to equilibrate at room temperature (25 ± 1 °C) in a controlled moisture atmosphere for 4 weeks in a desiccator, placed above a large quantity (≈ 250 cm³) of NaCl or Na₂SO₄ solutions which provided a 75 % or 93 % relative humidity. The samples were weighed, dried over night in a vacuum oven at 50 °C, and weighed again until no significant mass loss was recorded. The results were tabulated in the table 5-13 and summarised in table 5-4.

Table 5-4: Mole number of water retained per monomer equivalent mole of the cross-linked polymers.

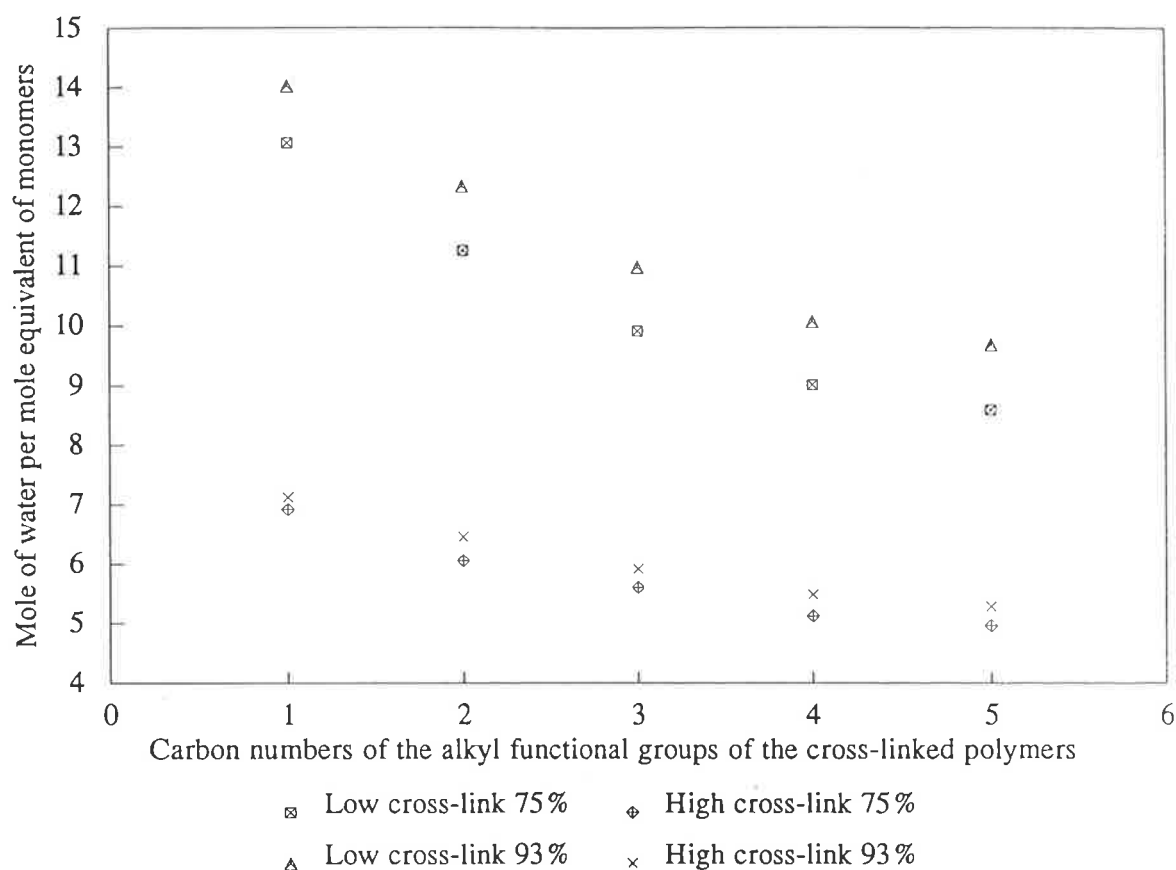
Relative humidity	cross-linking	methyl	ethyl	propyl	butyl	pentyl
75 %	9% DVB	13.06	11.26	9.92	9.02	8.59
75 %	22 % DVB	6.92	6.06	5.63	5.13	4.96
93 %	9 % DVB	14.02	12.34	10.99	10.08	9.69
93 %	22 % DVB	7.12	6.45	5.92	5.49	5.27

In a 75% relative humidity, the number of mole of water retained per equivalent of monomer varied from 8.5 up 13 and from 5 to 7 for the low and high cross-linked polymers respectively. This amount was large. It was enhanced by the small functional groups such as methyl. They possibly provided a less hydrophobic environment around the charge of the functional group, than larger one like butyl or pentyl. G. Owens [59] showed that the solubility in water decreased with the size of the alkyl functional groups. It was not surprising that the low cross-linked polymers would retain more water than the high one since the cross-linker agent, DVB, was quite hydrophobic. A higher cross-linking also meant a more rigid structure which would hindered a high water retention.

In a 93 % relative humidity, the phenomena observed previously in a 75 % relative humidity was even augmented. The moles of water kept by monomer unit of the polymer raised from 9.7 up 14 and from 5.2 to 7.1 for the low and high cross-link polymers respectively.

A plot of the water retained for the different polymers in the different atmosphere versus the size of the functional group was included, graph 5-1. It showed that 1) a high moisturised atmosphere let the polymers absorb more water, in a non linear way; 2) that water retention decreased with the length of the alkyl functional group and the cross-linking degree. Long alkyl chains were responsible for the hydrophobic behaviour of the monomers, the benzyltriethylammonium chloride was hardly soluble in water [59]. The

cross-linker was DVB, which is also hydrophobic. A similar trend was observed by Boyd and Soldano [83] with a 6 % and 12 % DVB Dowex-1 anion-exchanger. Water molecules were more numerous when the polymer network was more hydrophilic.



Graph 5-1: Water retained by the different polymers in 75 % and 93 % controlled humidity atmosphere

5-2-4-4 Conclusion

The polymers studied were able to retain a large amount of water. This amount decreased with the cross-linking and the long alkyl groups. These results confirmed a certain hydrophilic character shown by the monomers which decreased with the length of the alkyl groups [59]. The amount of water retained by the 2 different cross-linked sets of polymers decreased regularly with the length of the alkyl groups. It indicated that cross-linking degree was homogeneous among the different polymers of either low or

high DVB ratio. This ratio was previously established by microanalysis for five samples measured and they were 9.0 and 21.4 % mole of DVB for the low and high cross-linked degree respectively. This result was promising since water retention was directly related to the cross-linking degree and that this trend had been previously observed with another anionic exchanger [83]. For further calculations, low and high cross-link degrees were taken as they were given by microanalysis when measured, and as 9.0 and 21.4 %, for the other polymers.

5-3 THE EMF EXPERIMENTATION

Polymers were initially in the chloride or nitrate form. Adding a nitrate and a sulphate solution and using the corresponding ion selective electrodes I.S.E., the nitrate/chloride, sulphate/chloride, nitrate/sulphate selectivities were studied. The electrodes were calibrated. The experimental conditions and the materials used were the same as described for the selectivity study of the linear polymers.

5-3-1 The chloride nitrate affinity

5-3-1-1 Calibration of the working electrodes

Four reference solutions were prepared by weight with some AR grade BDH potassium chloride. The molalities covered a range from 1.1654×10^{-1} to 7.4×10^{-4} mole kg^{-1} . A plot EMF(mV) versus $\log ([\text{Cl}^-])$ allowed us to check the reliability of the electrode through the slope of the function. Chloride activity coefficients were calculated and compared to the literature following the procedure described in chapter 2.

Four new potassium nitrate reference solutions were prepared by weight; the concentrations covered a range from 4.969×10^{-2} to 7×10^{-5} mole kg^{-1} . The slope of the function emf (mV) versus $\log ([\text{NO}_3^-])$ were verified, the activity coefficients calculated. Both electrode systems gave satisfactory results and a daily calibration has been done. The activity coefficients of the anion species were in agreement with those found in the literature.

5-3-1-2 Experimental and results

Experimental: About 0.45 g of the cross-linked polymer in chloride form (dried in the vacuum for two hours at least) was mixed with 32 g of MQ water in a cell. Some aliquots of a potassium nitrate stock solution (5.70021 g of AR grade BDH salt in 445.70 g of MQ water) were weighed and added. The emf readings were recorded after 10 and 30 min, to check that the electrodes were stable with the time.

The molecular masses of the cross-linked polymers were worked out taking into account the identical vinyl monomers and the cross-linker. A DVB contribution ($M_{\text{DVB}} = 131.18$) was added. Knowing that one polymer was 9.0 % mole cross-linked and the others 21.4 %, a molecular mass contribution was calculated. The monomer analog mass M_{ma} were $M_{\text{ma}} = 0.910 \times M_{\text{m}} + 0.090 M_{\text{DVB}}$ and $M_{\text{ma}} = 0.786 \times M_{\text{m}} + 0.214 M_{\text{DVB}}$ for the low and high cross-linked respectively where M_{m} was the monomer masses. Data were included in table 5-5. The polymer equivalent molality varied from 0.066 down to 0.044 and from 0.061 down to 0.037 mol kg^{-1} for both sorts of polymers during the experiment.

Table 5-5: Masses of the analog monomers and amount of reactant input in the cell.

Low cross-linked	methyl	ethyl	propyl	butyl	pentyl
M_{ma} 9.0 %	204.41	242.76	281.03	319.34	358.11
Mass polymer (g)	0.44240	0.43203	0.40837	0.49429	0.49406
Mass water (g)	32.8002	31.8522	32.0844	31.5138	31.5167

Table 5-5: continued.

High cross-linked	methyl	ethyl	propyl	butyl	pentyl
M _{ma} 21.4 %	195.18	227.80	260.39	293.45	323.17
Mass polymer (g)	0.38959	0.39034	0.38926	0.35731	0.34503
Mass water (g)	32.5536	22.5990	32.7525	32.9868	32.548

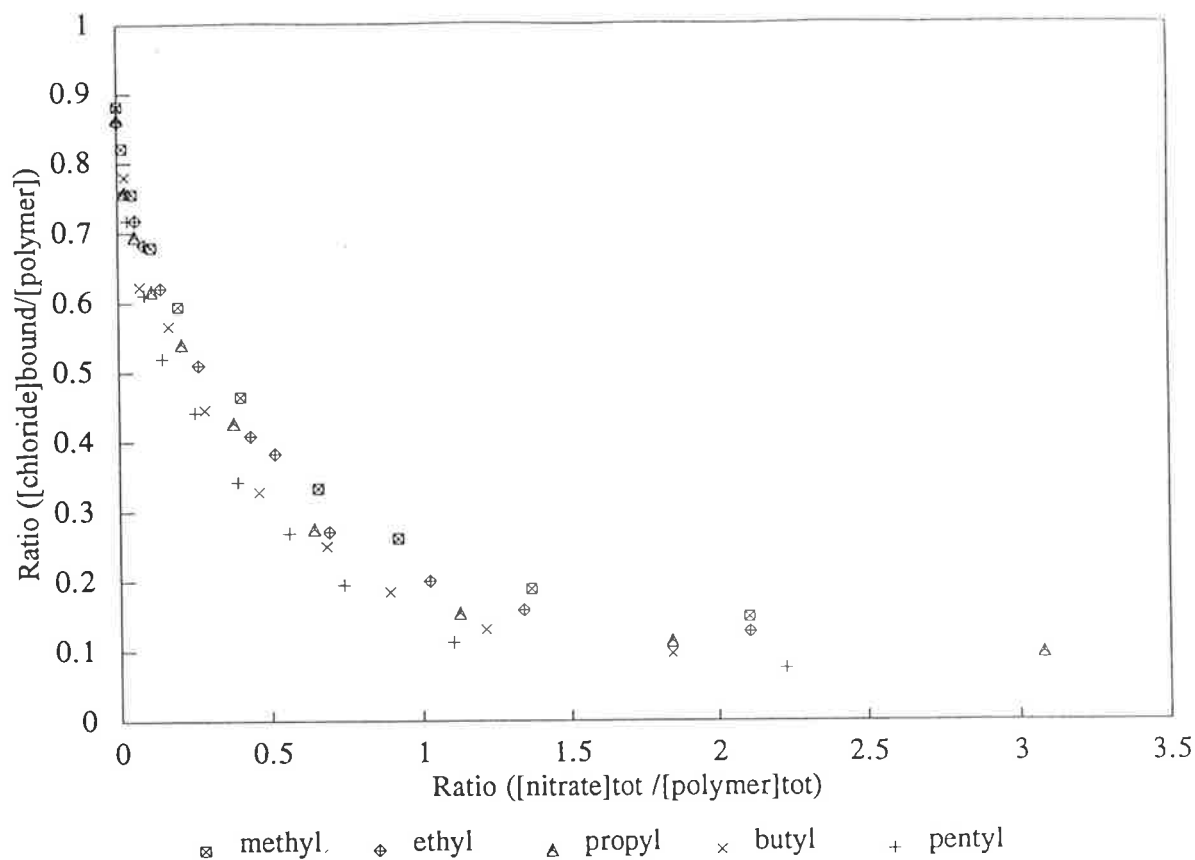
The chloride binding: Before adding any nitrates, the chloride binding to the cross-linked polymers in water was measured and expressed in mole ratio of chloride bound over the total chloride.

Table 5-6: Chloride binding to the polymers in water.

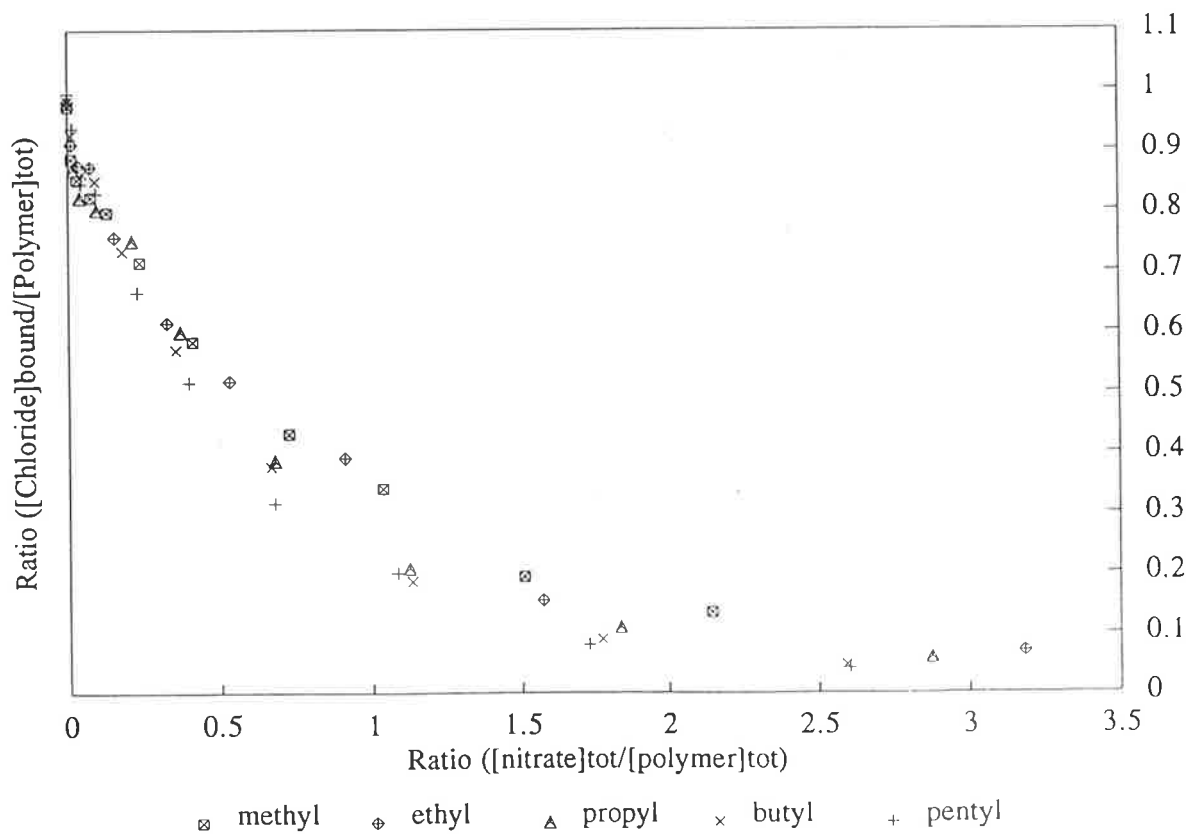
	methyl	ethyl	propyl	butyl	pentyl
Linear polymers	0.695	0.735	0.754	0.779	0.800
Low cross-linked polymers	0.882	0.859	0.864	0.879	0.865
High cross-linked polymers	0.927	0.939	0.935	0.943	0.949

The cross-linking raised the chloride binding ratio, above 0.85, higher than the linear polymer values. The binding increased slightly with the length of the alkyl groups and the cross-linking. ^A similar trend was observed for the monomers by Steel et al. [12]

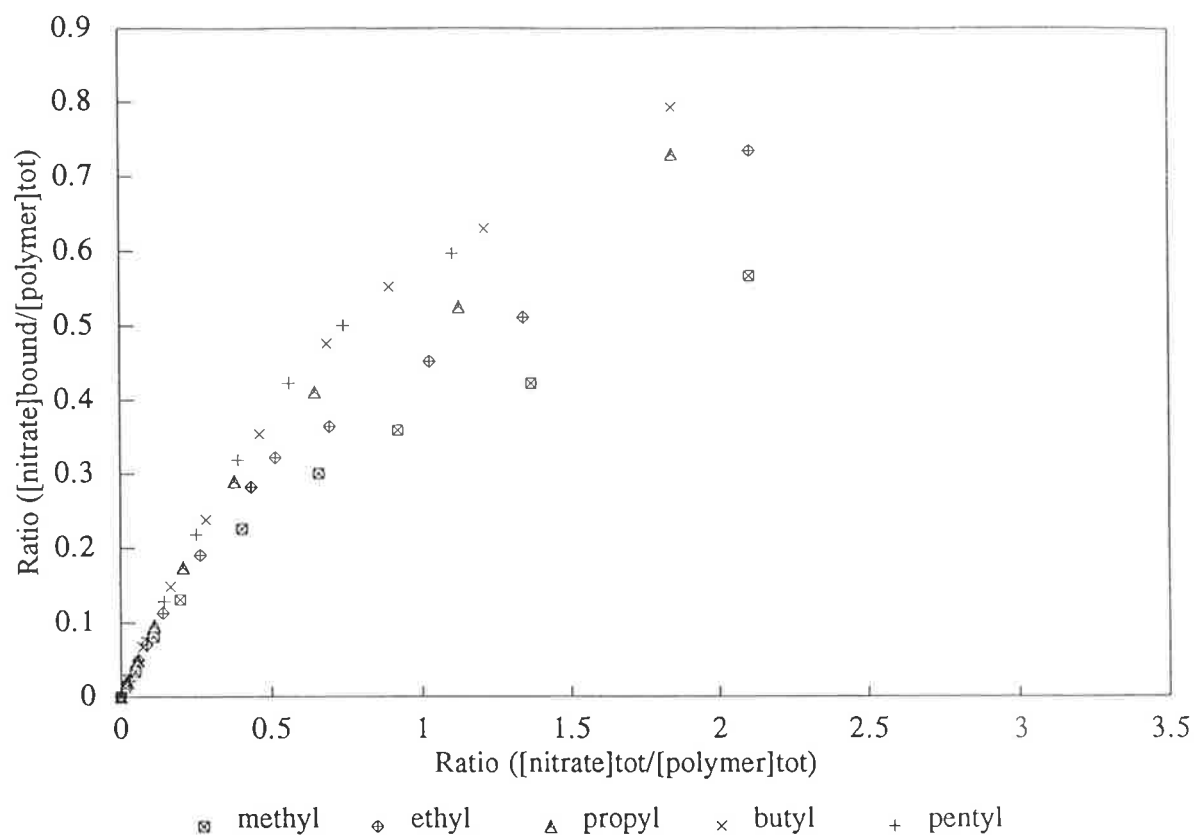
When the co-ion solution was added, the different bindings were illustrated on graphs 5-2, 5-3, 5-4, 5-5. The ratio of a bound species over the polymer equivalent base molality was plotted versus the ratio of the total concentration of the same species over the equivalent base molality of the polymer. This allowed us to visualise the trend of the fraction bound species versus the amount of polymer and versus the total amount of that particular species.



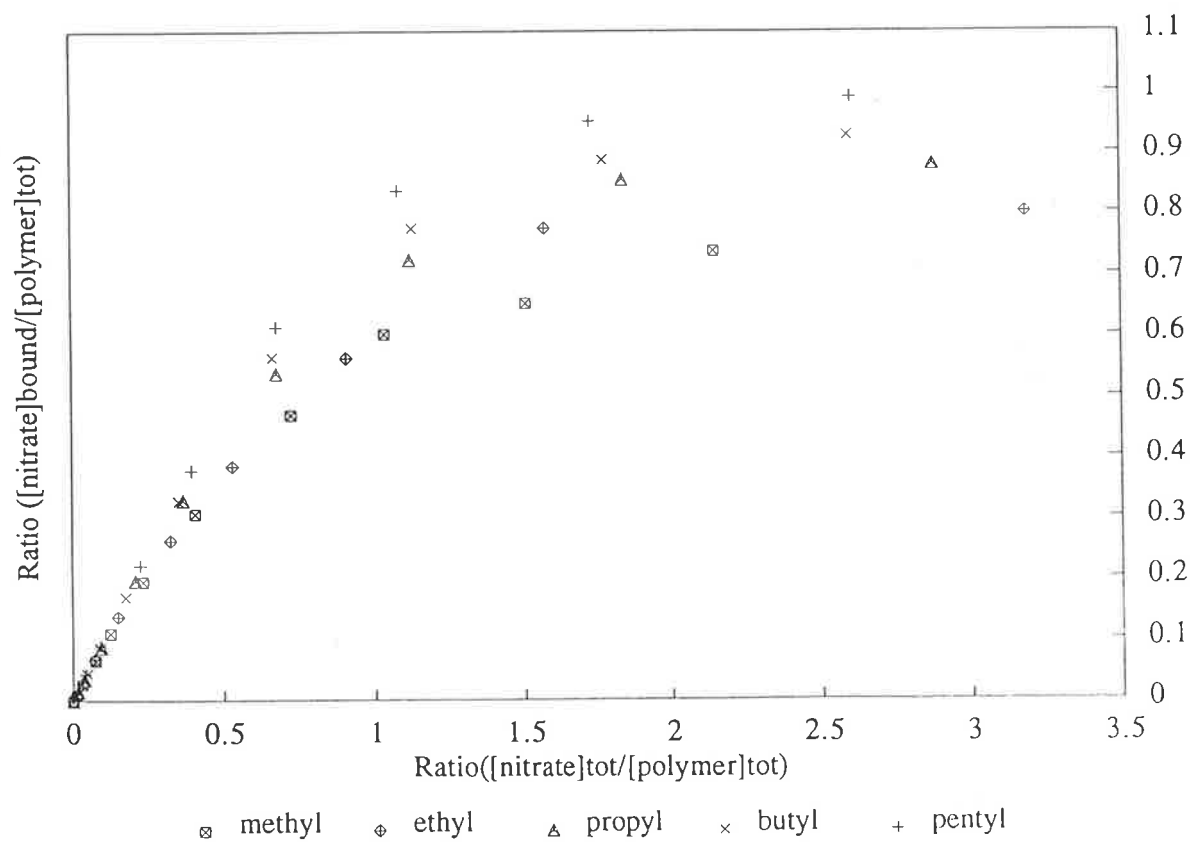
Graph 5-2: Chloride bound to low cross-linked polymers, nitrates as co-anions.



Graph 5-3: Chlorides bound to high cross-linked polymers, nitrates as co-anions.



Graph 5-4: Nitrates bound to low cross-linked polymers, chlorides as co-anions.



Graph 5-5: Nitrates bound to high cross-linked polymers, chlorides as co-anions.

The chloride binding diminished steadily, when the nitrate solution was introduced, graph 5-2, 5-3. The bound chlorides remained higher for the high cross-link polymers, and for the shorter alkyl chain attached on the quaternary ammonium binding site of the polymers. At the end of the experiment, the nitrate concentration was about three times the nitrate polymer base molality and the ion exchange rate was found stable. For both polymers, most of the chloride ions were already free when nitrates and chlorides had the same concentration.

The nitrate binding: Most of the nitrates first added would bound, see graph 5-4 and 5-5. Then a limit was reached and the bound nitrate curve flattened off well displayed for the low cross-link degree. Most of the further nitrates added were measured free. The level of that limit depended on the sample and was a measure for the resin affinity with the chloride dissociation. On graph 5-5, for example, this saturation phenomena was already observed for all the samples at a ratio nitrate/polymer of 1.5. The low cross-linked polymers, graph 5-4, were still able to fix more nitrates from the solution added. The high cross-link polymers were able to retain more nitrates faster. Nitrates bound more to the long functional groups, pentyl and butyl, for both polymers.

5-3-1-3 Conclusion

When nitrates were introduced as co-ions, chloride association decreased, and remained slightly higher with short alkyl groups and high cross-link polymers. Nitrate association was enhanced by longer functional alkyl groups and high cross-linked degrees. Low cross-linked polymers had a looser structure, which probably allowed anions to be easily freed, but the same loose structure could not keep as many nitrates. The stoichiometry, for the exchange one free chloride against one bound nitrate, was respected for the low cross-linked polymers. The high cross-linked polymer could fixed more nitrates. When both anions were equally present in the solution, nitrates tended to be more associated to the polymer, especially with long alkyl chain and a high cross-linking. We showed that

nitrate were preferred by high cross-linked polymers, and large hydrophobic groups fixed on the quaternary ammonium.

5-3-2 The chloride sulphate affinity

5-3-2-1 The lead ion-selective electrode

The sulphate concentrations were estimated indirectly by potentiometric titration. It consisted of determining the end point in the direct titration of free lead which had not precipitated under the PbSO_4 form when a standard sulphate solution was added.

The insolubility of the lead sulphate can be improved by addition of a less polar solvent, for example methanol [83], ethanol [84], dioxan [83-87], or isopropanol [83,84,86]. Therefore, titration of smaller concentration was possible. A potassium sulphate solution, $0.07411 \text{ mol kg}^{-1}$, was titrated using a lead nitrate solution, $0.33938 \text{ mol kg}^{-1}$. Some organic solvents, such as ethanol (BDH), dioxan (M&B) and isopropanol (BDH), all AR grade, were tested one at the time, and represented 55 % of the initial solvent present in the cell. This ratio diminished to 45 % at the end of the titration. The inflection point was determined experimentally and compared to the calculated value. Dioxan gave a result more accurate, within 1 % of the calculated answer, and it improved the shape of the titration.

This good result may be explained by the concentration ranges used were 100 times above than the threshold cited [83,85-87]. Attempts with water as a solvent gave results within 12 % when compared to the water dioxan solvent. The second problem involved contamination by chlorides coming from the initial form of the cross-linked polymer introduced. Some titrations were made with a ratio sulphate/chloride (1:3) and (1:10). They were compared to a chloride free control. For the (1:10) ratio, the end point was within 4 % of the calculated one, and the shapes of both curves were very similar.

The outer chamber of the double junction reference electrode was filled with NaNO_3 0.1 M mixed with the same volume of organic solvent used [86]. The lead electrode was

polished before each experiment using 0.3 micron alpha alumina (Buehler micropolish) [83,86]. The samples were vigorously stirred; a failure of the stirrer gave some erratic data. The other experimental conditions were previously described.

Calibration tests were made from the slope of the direct lead measurements by a known concentration sulphate solution and the effect of adding dioxan to obtain the end point. The slope of the function emf versus $\log([\text{Pb}^{2+}])$ was $25.2 \pm 0.2 \text{ mV mol}^{-1}$ compared to $27 \pm 3 \text{ mV mol}^{-1}$ given in the Orion notice.

The freshly polished ion-specific lead electrode was optimised using a 50 % water/dioxan mixture as a solvent (v/v). In the working range employed here, the chloride did not interfere considerably as already mentioned [83-85].

5-3-2-2 Experimental and results

The experimental conditions were similar to the other potentiometric measurements, done at $25.00 \pm 0.02 \text{ }^{\circ}\text{C}$, stirred constantly and high purity argon was bubbling through during all of the measurement.

The polymers were dried in a vacuum oven, kept in desiccator containing P_2O_5 as a drying agent. Nine cells were filled with from 0.3 up to 0.5 g of polymer, depending on the molecular weight to get the same mole number, and around 40 g of water was added. Free chloride molalities were measured using the chloride I.S.E.. Ammonium sulphate (BDH AR grade) solution was added to cover a range ratio (sulphate/equivalent chloride) from 0.07 up to 3 among the 9 samples. Then the free chlorides were measured again (emf). The total chlorides were known from the mass of polymer first introduced.

The polymer was filtered off using a sintered glass funnel and a tap vacuum. Sulphate indirect titrations were performed on each sample. A known mass (around 10 g) of the solutions was titrated using one of the 3 different lead nitrate (BDH, AR grade) concentration solutions, respectively $m = 0.003, 0.050$ and $0.150 \text{ mole kg}^{-1}$, depending on the sulphate concentration expected. The solvent was a dioxan MQ water mixture 70-30 (v/v). A 10 % KNO_3 outer filling solution for the outer chamber of the reference

electrode was prepared from the same solvent. The titration was done by weight and the emf values were recorded when they had stabilised (usually after 5 min when vigorously stirred). The end point of the curves emf versus the number of lead moles added, (n_{Pb} added), also indicated the free sulphate amount in mole.

From the total mass of solution input, the solvent mass was obtained and the sulphate molalities calculated. Emf measured the free chlorides, after each addition of a sulphate aliquot. The total chloride concentrations were calculated from the total mass of polymer input, and the bound chlorides deduced from the total minus the free ones. The bound concentrations were expressed in mole numbers over the mass of polymers, or "solid molality". The reactant masses input initially in the cell were gathered in table 5-7:

Table 5-7: Amount of polymer and water input in cells.

	methyl	ethyl	propyl	butyl	pentyl
M_{MA} 9.0 %	204.41	242.76	281.03	319.34	458.11
Mass polymer (g)	0.28792	0.30940	0.37168	0.39714	0.45195
Mass water (g)	40.9628	39.3729	39.7122	39.9500	39.5011
M_{MA} 21.4%	195.18	227.80	260.39	293.45	323.17
Mass polymer (g)	0.26907	0.30494	0.36311	0.39855	0.42933
Mass water (g)	41.1072	39.8490	40.7371	40.1293	40.4460

5-3-2-3 The anion binding

Before adding any sulphate, the initial amount of chloride bound to the cross-linked polymers were measured, data were input in table 5-8. Most of the chlorides remained bound to the cross-linked polymers in aqueous solution. A long alkyl chain and high cross-linking degree increased the binding.

Table 5-8: chloride binding in water before co-ion was added.

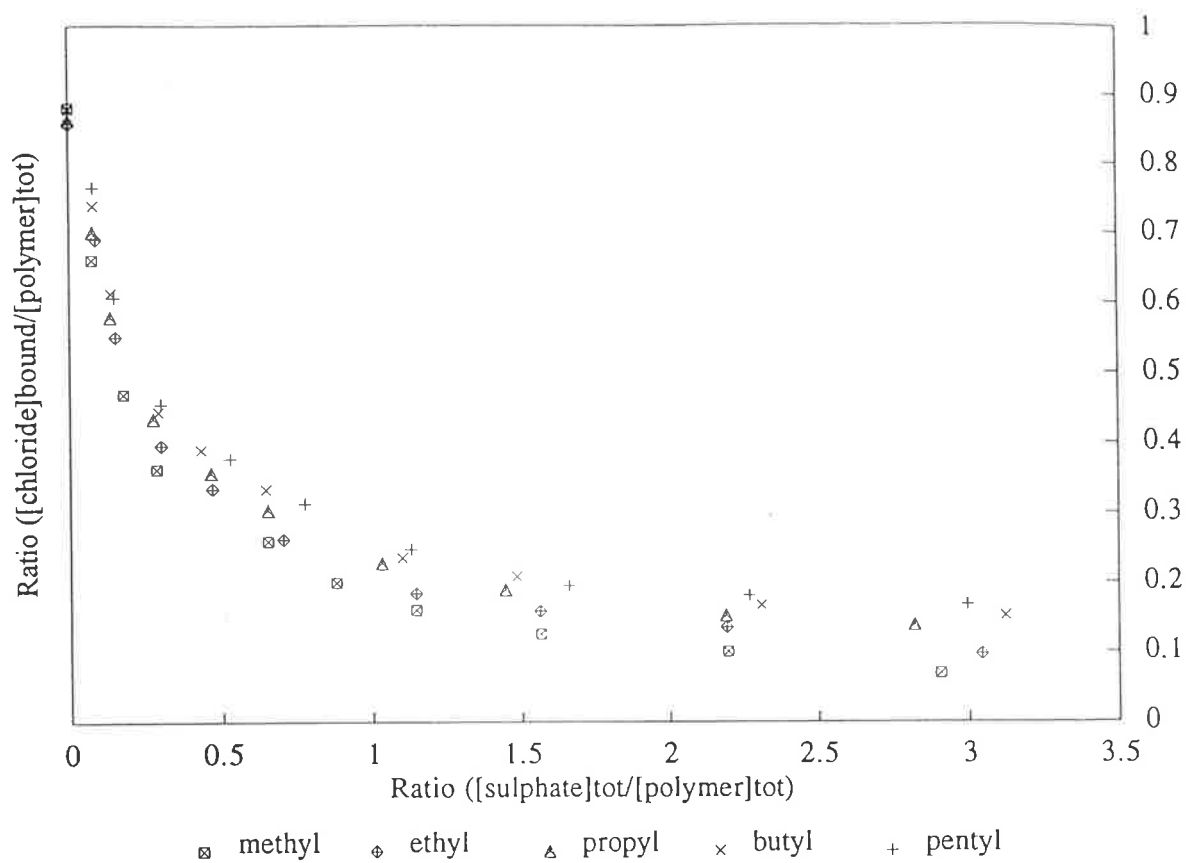
	methyl	ethyl	propyl	butyl	pentyl
Low cross-linked Cl/NO ₃	0.882	0.859	0.864	0.879	0.865
High cross linked Cl/NO ₃	0.927	0.939	0.935	0.943	0.949
Low cross-linked Cl/SO ₄	0.876	0.884	0.868	0.866	0.863
High cross linked Cl/SO ₄	0.924	0.922	0.927	0.910	0.933

When sulphates were added, the concentration of bound chlorides diminished steadily, graph 5-6 and 5-7. It decreased more for shorter alkyl groups, and for the low cross-linked polymer. The phenomena flattened off for a ratio sulphate/chloride of 1.5, thus when the ionic strength due to the sulphates was thrice the chloride contribution. At the end of the experiment, sulphate concentrations were thrice chloride equivalent base molalities. The chloride binding remained slightly higher with sulphate as co-ions than with nitrates.

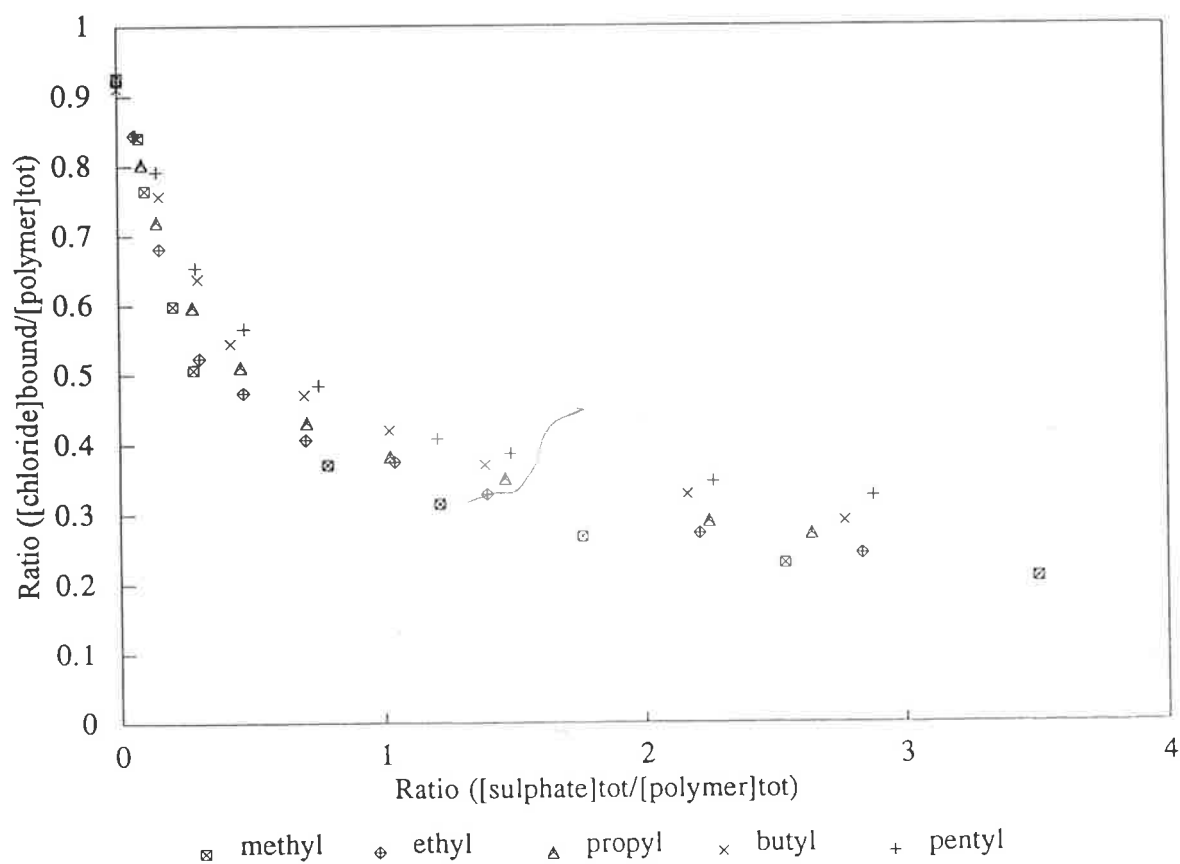
Graphs 5-8 and 5-9 illustrated the regular increase of bound sulphates when the ammonium sulphate solution was added. Bound sulphates amount increased notably for both the low and high cross-linked polymers and, in a less extent, for short alkyl groups. It was interesting to notice that the stoichiometry of the chemical exchange $\text{SO}_{4,\text{bound}}^{2-} = 2 \times \text{Cl}_{\text{free}}^{-}$ was not respected. The sulphate fixation kept on increasing when almost as many sulphates were measured bound as the polymers capacity, even if the slope of the bound sulphate curves tended to flatten off for the higher ratio (sulphate/polymer). It implied that most of the sulphates were bound to a single polymer positive charge. For the low cross-linked polymer, the amount of bound sulphates was even larger. It was then likely that electrostatic neutralisation was not the only binding way for sulphates.

5-3-2-4 Conclusion

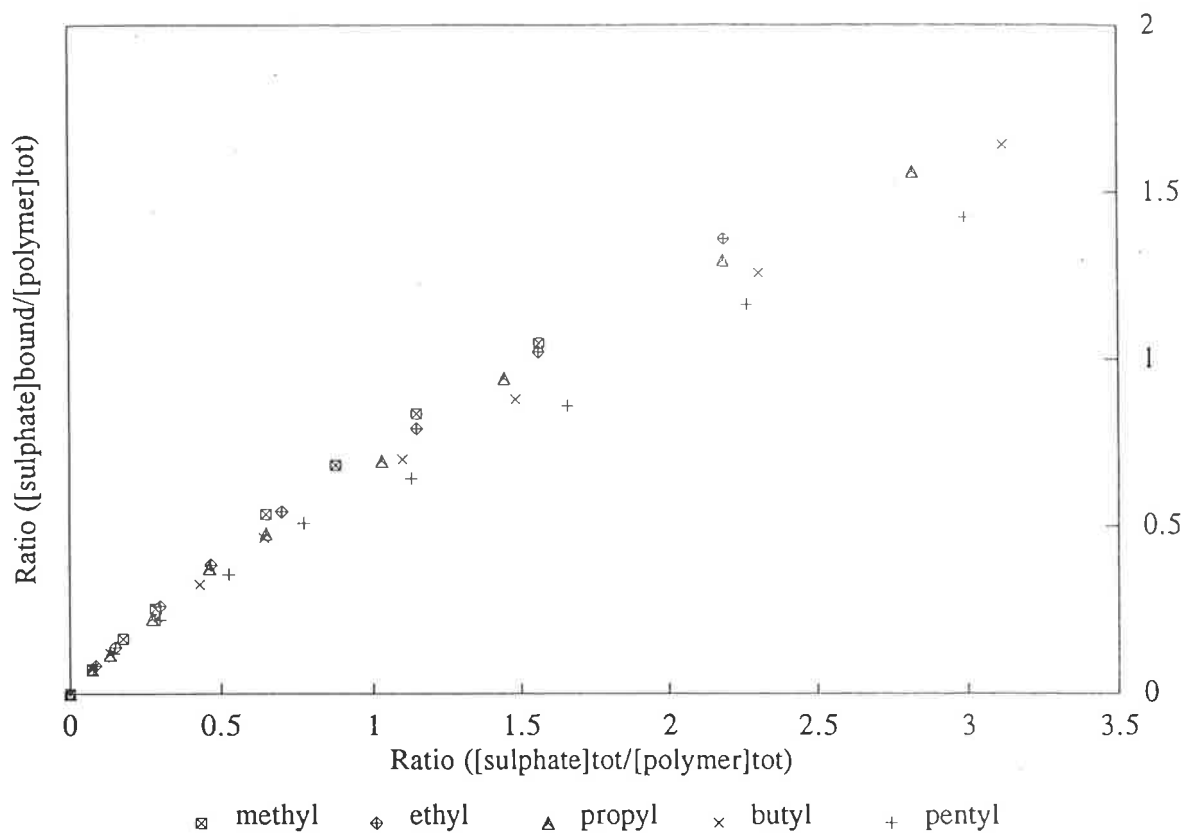
When a sulphate solution was introduced, chloride association to the polymer was low. However, the chloride association was slightly higher for high cross-linked polymers and



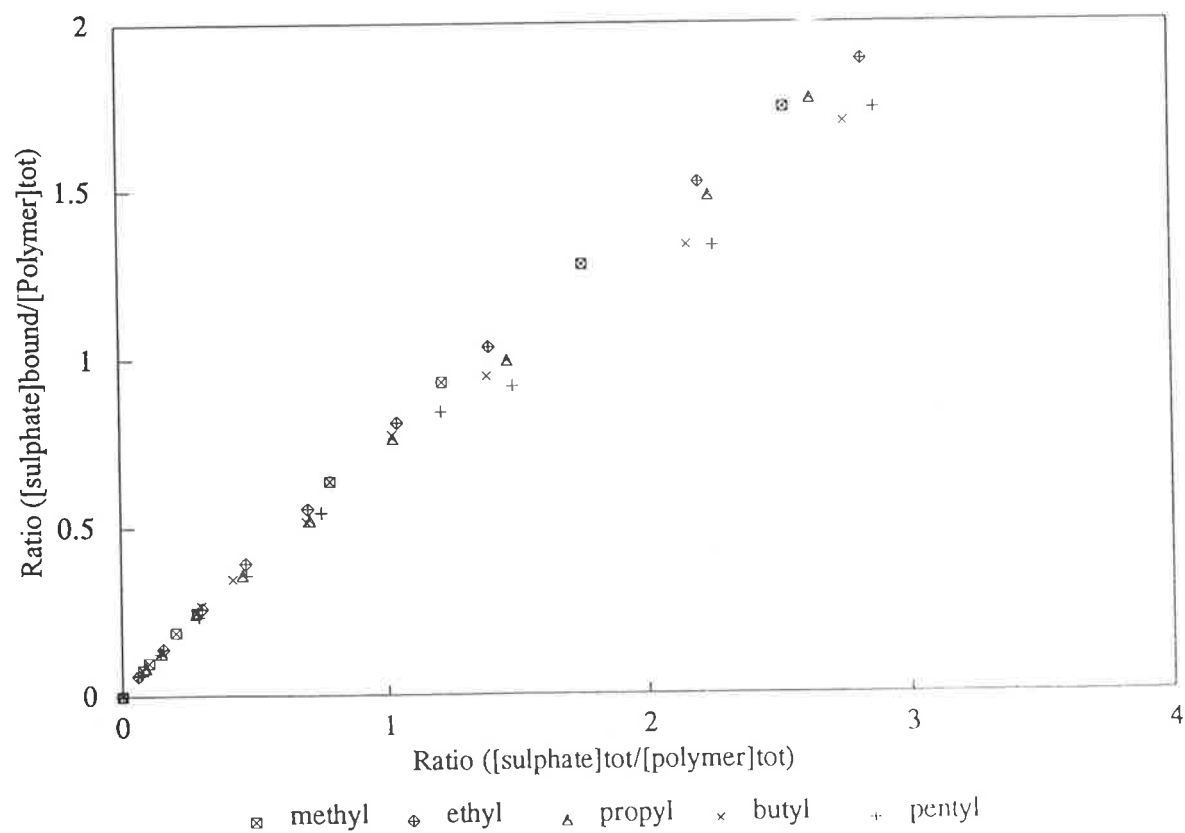
Graph 5-6: Chlorides bound to low cross-linked polymers, sulphates as co-anions.



Graph 5-7: Chlorides bound to high cross-linked polymers, sulphates as co-anions



Graph 5-8: Sulphates bound to low cross-linked polymers, chlorides as co-anions.



Graph 5-9: Sulphates bound to high cross-linked polymers, chlorides as co-anions.

long alkyl chain. The sulphate association was favoured by low cross-linked polymers and short alkyl groups. When both chlorides and sulphates were equally present in solution, sulphates were more associated with the polymer than chlorides. An abnormal amount of bound sulphates, which surpassed the stoichiometric predictions, was measured. The sulphate fixation could not be explained by electrostatic neutralisation processes only. This phenomena could partly explain the existence of an affinity for sulphates, and showed that one could not predict the behaviour of the co-ion from the release measurement of the first one. Therefore, the third selectivity, nitrate/sulphate could not be deduced from the two first as originally thought, and had to be measured as well.

5-3-3 The nitrate sulphate affinity

5-3-3-2 Experimental and results

Calibration of the nitrate working electrodes: four reference solutions were made up by weight with AR grade BDH potassium nitrate. Their molalities varied from 1.2548×10^{-1} down to 8.8×10^{-4} mole kg^{-1} , covering the full experiment range.

The usual checks were made by plotting EMF (mV) versus $\log([\text{NO}_3^-])$, and the activity coefficients were calculated and compared to the literature.

The sulphate concentrations were measured indirectly as described in section 3-3. The slope of a direct lead solution measurement emf (mV) versus $\log([\text{Pb}^{2+}])$ was 25.7 ± 0.2 mV mol^{-1} compared to 27 ± 3 mV mol^{-1} given in the Orion notice. A 50 % water/dioxan mixture was used as solvent (v/v).

The experimental conditions were similar to the other potentiometric measurements. The polymers had been converted from chloride to nitrate form by repeated washing with 2 M NaNO_3 solution, until no free chlorides were detected using the chloride I.S.E. The polymers were dried in a vacuum oven, and kept in desiccator containing P_2O_5 as a drying agent. Nine cells were filled with from 0.3 to 0.5 g of polymer, to work in the

same concentrations. The exact proportion of solutes present was determined. The nitrate and sulphate total concentrations were determined as for the other experiments. The outer chamber solution of the reference electrode was KCl 10 %. The averaged data concerning each samples were tabulated:

Table 5-9: Reactant input before experimentation

	methyl	ethyl	propyl	butyl	pentyl
M_{MA} low cross-linked	228.51	267.06	305.10	343.41	381.72
Mass polymer input (g)	0.32134	0.37350	0.40589	0.45459	0.52493
Mass water (g)	38.1255	38.3905	38.3277	35.7594	37.7573
M_{MA} high cross-linked	216.30	248.67	281.26	314.36	343.67
Mass polymer input	0.30441	0.35508	0.37283	0.42432	0.50490
Mass water (g)	38.6287	36.5361	38.7341	36.8832	38.6935

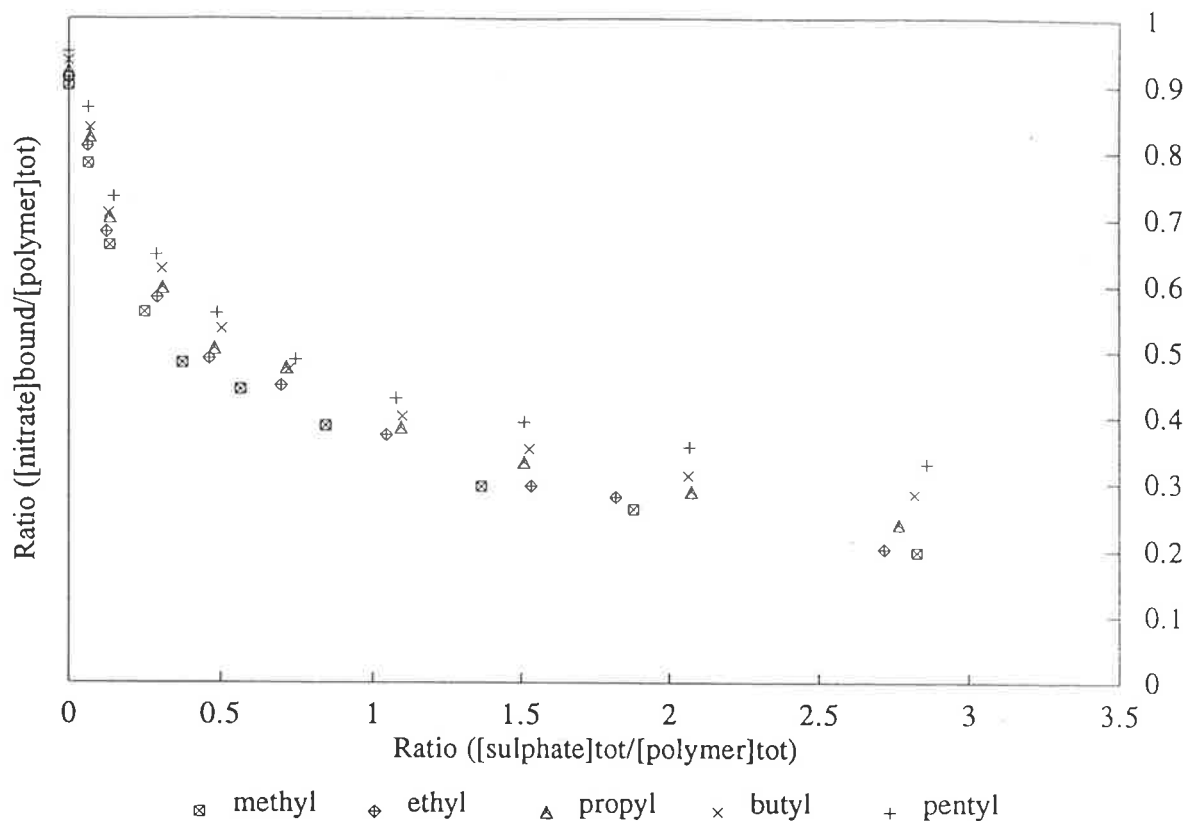
5-3-3-2 The anion bindings

Before adding any sulphates, the initial bound nitrate ratios to the cross-linked polymers were measured. These ratios were high, at a similar level as chlorides.

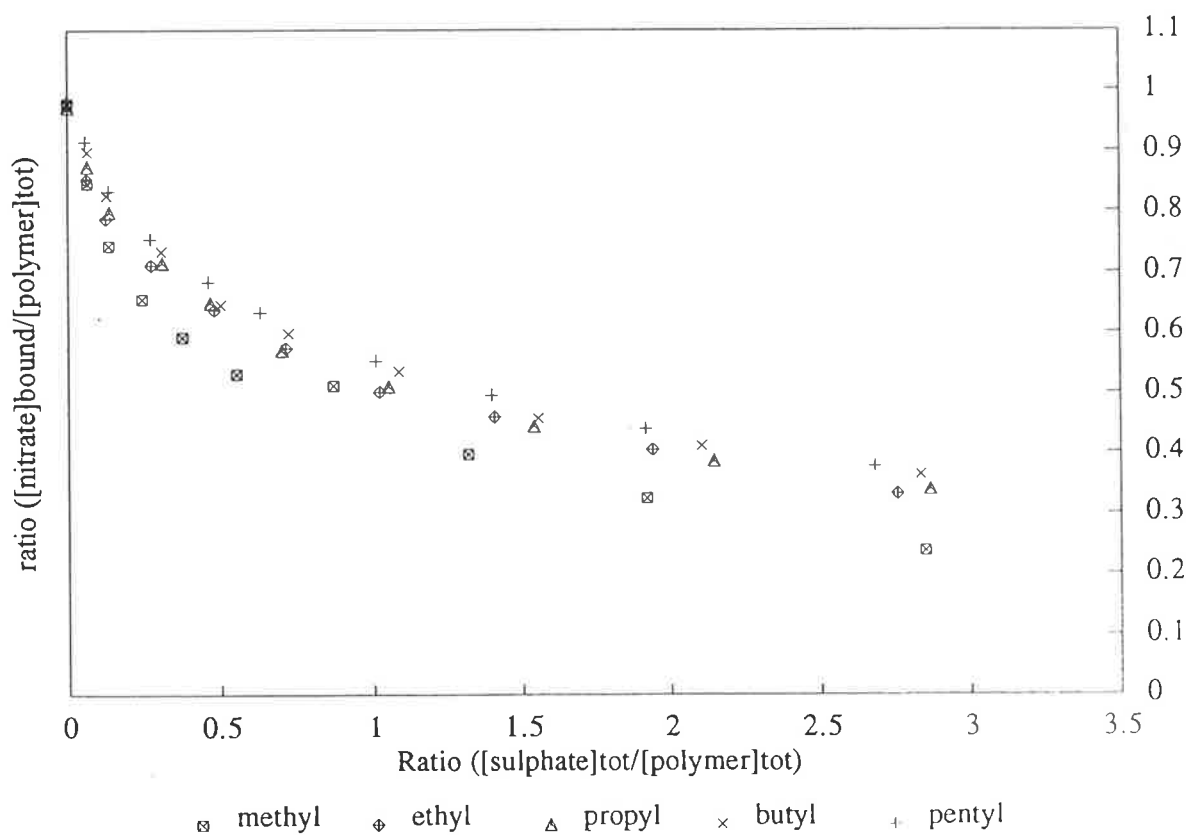
Table 5-10: Nitrate fraction bound to the cross-linked polymer in aqueous solution

	methyl	ethyl	Propyl	Butyl	Pentyl
Low cross-linked	0.935	0.945	0.951	0.972	0.985
High cross-linked	0.950	0.953	0.964	0.979	0.994

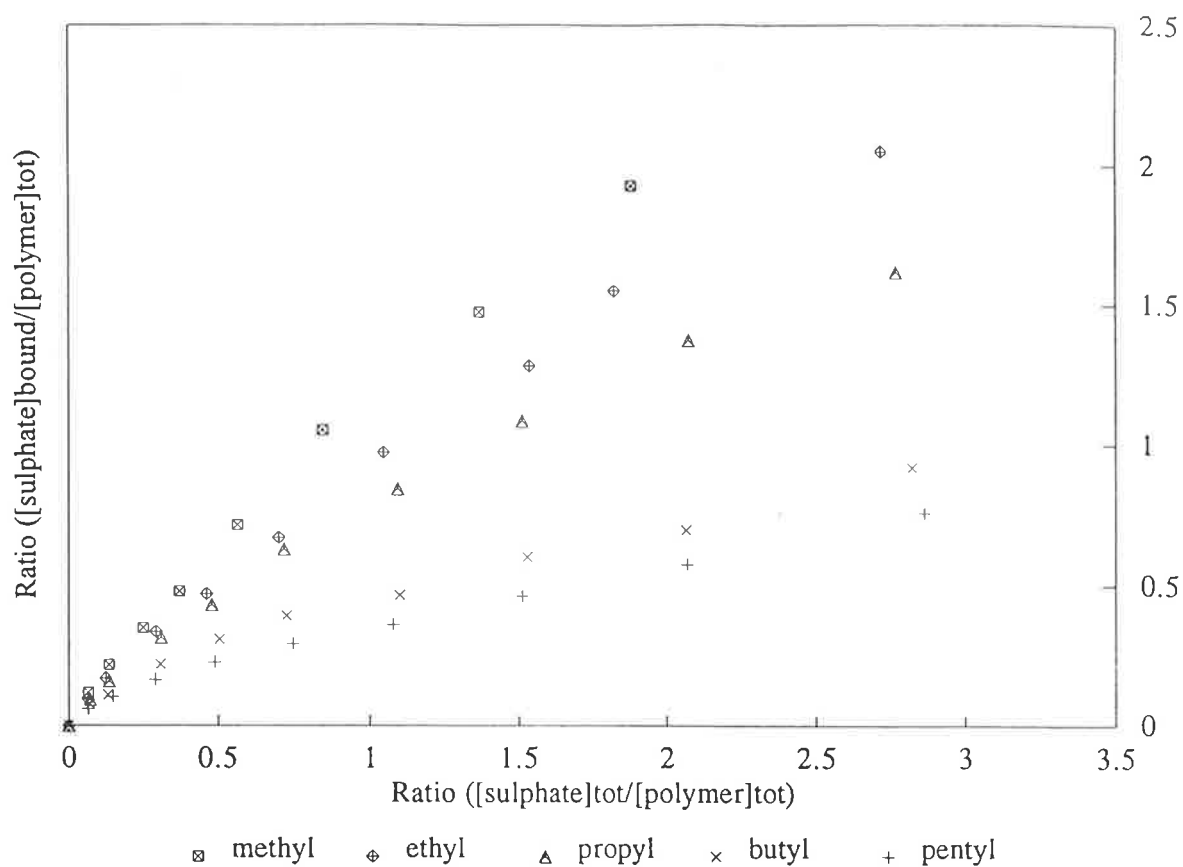
Nitrate binding diminished when sulphates were added, graph 5-10 and 5-11. It slightly decreased more for the low cross-linked polymers. The phenomena tended to flatten off for a ratio sulphate/nitrate polymer of 2. High cross-linkings and long functional groups



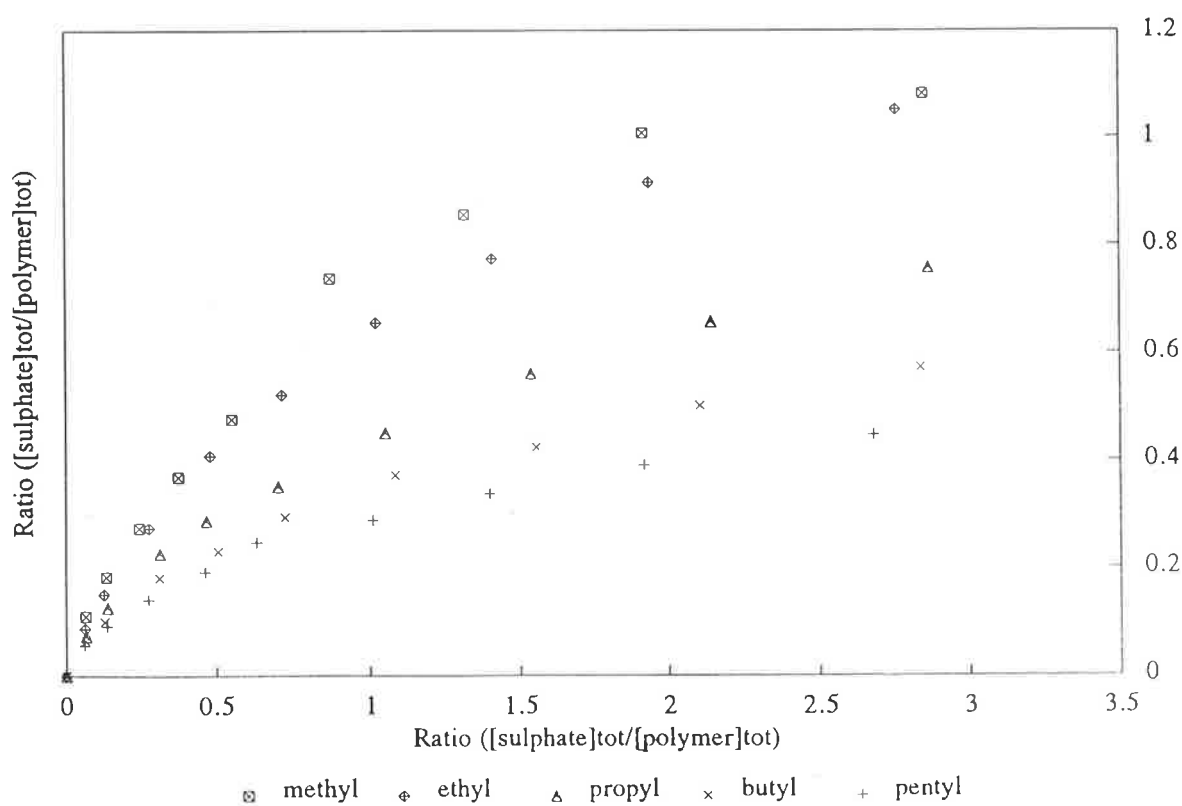
Graph 5-10: Nitrate bound to low cross-linked polymers, sulphates as co-anions.



Graph 5-11: Nitrates bound to high cross-linked polymers, sulphates as co-anions



Graph 5-12: Sulphates bound to low cross-linked polymers, nitrates as co-anions.



Graph 5-13: Nitrates bound to high cross-linked polymers, sulphates as co-anions.

enhanced a higher nitrate association. At the end of the experiment, sulphate concentrations were thrice polymer equivalent base molalities, the exchange did not evolve further, and the experiment was stopped.

Sulphates binding, illustrated on graph 5-12 and 5-13, was enhanced by low cross-linking and small alkyl functional groups such as methyl. As for the sulphate/chloride system, the amount of bound sulphates were again higher than the whole capacity of the resins input in the cell. When the sulphates concentration was thrice the nitrate ones, the amount of sulphate measured bound tended to flatten off for the high cross-linked. the bound sulphate over polymers capacity varied from 0.5 to 1.1 from pentyl to methyl alkyl chain respectively. For the low cross-linked polymers, bound sulphate amount was still increasing for the short alkyl group polymers. The stoichiometry of the exchange two free nitrates for one bound sulphates, was not fully respected, as already noticed [15] for sulphate/nitrate system.

5-3-3-3 Conclusion

When the sulphate solution was added, bound nitrates remained higher than chlorides measured in similar conditions. Nitrate association was favoured by high cross-linked and long alkyl chains. This property has already been reported [13-16] In contrary, bound sulphates increased with short functional groups and with low cross-linking. This more flexible polymer structure eased the association of the large sulphates ions. An excess of sulphate bound was recorded for this system as for chloride/sulphate ones, especially for low cross-linked degrees and short alkyl groups. If excesses of bound ions to polyelectrolytes in solution are commonly reported [91-92], excess of ion bound to insoluble material has not really been mentioned. However, Clifford [14] discussed that porosity of a resin favours sulphate selectivity against nitrates. The image of larger and more charged sulphates temporally blocked in the cross-linked polymer structure could explain this surprising but consistent result.

5-3-4 Stability in the time

The emf readings of any solution were quite stable with the time using the chloride I.S.E.. The first reading was taken after 10 min and the second one after 30 min. Usually, a shift of 1 to 3 mV was observed. The nitrate electrode shift were up to 5 mV difference, sometimes. The potential drift occurred essentially in the first minutes after the adding of the co-ion solution. The drift was independent of type of solution measured. It was not smaller with the linear polymer solutions, more viscous and where the ionic dissociation was higher, and decreased when solution were more concentrated. Some emf readings had been recorded for a few up to 14 days. At the same time, the reference solution used to calibrate the electrode, were measured. They showed that the emf drift was in the order of 15 mV, but a similar shift was recorded by the control reference. The drift would have a technical origin, such as a change in the junction potential of the electrodes, rather than a real evolution of the equilibrium formed in between the resin and the other components. The equilibrium was reached after few minutes only. Bolto et al [13] mentioned time length of 3 months before obtaining equilibration. About the indirect sulphate titrations, it was noticed that the agitation had to be constant to get a stable emf reading, addition of dioxan as solvent and fresh polishing of the lead I.S.E. were essential to get satisfactory results.

5-4 SELECTIVITY SURVEY

From the different total, free and bound concentrations recorded for affinity studies, different parameters such as separation factors α , equilibrium and selectivity constants, K and S respectively [15], were introduced to quantify the equilibrium. Establishments and comparisons, between the affinities found for the different systems studied, were done. Trends of those affinities were discussed

5-4-1 The separation factor α

For an ion-exchange such as:



where $\overline{B}$ where the overbar meant bound species.

The separation factor α_B^A was given by the mole fraction ratio (2-58):

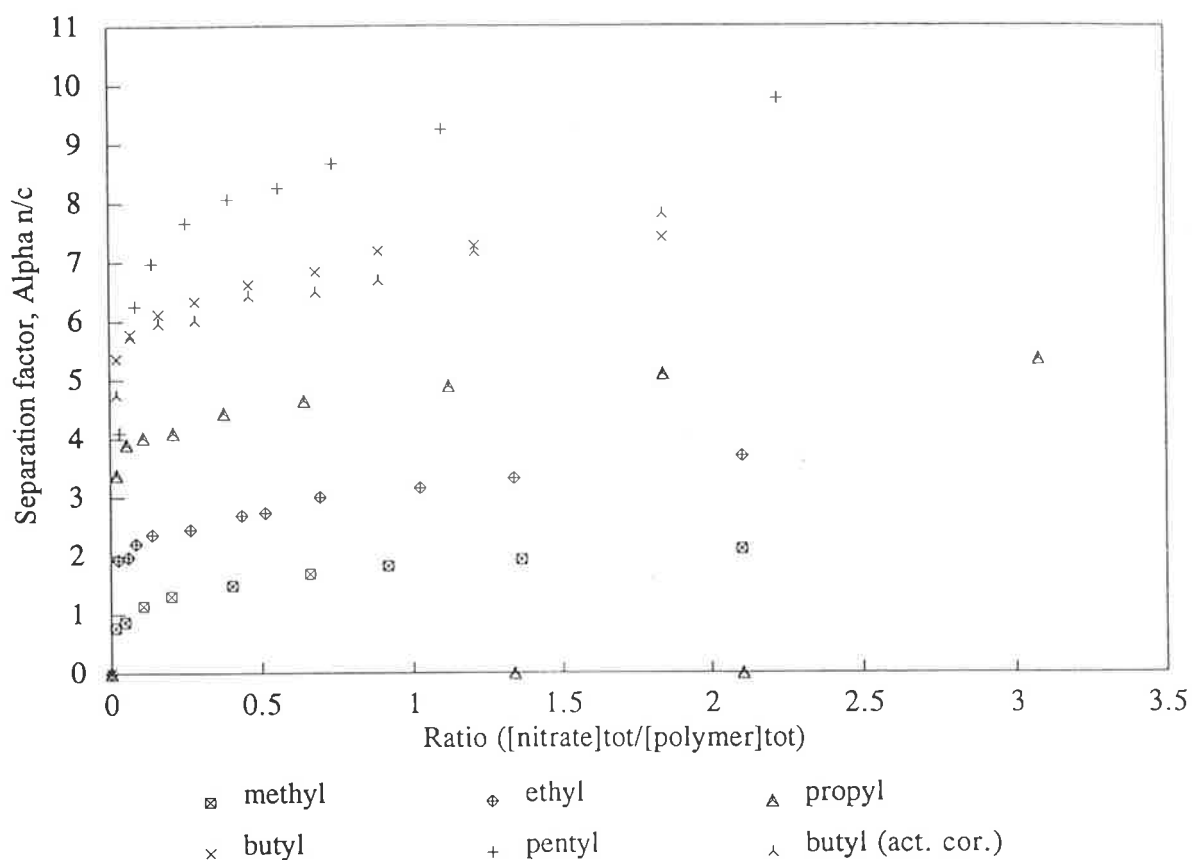
$$\alpha_B^A = \frac{\overline{X}_A \times X_B}{X_A \times \overline{X}_B} \quad (5-8)$$

where X_A and $\overline{X}_A$ were the equivalent mole fraction free and bound of the species A.

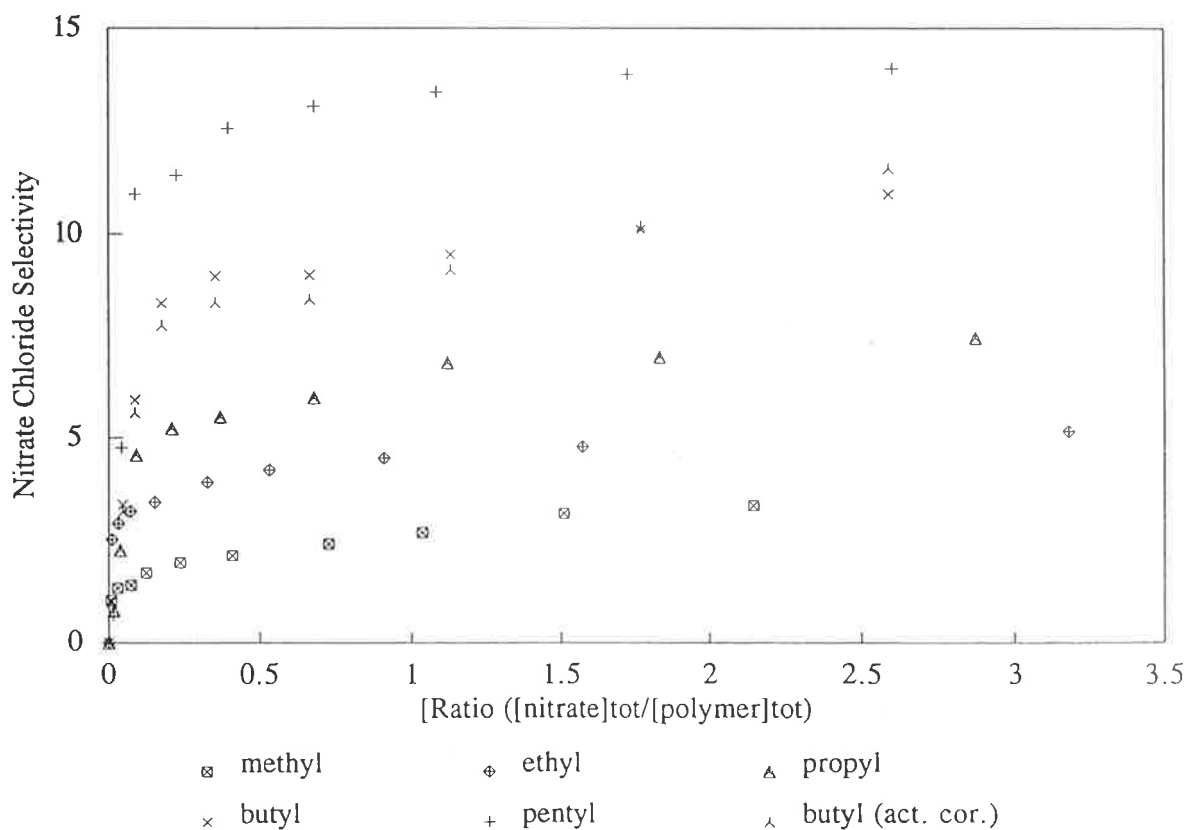
The separation factors were included, for each system, in the tables 5-14 to 5-18. They were plotted versus the concentration fraction of the anions present in solution, on graphs 5-15 to 5-19.

Chloride/nitrate systems were illustrated on graphs 5-14, 5-15. All the polymers had an affinity towards nitrates compared to chlorides, since $\alpha_{Cl}^{NO_3} > 1$. The separation factors increased when nitrate was added, the resin bound more nitrate when nitrate concentrations increased. High cross-linking favoured nitrate associations which increased from 1.8 to 10 from methyl to pentyl low cross-link, and from 2.5 to 14 for the high one. The influence of the size of the alkyl group was also of prime importance. The butyl (act. cor.) curves were the corrected equilibrium constants. No much difference could be observed.

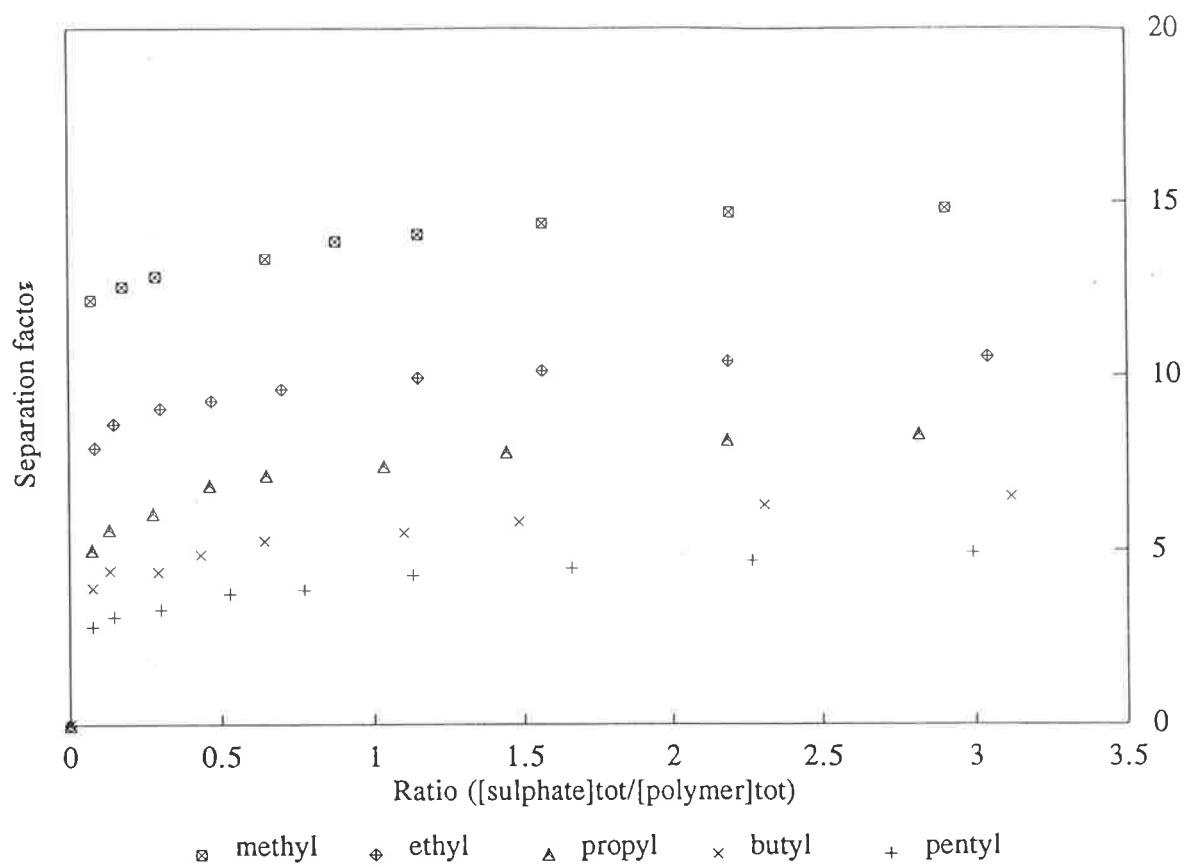
Chloride/sulphate systems were illustrated on graph 5-16, 5-17. The polymers had all an affinity towards sulphates compare to chlorides, $\alpha_{Cl}^{SO_4} > 1$. The separation factors increased with sulphate addition in the cell. They reached highest values for the methyl polymers, respectively 12 and 15 for the high and low cross-link polymers, and varied with the amount of sulphate added. No activity correction was possible on mole fractions, from which the separation factors were calculated. The sulphate affinity



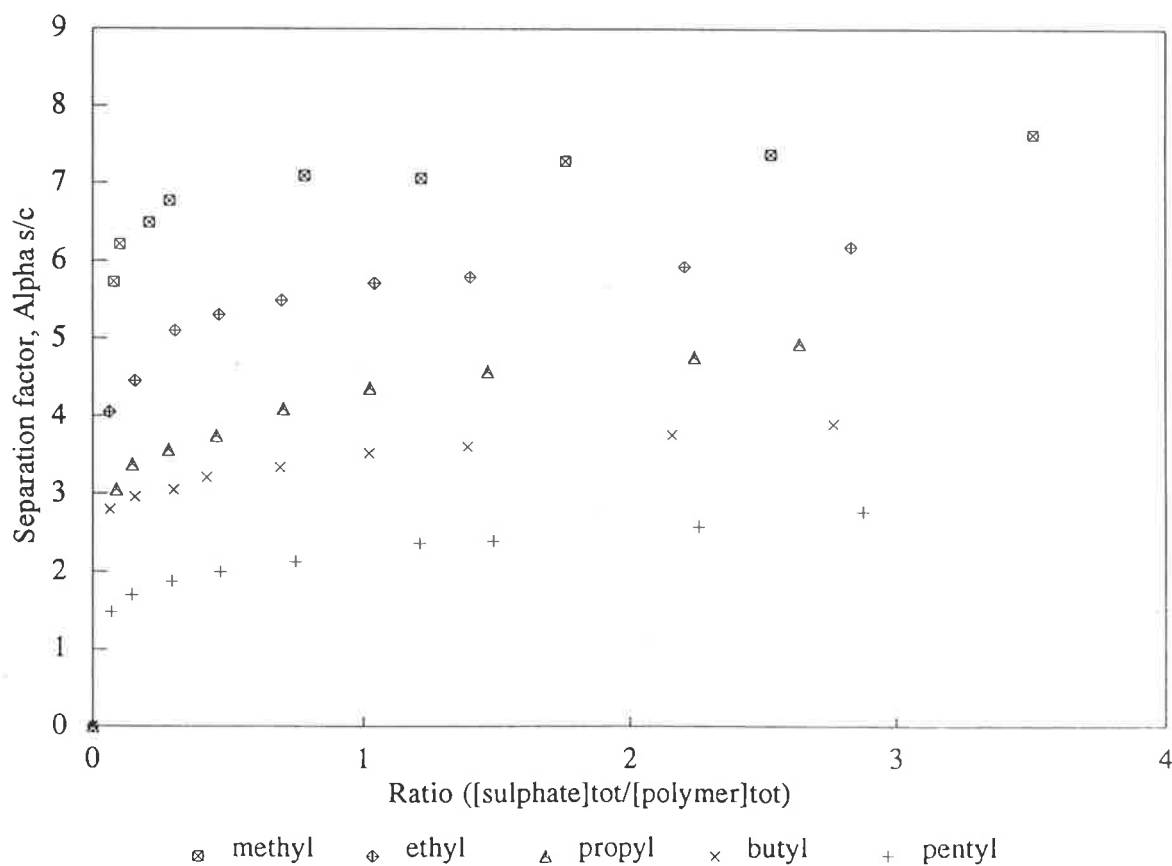
Graph 5-14: Separation factors $\alpha_{Cl^-}^{NO_3^-}$ for the low cross-linked polymers.



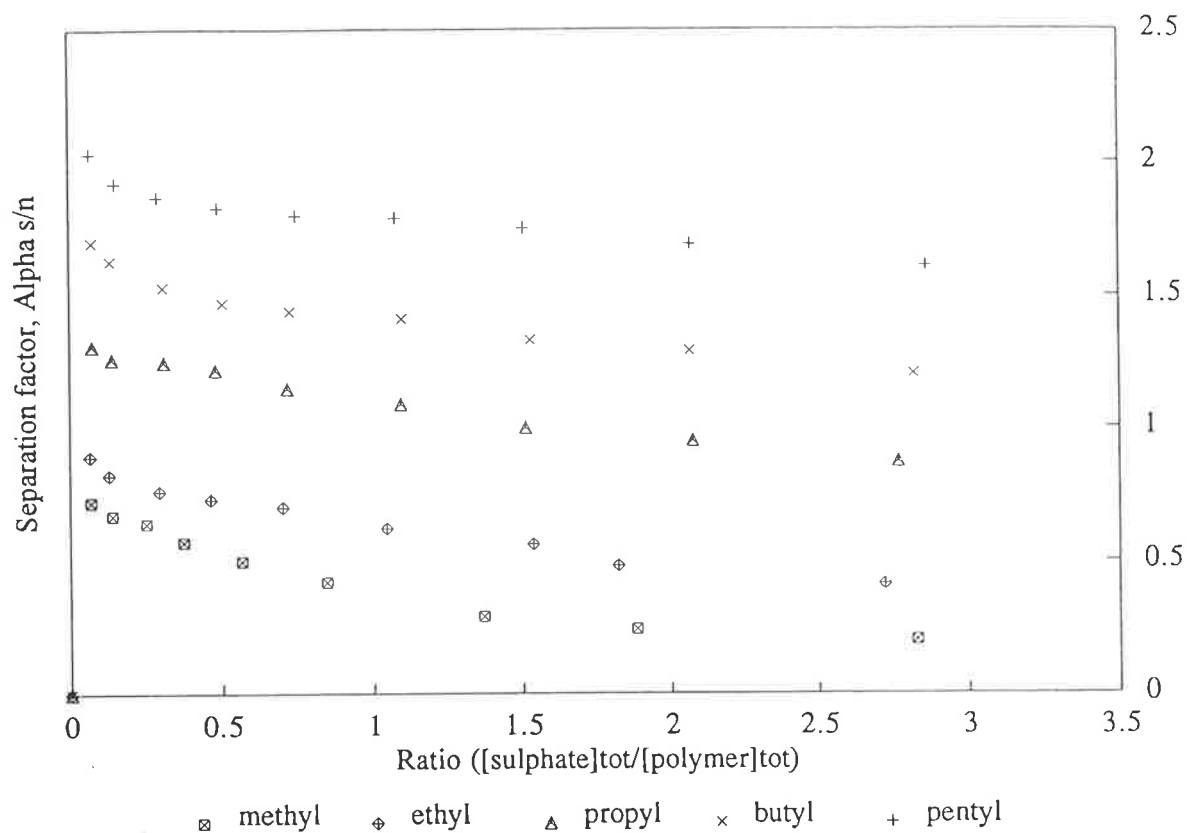
Graph 5-15: Separation factors $\alpha_{Cl^-}^{NO_3^-}$ for the high cross-linked polymers.



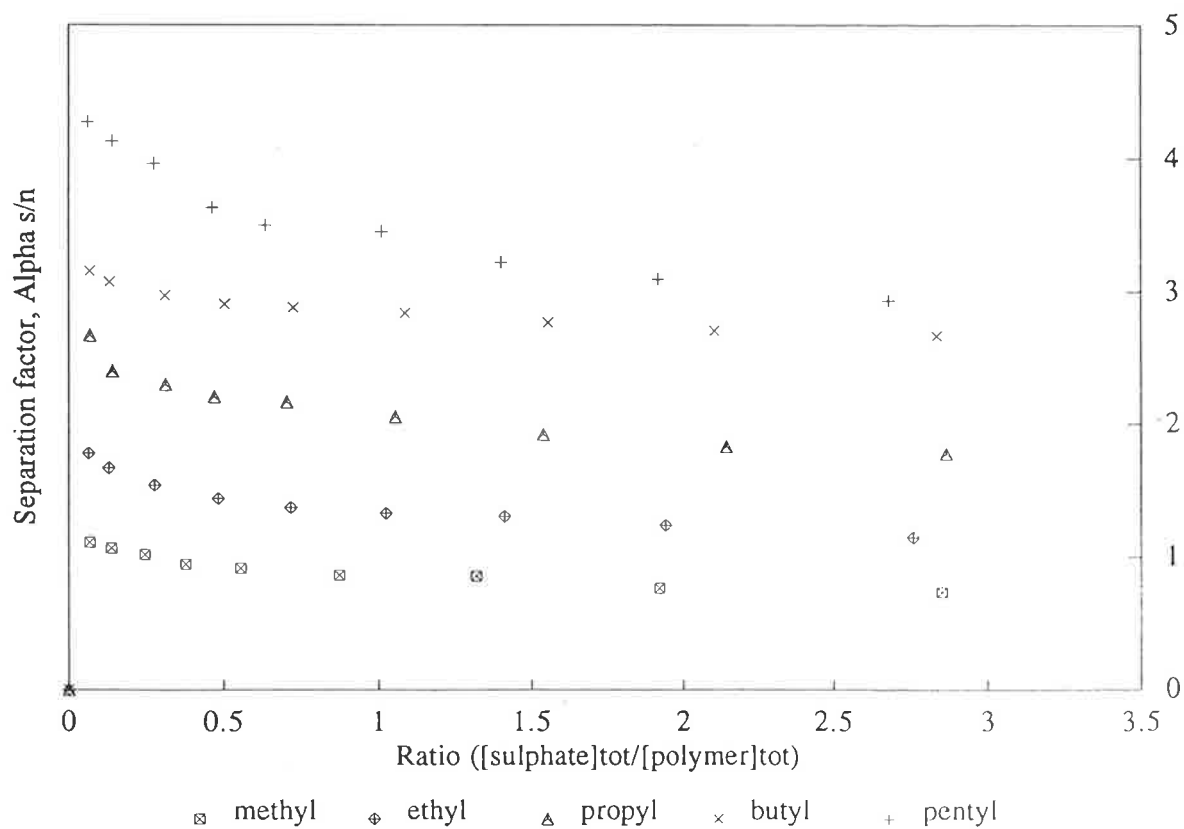
Graph 5-16: Separation factors $\alpha_{Cl^-}^{SO_4^{2-}}$ for the low cross-linked polymers.



Graph 5-17: Separation factors $\alpha_{Cl^-}^{SO_4^{2-}}$ for the high cross-linked polymers.



Graph 5-18: Separation factors $\alpha_{SO_4}^{NO_3}$ for the low cross-linked polymers.



Graph 5-19: Separation factors $\alpha_{SO_4}^{NO_3}$ for the high cross-linked polymers.

increased with the low cross-linking and with small alkyl functional groups such as methyl and ethyl.

Nitrate/sulphate systems were illustrated on graph 5-18 and 5-19. For most of the polymers, an affinity toward nitrates relative to sulphate was recorded, $\alpha_{\text{SO}_4}^{\text{NO}_3} > 1$ which tended to diminished when more sulphates were added. The nitrate affinity was enhanced by the long alkyl chains and high cross-linking. It reached 3 for the high poly pentyl. A sulphate selectivity was observed for the low cross-linked methyl and ethyl, since their separation factors were below 1.

Conclusion: the separation factors gave consistent results whose trends indicated that our polymers had an affinity for nitrates then sulphates against chlorides. The nitrate affinity was confirmed against sulphates and chlorides. A long chain group and a high cross-linking improve the nitrate selectivity. Polymers were sulphate selective against chlorides.

5-4-2 The equilibrium constants

The equilibrium constants K were calculated from the equation 2-60, (previously detailed in chapter 2) from an equilibrium such as 5-7:

$$K_B^A = \frac{[\bar{A}] \times [B^-]^{Z_A}}{[\bar{B}]^{Z_A} \times [A^{Z_A-}]} \quad (5-9)$$

where the liquid and the overbarred resin phase concentrations were expressed in molalities. This expression was identical to the separation factor for a 1:1 electrolyte. The apparent equilibrium constants varied slightly with the total ion concentration as already observed [14]. The activity coefficients partly corrected this trend. The equilibrium constants were determined at the same concentration ratio to be discussed. A data regression was used to obtain the equilibrium constant at a one to one ratio between of both anion concentrations present in the cell. The values were in table 5-11.

Table 5-11: Selected value of the equilibrium constant for the different systems and polymers.

Low cross-linked	$K_{Cl}^{NO_3}$	$K_{Cl}^{SO_4}$	$K_{NO_3}^{SO_4}$
methyl	1.84	0.455	0.053
ethyl	3.14	0.326	0.031
propyl	4.82	0.294	0.032
butyl	7.20	0.182	0.020
pentyl	9.01	0.145	0.013
High cross-linked	$K_{Cl}^{NO_3}$	$K_{Cl}^{SO_4}$	$K_{NO_3}^{SO_4}$
methyl	2.65	0.173	0.012
ethyl	4.56	0.071	0.008
propyl	6.83	0.057	0.006
butyl	9.02	0.051	0.005
pentyl	13.36	0.043	0.003

Chloride nitrate system: No activity correction were done. Both chloride and nitrate activity coefficients were similar, especially in our working range concentrations, and would have cancelled out in the ratio of the formula.

Equilibrium constants showed that more nitrates were bound to the polymers than chlorides, and this trend increased with the size of the alkyl group and the cross-linking of the polymer. The association constants of the nitrate monomer analogues in aqueous solution [12], were half as much as the nitrate chloride equilibrium constant calculated here for the low cross-linked polymers. A 50 % increase was observed when $K_{Cl}^{NO_3}$ were compared between the high cross-linked and the linear polymers.

Chloride sulphate system: The activity coefficients were introduced in the equilibrium constant calculations, to take into account the activity difference in between mono and divalent anions. The correction was applied using the activity coefficients calculated from

the Debye-Hückel limiting law:

$$\log \gamma_{\pm} = -0.5115 \times |z_+ z_-| \times \sqrt{I} \quad (5-10)$$

where I was the anionic strength $I = \frac{1}{2} \sum Z_i^2 m_i$, the activity of a species i was given by the product of the activity coefficient and the molality by $a_i = \gamma_i \times m_i$.

The equilibrium constants marked a sulphate preference over chloride, which decreased with large alkyl group and with high cross-linking.

Nitrate sulphate system: an activity correction was made to obtain the equilibrium constants, as explained in chloride sulphate system. The small equilibrium constants $K_{NO_3}^{SO_4}$ displayed an affinity of the resin towards nitrates, which increased with high cross-linking and large alkyl groups.

Conclusion: Equilibrium constants calculated showed a nitrate affinity against chlorides, and in a less extent the sulphates. It was also found that monovalent anion affinity was improved by high cross-linking and long alkyl chains. They confirmed the results found by the molar fraction bound or the separation factors. Furthermore, the equilibrium constants $K_{Cl}^{NO_3}$ obtained with cross-linked polymers were compared to the equilibrium constant $K_{Cl}^{NO_3}$ obtained with the linear polymers. The trends observed in the values of the equilibrium constants were identical, showing the same affinity order which was nitrate then sulphate and chloride from both linear and cross-linked polymers. The nitrate association was multiplied by a factor between 2 and 3. This illustrated the relative importance of the cross-linked structure. The increasing nitrate affinity with an increasing size of the alkyl group observed for the cross-linked polymers represented an identical trend as Steel et al. [12] had previously discussed. They also found that the nitrate/monomer analogues association in aqueous solution increased the size of the alkyl group. The sulphate/monomer analogues association, about in the same order, was favoured by short alkyl groups and was higher than the chloride/monomer analogues association.

Equilibrium constants have not been a popular way to express the selectivity of a resin. Often [13, 14, 18] separation factors were chosen to discuss the resin affinity for one anion rather than equilibrium constants. The discussion of the equilibrium constants at a certain anion / co-anion ratio was found restrictive when discussing the behaviour of a polymer which if used as a resin will not meet such concentration ratios.

5-4-3 The selectivity:

A quantitative measure of the selectivity was defined by Guter [18]. For an equilibrium involving a monovalent and a divalent anion such as $A + \bar{B} \rightleftharpoons \bar{A} + B$, the selectivity coefficient is:

$$BAS = \log K_B^A - \log \bar{C}_p + 1 \quad (5-11)$$

where $\bar{C}_p$ was the resin capacity (meq/L).

When the selectivity is positive, the affinity goes to the co-anion A. A strong affinity occurs when the selectivity approaches 2 [15].

When two monovalent anions were involved in the exchange, such as chloride nitrate, the equilibrium CNS was simplified to :

$$CNS = \log K_{Cl}^{NO_3} \quad (5-12)$$

All the data calculated were gathered in tables of the table 5. The data were averaged and input in the table 5-12:

Table 5-12: Averaged selectivity for the different systems.

Low cross-linked	CNS (a)	CSS (b)	NSS (c)
methyl	0.14 ± 0.14	-2.86 ± 0.41	-3.95 ± 0.67
ethyl	0.42 ± 0.08	-3.09 ± 0.44	-4.05 ± 0.54
propyl	0.64 ± 0.07	-3.23 ± 0.47	-4.01 ± 0.48
butyl	0.81 ± 0.04	-3.36 ± 0.48	-4.28 ± 0.48
pentyl	0.87 ± 0.10	-3.43 ± 0.49	-4.47 ± 0.52

Table 5-12: continued.

High cross-linked	CNS (a)	CSS (b)	NSS (c)
methyll	0.30 ± 0.16	-3.40 ± 1.10	-4.34 ± 0.49
ethyl	0.57 ± 0.09	-3.57 ± 0.44	-4.51 ± 0.44
propyl	0.67 ± 0.30	-3.68 ± 0.41	-4.66 ± 0.50
butyl	0.79 ± 0.31	-3.69 ± 0.47	-4.82 ± 0.48
pentyl	0.91 ± 0.41	-3.84 ± 0.61	-5.13 ± 0.37

CNS(a): The chloride/nitrate selectivity had positive values. It followed that the polymers were nitrate selective, and this selectivity increased with larger alkyl groups and higher cross-linking degrees.

CSS(b): The chloride/sulphate selectivity had negative values, the polymers would be chloride selective, and this selectivity increased with long alkyl chain and high cross-linked degrees.

NSS(c): The nitrate/sulphate selectivity had negative values, the polymers were nitrate selective, and this selectivity increased larger alkyl groups and higher cross-link degrees.

For mono-/di-valent exchange, all selectivities were found negative, meaning that no affinity for the co-ion added was measured. This was due to $\bar{C}_p$ which had to be expressed in meq L⁻¹, and which became larger than a thousand. Their log was negative enough to bring the all expression below zero. For example, for a capacity of 2000 meq L⁻¹, an equilibrium constant of 5437 was necessary to get a selectivity equalled to 0!

Equation 5-11 was derived by Guter [89]. He derived the selectivity from the equilibrium constants expressed on molarity scale, and substituting mole fractions and total concentration of anions in both the liquid and solid phases. It became:

$$\frac{\bar{X}_s}{(1-\bar{X}_s)^2} = K_N^S \times \frac{\bar{C}_p}{C} \times \frac{X_s}{(1-X_s)^2} \quad (5-13)$$

where X_s and $\bar{X}_s$ were the equivalent fraction of sulphate in solution and in resin, C and

$\bar{C}_p$ were the total aqueous anion concentration and the resin capacity and K_N^S was the equilibrium constant already defined. The equation 5-13 was be modify to:

$$\frac{K_N^S \times C}{\bar{C}_p} = \frac{\frac{X_s}{(1-X_s)^2}}{\frac{\bar{X}_s}{(1-\bar{X}_s)^2}} \quad (5-14)$$

A resin was nitrate selective when X_s was larger than $\bar{X}_s$ and consequently:

$$\frac{K_N^S \times C}{\bar{C}_p} = 1 \text{ or more} \quad (5-15)$$

The nitrate to sulphate equivalent of equation 5-16 was obtained by fixing $C = 10 \text{ meq dm}^{-3}$. This latter adapted the whole formula to low concentration ranges.

$$NSS = \log K_N^S - \log \bar{C}_p + 1 \quad (5-16)$$

The choice for the resin capacity to be in meq dm^{-3} instead of meq cm^{-3} was justified by the fact that the ratio of both concentrations $\frac{\bar{C}_p}{C}$, from equation 5-13, had to be dimensionless. The concentration of 10 meq dm^{-3} was choosen because it represented the range of concentration of nitrate expected in water. However, this fixed concentration gave a factor of "+ 1" in the equation 5-16 and was quite arbitrary. Further more, from equation 5-16, it appeared that a low capacity resin would be more nitrate selective, since $\bar{C}_p$ would be less negative. The link between capacity and selectivity is maybe not that straightforward.

One can argue that a simpler formula like 5-12 used for 1:1 anion exchange was sensible. For a 2:1 exchange, all the selectivities were for the ion originally bound to the polymers, which was suspicious. Nevertheless, a trend could be seen where nitrate and chloride selectivities were larger with a long alkyl chain and a high cross-linking, and the opposite for sulphate.

5-4-4 Equilibrium isotherms

The relative affinity of an ion-exchange resin for an ion can be expressed on a isotherm diagram. The mole fractions of the component in the solid phase are plotted against the mole fraction of the equivalent ion in the solution phase. No affinity would display a straight line crossing in diagonal the graph. A curve lying above the diagonal indicates that the ions are preferably found in the solid phase, a curve located below the diagonal indicates that the ions are mainly in the liquid phase. Isotherms allow to visualise well the different affinities from different polymers towards one anion and are widely used to study resins.

The free and bound chloride mole fraction were tabulated, 5-13 to 5-18. For an equilibrium such as 5-6, the corresponding mole fractions of the anion A and B can be deduced, applying:

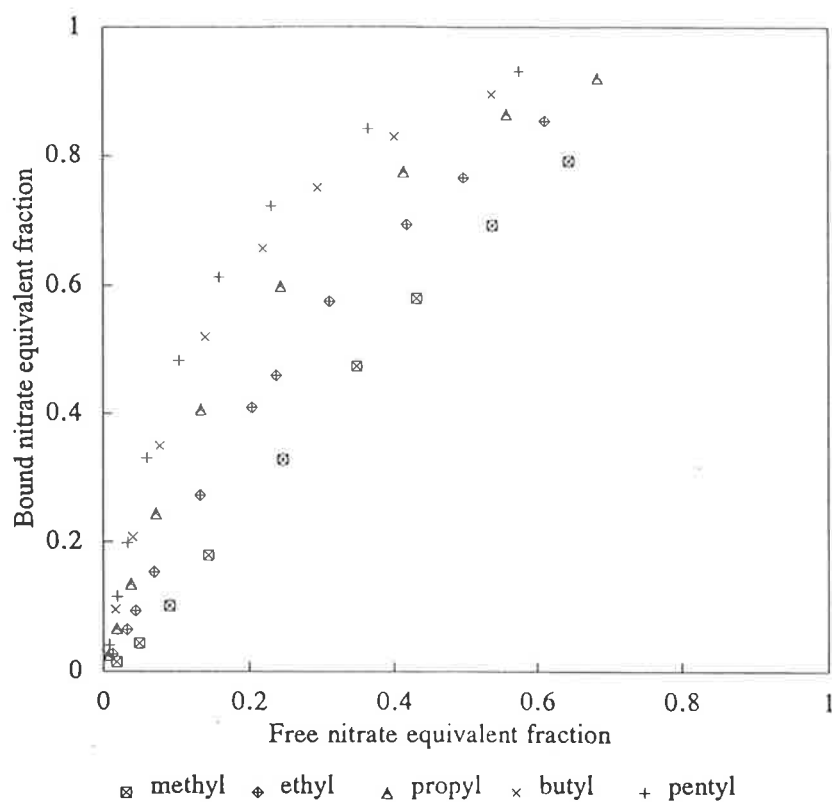
$$X_A = 1 - X_B \quad (5-17)$$

Therefore, only the isotherm of the co-ions, species added, were included in graphs 5-20 to 5-25, the first ion ones would the mirror image.

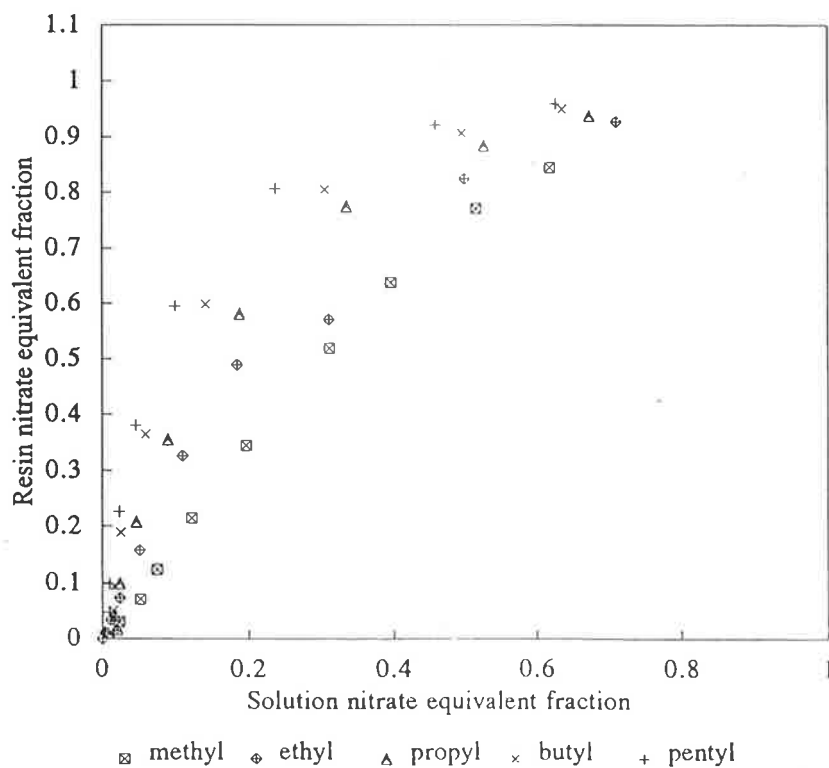
Chloride/nitrate systems were illustrated on graphs 5-20 and 5-21; the diagram showed clearly that nitrates were more in the solid phase, this regular trend increasing as already noticed, for the high cross-linked polymers and for the long alkyl chains.

Chloride/sulphate systems were illustrated on graphs 5-22, 5-23; the sulphate added were found mainly in the resin phase, showing the affinity to the divalent species. The trend was clear, increasing for low cross-linking and little alkyl groups.

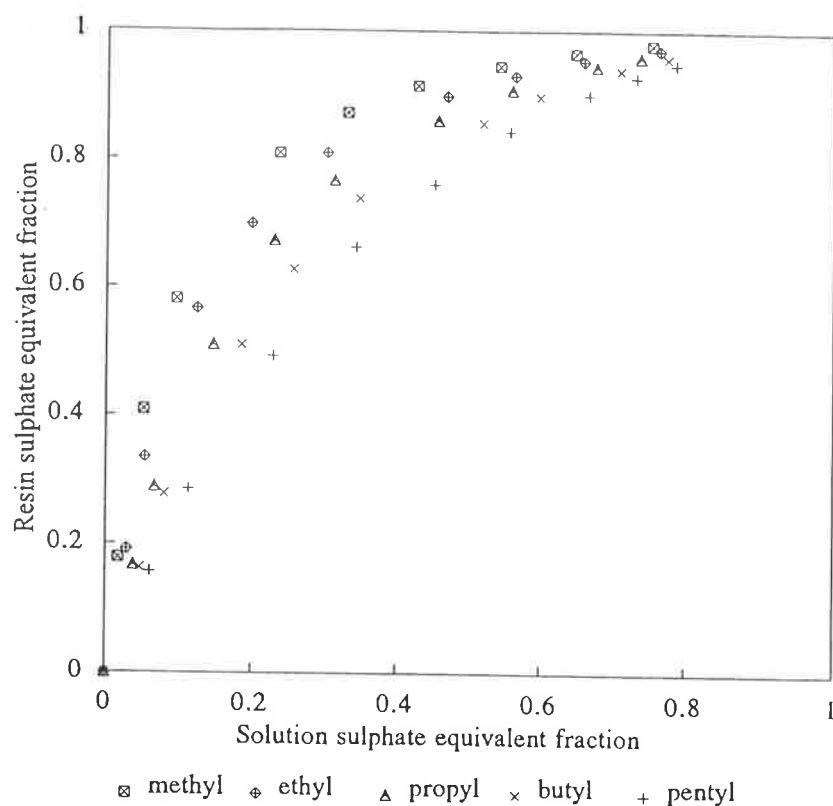
Nitrate/sulphate systems were illustrated on graphs 5-24, 5-25; most of the sulphate stayed in the liquid phase, displaying the affinity for nitrate of the polymers. Solution sulphate fractions were enhanced by long alkyl chain and higher cross-link degree.



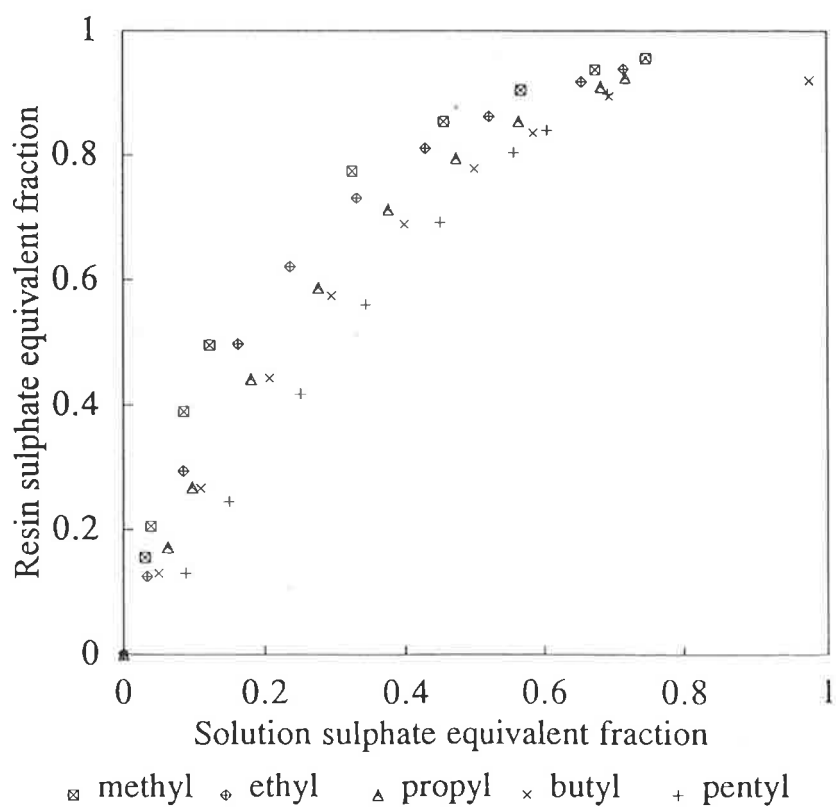
Graph 5-20: Nitrate isotherm for the chloride low cross-linked polymers.



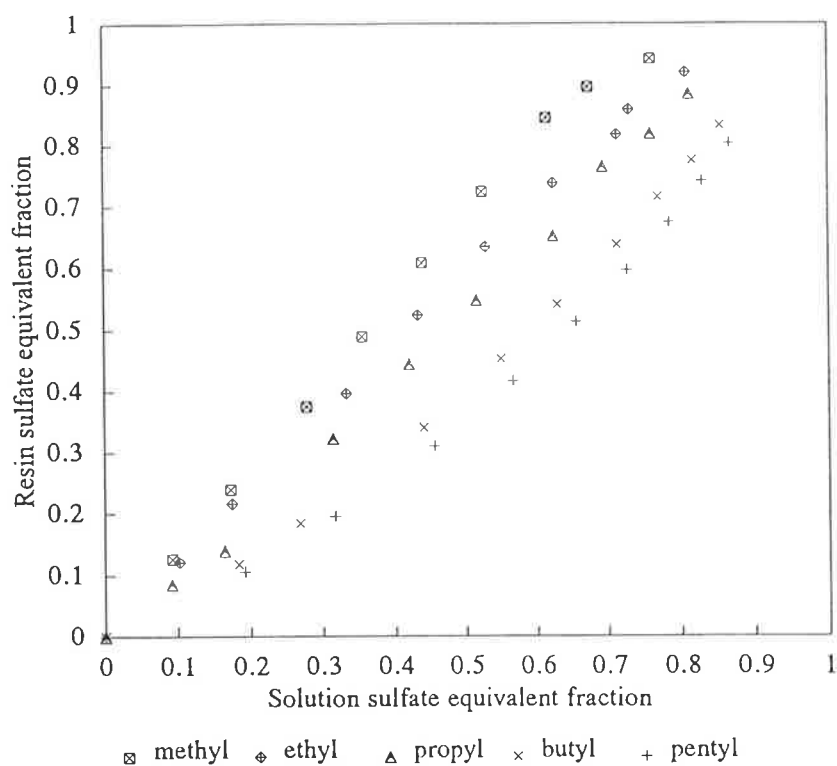
Graph 5-21: Nitrate isotherm for the chloride high cross-linked polymers.



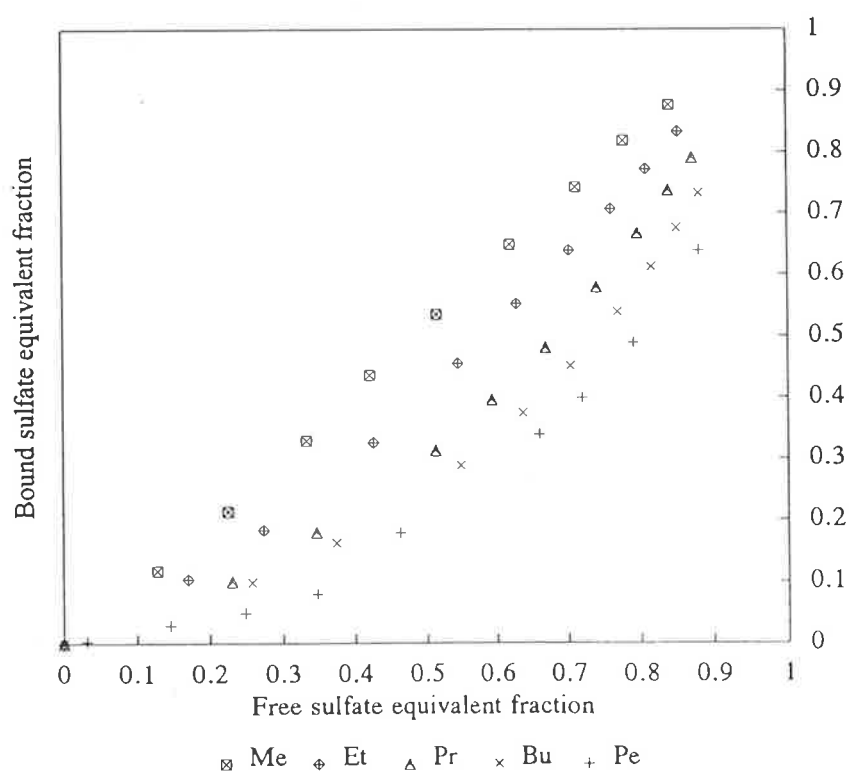
Graph 5-22: Sulphate isotherm for the chloride low cross-linked polymers.



Graph 5-23: Sulphate isotherm for the chloride high cross-linked polymers.



Graph 5-24: Sulphate isotherm for the nitrate low cross-linked polymers.



Graph 5-25: Sulphate isotherm for the nitrate high cross-linked polymers.

Isotherms are popular in discussing resin affinities. They are visual and easy to interpret and can cover a wide range of concentration studied. It can be noticed that our solution did not have a constant ionic strength, contrary to most of the other studies [13-18].

Nevertheless, the addition of the co-ion solution increased, at the most, the solution concentration 3 times, less for most of the measurements. The effect of an increase of the concentration was the same for the different samples, and should not alter the results of a comparison between them.

5-5 CONCLUSION

Two sets of cross-link polymers were synthesised from vinylbenzyltrialkylammonium chloride and DVB, which was the cross-linker. It was established that the cross-linking degree was homogeneous among both sorts of polymers, called low and high cross-linked. Microanalysis and water retention experiments established that the ratio DVB, monomer was around 9.0 and 21.4 % (mole/mole).

The affinity for chloride/nitrate, chloride/sulphate, nitrate/sulphate were carried out using I.S.E. This allowed a direct measurement of the free anion concentrations. From the mass input at the beginning, and the proportion of monomer, containing the quaternary functional groups in the polymer, the total amount of anions capable of reacting was calculated. The bound concentrations were obtained by subtraction of the free from the total concentrations and expressed in mole per resin masses (solid molality), and the affinities of the different polymers studied for chlorides, nitrates, and sulphate were evaluated. It makes electrochemistry and I.S.E. an ideal tool to measure the affinity from a polymer towards different ions.

Separation factors and ion isotherms were found the most appropriate ways to express the affinity towards one species. Equilibrium constants were varying with addition of the co-anion solution, and could not be properly corrected with the activity coefficients. For

a 2:1 anion exchange, selectivity as defined by Guter [18] gave conclusion always in favour of the ions originally bound to the polymers, even when the equilibrium constant was showing an affinity for the co-ions introduced.

Chloride/nitrate survey showed that polymers had a stronger affinity towards nitrates, which increased with the length of the alkyl group and the cross-linking degree.

Chloride/sulphate survey showed that polymers had a stronger affinity towards sulphates which increased mainly when the alkyl groups were smaller.

Nitrate/sulphate survey showed that polymers had a stronger affinity towards nitrates, which increased with the length of the alkyl group and the cross-linking degree.

Using ion transport properties, [17 h] and the modified Stoke's law [17, g], it was calculated that chloride radius were 7 % larger than nitrates and sulphates 118 % larger than nitrates. The size parameters of the binding sites due to the cross-linking degree was relevant for sulphate versus either of the monovalent ions. Indeed, sulphate binding was always smaller with high cross-linked degree.

Long and hydrophobic alkyl groups tended to favour the fixation of monovalent species against sulphates, and nitrate against chlorides.

An affinity towards nitrate was measured even when the co-ion was sulphates. In that respect, these results were interesting, since previous studies [13-15] measured opposite trends.

It was noticed that affinity for sulphate could be due to other parameters than the nature of the electrostatic sites, since anion amounts bound were measured sometimes much higher than the resin capacity. Such phenomena was observed, in a much larger extent, with the linear polymers or in the literature [15]. With a rigid structure like cross-linked polymers, relatively large sulphates could be trapped in the lattice structure, and therefore not detected as free.

Table 5-13:

**WATER RETENTION FROM POLY(VINYL BENZYL AMMONIUM
triALKYL CHLORIDE) IN HUMIDITY CONTROLLED ATMOSPHERE**

Low cross-link polymers in 75 % humidity atmosphere:

	Methyl	ethyl	Propyl	Butyl	Pentyl	Amberlite
mass _{wet} (g)	1.44896	1.22863	1.70263	1.23467	2.19861	3.51252
mass _{dried} (g)	0.67382	0.66958	1.04111	0.81856	1.53553	2.35080
mass _{H₂O} (g)	0.77514	0.55905	0.66152	0.41611	0.66308	1.16172
mole polymer	0.0033	0.0028	0.0037	0.0026	0.0043	
mole ratio	13.06	11.26	9.92	9.02	8.59	

High cross-link polymers in 75 % humidity atmosphere:

	methyl	ethyl	propyl	butyl	pentyl
mass _{wet} (g)	1.71135	1.30609	1.45833	0.31951	0.85811
mass _{dried} (g)	1.04469	0.88342	1.05088	0.24306	0.67230
mass _{H₂O} (g)	0.66666	0.42267	0.40745	0.07645	0.18581
mole polymer ^a	0.0054	0.0039	0.0040	0.0008	0.0021
mole ratio ^b	6.92	6.06	5.63	5.13	4.96

Low cross-link polymers in 93 % humidity atmosphere:

	methyl	ethyl	propyl	butyl	pentyl	Amberlite
mass _{wet} (g)	1.50367	1.28112	1.77357	1.28521	2.28324	3.53050
mass _{dried} (g)	0.67283	0.66910	1.04071	0.81963	1.53557	2.36946
mass _{H₂O} (g)	0.83084	0.61202	0.73286	0.46558	0.74767	1.16104
mole polymer ^a	0.0033	0.0028	0.0037	0.0026	0.0043	
mole ratio ^b	14.02	12.34	10.99	10.08	9.69	

High cross-link polymers in 93 % humidity atmosphere:

	methyl	ethyl	propyl	butyl	pentyl
mass _{wet} (g)	1.72835	1.33384	1.48116	0.32486	0.86959
mass _{dried} (g)	1.04309	0.88344	1.05100	0.24307	0.67215
mass _{H₂O} (g)	0.68526	0.45040	0.43016	0.08179	0.19744
mole polymer ^a	0.0053	0.0039	0.0040	0.0008	0.0021
mole ratio ^b	7.12	6.45	5.92	5.49	5.27

^a mole polymer was number of mole of equivalent monomer unit

^b mole ratio of the mole number of water over polymer

Table 5-14:

BINDING by LOW CROSS-LINKED
POLY(VINYLBENZYLtriALKYLAMMONIUM CHLORIDE) to NITRATES
in AQUEOUS SOLUTION

Poly(vinylbenzyltrimethylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.0659		0.00778	0.00005				
0.06552	0.00108	0.01167	0.00024	0.980	0.985	0.767	-0.12
0.06465	0.00308	0.01586	0.00084	0.950	0.956	0.868	-0.06
0.06300	0.00687	0.02024	0.00202	0.909	0.898	1.138	0.06
0.06072	0.01213	0.02472	0.00420	0.855	0.820	1.295	0.11
0.05619	0.02257	0.03022	0.00990	0.753	0.672	1.490	0.17
0.05132	0.03378	0.03420	0.01835	0.651	0.526	1.679	0.23
0.04717	0.04335	0.03491	0.02643	0.569	0.420	1.823	0.26
0.04144	0.05656	0.03364	0.03905	0.463	0.308	1.934	0.29
0.03450	0.07254	0.02936	0.05301	0.356	0.208	2.106	0.32

Poly(vinylbenzyltriethylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.05587		0.00789	0.00003				
0.05537	0.00137	0.01334	0.00019	0.986	0.973	1.931	0.29
0.05465	0.00332	0.01411	0.00050	0.966	0.935	1.976	0.30
0.05417	0.00463	0.01717	0.00081	0.955	0.906	2.200	0.34
0.05311	0.00752	0.02017	0.00155	0.929	0.847	2.355	0.37
0.05088	0.01358	0.02497	0.00384	0.867	0.727	2.444	0.39
0.04817	0.02096	0.02854	0.00737	0.795	0.591	2.679	0.43
0.04697	0.02422	0.02912	0.00908	0.762	0.541	2.723	0.44
0.04451	0.03092	0.03249	0.01468	0.689	0.425	2.992	0.48
0.04059	0.04158	0.03249	0.02329	0.582	0.307	3.150	0.50
0.03744	0.05015	0.03158	0.03105	0.504	0.235	3.314	0.52
0.03150	0.06632	0.02751	0.04320	0.389	0.147	3.693	0.57

X_{Cl} and $\bar{X}_{Cl}$ were the chloride mole fraction free and bound when overbarred.

Poly(vinylbenzyltripropylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.04529		0.00615	0.00006				
0.04499	0.00099	0.01090	0.00009	0.992	0.974	3.392	0.53
0.04455	0.00248	0.01358	0.00027	0.980	0.933	3.552	0.55
0.04383	0.00492	0.01680	0.00067	0.961	0.864	3.912	0.59
0.04263	0.00895	0.01964	0.00154	0.927	0.756	4.097	0.61
0.04069	0.01545	0.02336	0.00361	0.866	0.594	4.428	0.65
0.03800	0.02447	0.02758	0.00889	0.756	0.401	4.636	0.67
0.03393	0.03814	0.02876	0.02029	0.586	0.225	4.887	0.69
0.02923	0.05390	0.02591	0.03263	0.443	0.135	5.089	0.71
0.02363	0.07269	0.02133	0.04610	0.316	0.080	5.338	0.73

Poly(vinylbenzyltributylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.04912		0.00593	0.00004				
0.04875	0.00112	0.01073	0.00006	0.995	0.973	5.356	0.73
0.04799	0.00349	0.01816	0.00033	0.982	0.904	5.768	0.76
0.04661	0.00777	0.02030	0.00087	0.959	0.792	6.110	0.79
0.04497	0.01284	0.02496	0.00212	0.922	0.651	6.323	0.80
0.04273	0.01976	0.02876	0.00470	0.860	0.481	6.599	0.82
0.04022	0.02754	0.03023	0.00846	0.781	0.344	6.822	0.83
0.03813	0.03401	0.03113	0.01302	0.705	0.250	7.171	0.86
0.03531	0.04274	0.03074	0.02056	0.599	0.171	7.257	0.86
0.03078	0.05675	0.02793	0.03233	0.464	0.105	7.397	0.87

poly(vinylbenzyltripentylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.04377	0.00001	0.00593	0.00012				
0.04336	0.00144	0.01230	0.00013	0.990	0.959	4.101	0.61
0.04269	0.00377	0.01672	0.00035	0.979	0.884	6.247	0.80
0.04202	0.00609	0.02024	0.00072	0.966	0.802	6.964	0.84
0.04080	0.01034	0.02278	0.00147	0.940	0.670	7.654	0.88
0.03932	0.01546	0.02596	0.00300	0.896	0.518	8.055	0.91
0.03769	0.02115	0.02761	0.00528	0.840	0.388	8.241	0.92
0.03608	0.02671	0.02912	0.00871	0.770	0.279	8.649	0.94
0.03323	0.03662	0.02949	0.01686	0.636	0.159	9.225	0.96
0.02668	0.05936	0.02472	0.03346	0.425	0.070	9.742	0.99

X_{Cl^-} and $\bar{X}_{Cl^-}$ were the chloride mole fraction free and bound when overbarred.

Table 5-15:

BINDING by HIGH CROSS-LINKED
POLY(VINYLBENZYLtriALKYLAMMONIUM CHLORIDE) to NITRATES in
AQUEOUS SOLUTION

Poly(vinylbenzyltrimethylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.06133		0.00165	0.00001				
0.06106	0.00057	0.00698	0.00006	0.991	0.991	1.021	0.01
0.06046	0.00179	0.00903	0.00021	0.977	0.970	1.322	0.12
0.05921	0.00438	0.01050	0.00058	0.947	0.928	1.403	0.15
0.05775	0.00738	0.01171	0.00095	0.925	0.877	1.722	0.24
0.05501	0.01304	0.01569	0.00221	0.877	0.784	1.959	0.29
0.05117	0.02096	0.02133	0.00526	0.802	0.655	2.135	0.33
0.04537	0.03293	0.02581	0.01167	0.689	0.479	2.404	0.38
0.04082	0.04232	0.02694	0.01777	0.603	0.361	2.682	0.43
0.03542	0.05344	0.02856	0.03033	0.485	0.229	3.173	0.50
0.03006	0.06450	0.02602	0.04235	0.381	0.155	3.361	0.53

Poly(vinylbenzyltriethylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.07620		0.00140	0.00002				
0.07572	0.00079	0.00678	0.00003	0.996	0.989	2.512	0.40
0.07477	0.00237	0.00930	0.00011	0.988	0.967	2.897	0.46
0.07303	0.00526	0.00930	0.00023	0.976	0.927	3.199	0.51
0.06971	0.01078	0.01700	0.00093	0.948	0.842	3.431	0.54
0.06365	0.02083	0.02765	0.00341	0.890	0.674	3.925	0.59
0.05768	0.03074	0.03359	0.00763	0.815	0.510	4.224	0.63
0.04921	0.04481	0.03492	0.01573	0.689	0.329	4.519	0.66
0.03914	0.06152	0.03307	0.03273	0.503	0.174	4.789	0.68
0.02615	0.08310	0.02432	0.05980	0.289	0.073	5.173	0.71

X_{Cl} and $\bar{X}_{Cl}$ were the chloride mole fraction free and bound when overbarred.

Poly(vinylbenzyltripropylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.04545		0.00086	0.00011				
0.04516	0.00079	0.00593	0.00013	0.979	0.983	0.770	-0.11
0.04484	0.00171	0.00794	0.00015	0.982	0.959	2.263	0.35
0.04398	0.00410	0.00868	0.00021	0.976	0.901	4.568	0.66
0.04225	0.00889	0.01055	0.00053	0.952	0.791	5.225	0.72
0.04012	0.01484	0.01606	0.00160	0.909	0.645	5.513	0.74
0.03651	0.02487	0.02236	0.00519	0.811	0.418	5.986	0.78
0.03238	0.03639	0.02562	0.01297	0.664	0.224	6.853	0.84
0.02738	0.05030	0.02436	0.02692	0.475	0.114	7.002	0.85
0.02236	0.06427	0.02101	0.04342	0.326	0.061	7.463	0.87

Poly(vinylbenzyltributylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.03683		0.00067	0.00002				
0.03671	0.00041	0.00274	0.00003	0.989	0.989	1.008	0.01
0.03633	0.00171	0.00502	0.00008	0.985	0.950	3.355	0.53
0.03589	0.00322	0.00542	0.00009	0.983	0.907	5.919	0.77
0.03501	0.00625	0.00935	0.00026	0.973	0.811	8.308	0.92
0.03337	0.01187	0.01435	0.00092	0.940	0.635	8.973	0.95
0.03084	0.02057	0.01921	0.00319	0.858	0.401	9.000	0.95
0.02770	0.03135	0.02254	0.00987	0.695	0.194	9.494	0.98
0.02429	0.04307	0.02210	0.02154	0.506	0.092	10.105	1.01
0.02099	0.05441	0.01998	0.03497	0.364	0.050	10.966	1.04

Poly(vinylbenzyltripentylammonium chloride)

Total chloride (mole kg ⁻¹)	Total nitrate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free nitrate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl^-}$	$K_{Cl}^{NO_3}$	NCS
0.03463	0.00001	0.00018	0.00004				
0.03449	0.00050	0.00217	0.00005	0.979	0.986	0.655	-0.18
0.03423	0.00148	0.00530	0.00005	0.990	0.953	4.748	0.68
0.03378	0.00310	0.00578	0.00006	0.990	0.902	10.974	1.04
0.03259	0.00746	0.00767	0.00020	0.975	0.774	11.422	1.06
0.03123	0.01243	0.01200	0.00059	0.953	0.619	12.561	1.10
0.02920	0.01984	0.01704	0.00192	0.899	0.404	13.086	1.12
0.02670	0.02896	0.02136	0.00663	0.763	0.193	13.438	1.13
0.02351	0.04062	0.02161	0.01827	0.542	0.079	13.868	1.14
0.02022	0.05263	0.01938	0.03263	0.373	0.041	14.013	1.15

X_{Cl^-} & $\bar{X}_{Cl^-}$ were the chloride mole fraction free and bound when overbarred.

Table 5-16

BINDING by LOW CROSS-LINKED
POLY(VINYLBENZYLtriALKYLAMMONIUM CHLORIDE) to SULPHATE
in AQUEOUS SOLUTION

Poly(vinylbenzyltrimethylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03318		0.00411	0.00001					
0.03537	0.00267	0.01175	0.00011	0.982	0.821	12.15	0.038	-3.78
0.03292	0.00587	0.01732	0.00048	0.948	0.591	12.05	0.081	-3.45
0.03360	0.00962	0.02134	0.00115	0.903	0.420	12.84	0.135	-3.23
0.03298	0.02143	0.02447	0.00381	0.763	0.194	13.32	0.244	-2.97
0.03471	0.03054	0.02774	0.00682	0.670	0.128	13.82	0.389	-2.77
0.03234	0.03714	0.02718	0.01013	0.573	0.087	14.05	0.520	-2.65
0.03243	0.05068	0.02842	0.01675	0.459	0.056	14.34	0.783	-2.47
0.03272	0.07181	0.02935	0.02681	0.354	0.036	14.64	1.108	-2.32
0.03158	0.09172	0.02947	0.04460	0.248	0.022	14.76	2.020	-2.06

Poly(vinylbenzyltriethylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03246		0.00369	0.00002					
0.03296	0.00285	0.01014	0.00015	0.971	0.808	7.92	0.025	-3.98
0.03236	0.00491	0.01444	0.00042	0.945	0.666	8.60	0.048	-3.69
0.03176	0.00959	0.01908	0.00137	0.875	0.435	9.04	0.094	-3.40
0.03138	0.01469	0.02088	0.00260	0.801	0.303	9.25	0.131	-3.25
0.03033	0.02128	0.02240	0.00484	0.698	0.194	9.59	0.196	-3.08
0.03139	0.03608	0.02567	0.01124	0.533	0.103	9.91	0.369	-2.80
0.03045	0.04757	0.02567	0.01648	0.438	0.071	10.12	0.472	-2.70
0.03073	0.06734	0.02654	0.02549	0.342	0.048	10.40	0.637	-2.57
0.03005	0.09138	0.02721	0.04351	0.238	0.029	10.52	1.118	-2.32

X_{Cl} and $\bar{X}_{Cl}$ were the chloride mole fraction free and bound when overbarred

Poly(vinylbenzyltripropylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03221		0.00615	0.00001					
0.03330	0.00255	0.00984	0.00020	0.961	0.833	5.01	0.02	-4.13
0.03312	0.00442	0.01381	0.00050	0.932	0.711	5.59	0.03	-3.85
0.03258	0.00899	0.01837	0.00158	0.853	0.490	6.05	0.07	-3.56
0.03331	0.01545	0.02137	0.00320	0.770	0.328	6.85	0.11	-3.33
0.03231	0.02100	0.02254	0.00512	0.688	0.235	7.15	0.15	-3.20
0.03150	0.03257	0.02427	0.01014	0.545	0.139	7.41	0.24	-2.99
0.03182	0.04590	0.02581	0.01628	0.442	0.092	7.81	0.35	-2.82
0.03154	0.06901	0.02668	0.02774	0.325	0.056	8.16	0.53	-2.65
0.03037	0.08552	0.02613	0.03636	0.264	0.041	8.33	0.63	-2.57

Poly(vinylbenzyltributylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03013		0.00404	0.00001					
0.03101	0.00244	0.00801	0.00020	0.952	0.837	3.89	0.012	-4.28
0.03110	0.00420	0.01189	0.00052	0.919	0.723	4.38	0.024	-3.98
0.03063	0.00899	0.01701	0.00194	0.814	0.491	4.53	0.052	-3.65
0.03046	0.01316	0.01861	0.00322	0.743	0.374	4.85	0.071	-3.51
0.03023	0.01946	0.02011	0.00534	0.653	0.264	5.25	0.102	-3.35
0.03051	0.03357	0.02331	0.01246	0.483	0.146	5.49	0.195	-3.07
0.02984	0.04419	0.02360	0.01745	0.403	0.104	5.80	0.252	-2.96
0.02898	0.06691	0.02409	0.02936	0.291	0.061	6.30	0.393	-2.77
0.02838	0.08843	0.02409	0.04092	0.227	0.043	6.52	0.503	-2.66

poly(vinylbenzyltripentylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03084		0.00266	0.00001					
0.03242	0.00255	0.00757	0.00025	0.938	0.844	2.79	0.009	-4.42
0.03178	0.00467	0.01238	0.00080	0.885	0.715	3.07	0.020	-4.06
0.03139	0.00947	0.01705	0.00253	0.771	0.508	3.26	0.041	-3.75
0.03036	0.01604	0.01891	0.00493	0.657	0.340	3.72	0.067	-3.54
0.03131	0.02423	0.02151	0.00880	0.550	0.241	3.84	0.101	-3.37
0.03036	0.03432	0.02280	0.01423	0.445	0.158	4.26	0.161	-3.16
0.03027	0.05020	0.02437	0.02416	0.335	0.102	4.45	0.258	-2.96
0.03043	0.06902	0.02488	0.03381	0.269	0.073	4.67	0.324	-2.86
0.02995	0.08747	0.02437	0.04417	0.216	0.053	4.89	0.397	-2.77

X_{Cl} and $\bar{X}_{Cl}$ were the chloride mole fraction free and bound when overbarred.

Table 5-17

**BINDING by HIGH CROSS-LINKED
POLY(VINYLBENZYLtriALKYLAMMONIUM CHLORIDE) to SULPHATE
in AQUEOUS SOLUTION**

Poly(vinylbenzyltrimethylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03128		0.00052	0.00001					
0.03271	0.00268	0.00455	0.00005	0.977	0.843	8.08	0.000	-6.00
0.03114	0.00324	0.00730	0.00010	0.974	0.791	9.82	0.001	-5.46
0.03057	0.00640	0.01224	0.00039	0.939	0.604	10.15	0.003	-4.81
0.03253	0.00842	0.01444	0.00069	0.912	0.494	10.67	0.006	-4.50
0.03246	0.03946	0.02226	0.00600	0.650	0.132	12.18	0.215	-2.93
0.03129	0.02459	0.01968	0.00313	0.759	0.213	11.61	0.131	-3.14
0.03160	0.05559	0.02314	0.00978	0.542	0.085	12.82	0.678	-2.43
0.03176	0.08067	0.02447	0.01651	0.426	0.054	13.06	1.015	-2.25
0.03047	0.10670	0.02413	0.02372	0.337	0.037	13.33	1.303	-2.14

Poly(vinylbenzyltriethylammonium chloride)

Total chloride (mole kg ⁻¹)	Total sulphate (mole kg ⁻¹)	Free chloride (mole kg ⁻¹)	Free sulphate (mole kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03246		0.00254	0.00002					
0.03317	0.00211	0.0051	0.00005	0.981	0.872	7.44	0.009	-4.27
0.03372	0.00528	0.0107	0.00030	0.947	0.698	7.73	0.025	-3.85
0.03374	0.01033	0.0161	0.00107	0.882	0.488	7.83	0.049	-3.55
0.03269	0.01536	0.0172	0.00226	0.792	0.372	8.00	0.050	-3.55
0.03160	0.02216	0.0187	0.00335	0.736	0.255	8.15	0.082	-3.33
0.03201	0.03337	0.0200	0.00554	0.643	0.178	8.33	0.102	-3.24
0.03285	0.04587	0.0221	0.00882	0.556	0.127	8.58	0.140	-3.10
0.03105	0.06865	0.0226	0.01559	0.414	0.074	8.82	0.198	-2.95
0.02127	0.08861	0.0237	0.02273	0.342	0.055	9.01	0.255	-2.84

X_{Cl} and $\bar{X}_{Cl}$ were the chloride mole fraction free and bound when overbarred.

Poly(vinylbenzyltripropylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03305		0.00243	0.00001					
0.03366	0.00306	0.00662	0.00015	0.957	0.823	4.83	0.009	-4.24
0.03295	0.00488	0.00919	0.00034	0.931	0.724	5.15	0.015	-4.03
0.03437	0.00967	0.01381	0.00105	0.867	0.544	5.48	0.030	-3.75
0.03393	0.01558	0.01654	0.00219	0.790	0.394	5.80	0.043	-3.58
0.03290	0.02331	0.01865	0.00420	0.689	0.272	5.95	0.060	-3.44
0.03343	0.03429	0.02059	0.00710	0.592	0.191	6.14	0.077	-3.33
0.03178	0.04652	0.02059	0.01046	0.496	0.134	6.34	0.087	-3.28
0.03169	0.07125	0.02247	0.01937	0.367	0.082	6.52	0.122	-3.13
0.03274	0.08648	0.02381	0.02479	0.324	0.067	6.64	0.142	-3.07

Poly(vinylbenzyltributylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03271		0.00294	0.00001					
0.03389	0.00229	0.00558	0.00012	0.959	0.867	3.55	0.006	-4.39
0.03412	0.00501	0.01000	0.00050	0.909	0.728	3.73	0.014	-4.04
0.03356	0.01012	0.01215	0.00130	0.824	0.548	3.85	0.020	-3.89
0.03184	0.01472	0.01447	0.00257	0.738	0.417	3.93	0.030	-3.72
0.03156	0.02199	0.01670	0.00466	0.642	0.300	4.17	0.044	-3.55
0.03312	0.03391	0.01919	0.00810	0.542	0.212	4.39	0.063	-3.39
0.03317	0.04606	0.02084	0.01226	0.459	0.154	4.66	0.087	-3.25
0.03155	0.06830	0.02119	0.02018	0.344	0.097	4.87	0.116	-3.13
0.03159	0.08745	0.02244	0.02864	0.282	0.072	5.04	0.157	-3.00

Poly(vinylbenzyltripentylammonium chloride)

Total chloride (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free chloride (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	X_{Cl^-}	$\bar{X}_{Cl}$	$\alpha_{Cl}^{SO_4}$	$K_{Cl}^{SO_4}$	SCS
0.03172		0.00308	0.00001					
0.03316	0.00236	0.00515	0.00020	0.928	0.866	1.91	0.004	-4.41
0.03280	0.00481	0.00683	0.00050	0.872	0.751	2.11	0.006	-4.09
0.03307	0.00971	0.01143	0.00162	0.779	0.572	2.34	0.014	-3.74
0.03205	0.01518	0.01390	0.00306	0.695	0.428	2.57	0.024	-3.50
0.03047	0.02298	0.01572	0.00538	0.594	0.295	2.77	0.038	-3.22
0.03173	0.03844	0.01876	0.01011	0.481	0.186	3.00	0.067	-2.96
0.03125	0.04647	0.01916	0.01253	0.433	0.151	3.07	0.079	-2.85
0.03055	0.06923	0.01996	0.01952	0.338	0.096	3.22	0.113	-2.67
0.02039	0.08924	0.02030	0.02509	0.288	0.073	3.31	0.136	-2.59

X_{Cl} & $\bar{X}_{Cl}$ were the chloride mole fraction free and bound when overbarred.

Table 5-18:

BINDING by LOW CROSS-LINKED
POLY(VINYLBENZYLtriALKYLAMMONIUM NITRATE) to SULPHATE
in AQUEOUS SOLUTION

Poly(vinylbenzyltrimethylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03575		0.00239	0.00001					
0.03688	0.00249	0.00810	0.00042	0.906	0.874	0.72	329.1	-4.88
0.03599	0.00501	0.01232	0.00130	0.826	0.761	0.67	167.5	-4.59
0.03676	0.00927	0.01633	0.00314	0.722	0.625	0.64	98.06	-4.35
0.03573	0.01334	0.01855	0.00510	0.645	0.511	0.57	64.46	-4.17
0.03680	0.02072	0.02054	0.00805	0.561	0.391	0.50	44.52	-4.01
0.03635	0.03072	0.02229	0.01229	0.475	0.276	0.42	28.37	-3.81
0.03535	0.04828	0.02492	0.01987	0.385	0.155	0.29	12.33	-3.45
0.03505	0.06593	0.02591	0.02679	0.326	0.105	0.24	8.06	-3.27
0.03280	0.09277	0.02636	0.04163	0.240	0.059	0.20	4.30	-3.00

Poly(vinylbenzyltriethylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03513		0.00193	0.00001					
0.03621	0.00241	0.00703	0.00040	0.897	0.879	0.84	3865	-4.96
0.03635	0.00464	0.01172	0.00125	0.824	0.784	0.78	179.2	-4.63
0.03532	0.01040	0.01489	0.00371	0.667	0.604	0.76	110.8	-4.42
0.03511	0.01625	0.01802	0.00687	0.567	0.477	0.69	66.6	-4.19
0.03489	0.02439	0.01929	0.01082	0.471	0.365	0.64	49.8	-4.07
0.03468	0.03631	0.02176	0.01807	0.376	0.262	0.59	30.8	-3.86
0.03486	0.05348	0.02455	0.06047	0.287	0.183	0.56	18.2	-3.63
0.03452	0.06282	0.02487	0.03364	0.270	0.142	0.45	13.3	-3.49
0.03425	0.09312	0.02736	0.05739	0.193	0.088	0.40	6.59	-3.19

X_{NO_3} and $\bar{X}_{NO_3}$ were the chloride mole fraction free and bound when overbarred.

Poly(vinylbenzyltripropylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03304		0.00092	0.00001					
0.03455	0.00237	0.00435	0.00068	0.762	0.899	2.79	294.7	-4.86
0.03389	0.00481	0.00679	0.00195	0.635	0.826	2.73	164.5	-4.55
0.03448	0.01084	0.00982	0.00567	0.464	0.705	2.75	90.67	-4.31
0.03305	0.01553	0.01155	0.00922	0.385	0.630	2.72	64.35	-4.13
0.03309	0.02326	0.01420	0.01555	0.313	0.551	2.69	41.93	-4.04
0.03292	0.03475	0.01612	0.02489	0.245	0.460	2.63	27.46	-3.82
0.03284	0.05056	0.01824	0.03835	0.192	0.374	2.51	16.81	-3.63
0.03134	0.06722	0.01952	0.05357	0.152	0.308	2.48	11.60	-3.48
0.03119	0.08938	0.02056	0.01372	0.122	0.253	2.43	7.706	-3.30

Poly(vinylbenzyltributylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03559		0.00225	0.00001					
0.03500	0.00258	0.00395	0.00061	0.828	0.881	1.53	664.5	-5.18
0.03700	0.00495	0.00618	0.00185	0.746	0.809	1.44	280.0	-4.81
0.03671	0.01135	0.01253	0.00508	0.578	0.645	1.33	166.5	-4.58
0.03608	0.01824	0.01724	0.00962	0.468	0.527	1.27	104.0	-4.38
0.03569	0.02586	0.02183	0.01494	0.387	0.435	1.22	74.1	-4.23
0.03566	0.03922	0.02819	0.02511	0.299	0.336	1.19	48.7	-4.05
0.03489	0.05330	0.03406	0.03625	0.238	0.265	1.15	35.5	-3.91
0.03472	0.07169	0.04122	0.05104	0.190	0.207	1.11	25.7	-3.77
0.03458	0.09752	0.05231	0.07130	0.148	0.157	1.08	19.1	-3.65

poly(vinylbenzyltripentylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03507		0.00177	0.00003					
0.03595	0.00242	0.00491	0.00059	0.807	0.865	2.03	191.8	-4.66
0.03671	0.00555	0.00993	0.00230	0.683	0.761	1.92	78.14	-4.27
0.03530	0.01034	0.01261	0.00528	0.544	0.577	1.87	48.63	-3.94
0.03575	0.01750	0.01592	0.01040	0.433	0.456	1.83	29.36	-3.75
0.03471	0.02592	0.01786	0.01700	0.344	0.351	1.80	19.78	-3.54
0.03502	0.03772	0.02005	0.02661	0.274	0.247	1.79	13.20	-3.39
0.03473	0.05249	0.02112	0.03835	0.216	0.180	1.75	8.93	-3.24
0.03399	0.07032	0.02195	0.05308	0.171	0.131	1.69	5.91	-3.12
0.03345	0.09567	0.02243	0.07327	0.133	0.096	1.61	3.68	-3.00

X_{NO_3} and $\bar{X}_{NO_3}$ were the chloride mole fraction free and bound when overbarred.

Table 5-19

BINDING by HIGH CROSS-LINKED
POLY(VINYLBENZYLtriALKYLAMMONIUM NITRATE) to SULPHATE in
AQUEOUS SOLUTION

Poly(vinylbenzyltrimethylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03532		0.00179	0.00001					
0.03693	0.00251	0.00568	0.00042	0.871	0.882	1.11	807.6	-5.17
0.03642	0.00504	0.00934	0.00135	0.775	0.786	1.07	407.8	-4.87
0.03527	0.00871	0.01214	0.00304	0.666	0.671	1.02	255.7	-4.67
0.03610	0.01362	0.01472	0.00538	0.578	0.565	0.95	169.3	-4.49
0.03605	0.01999	0.01692	0.00899	0.485	0.465	0.92	121.3	-4.34
0.03567	0.03115	0.01743	0.01419	0.381	0.350	0.87	99.38	-4.26
0.03487	0.04606	0.02103	0.02602	0.288	0.257	0.86	55.55	-4.00
0.03393	0.06516	0.02291	0.04020	0.222	0.181	0.77	33.48	-3.78
0.03265	0.09301	0.02487	0.06546	0.160	0.124	0.74	18.27	-3.52

Poly(vinylbenzyltriethylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03657		0.00058	0.00001					
0.03971	0.00260	0.00585	0.00061	0.828	0.895	1.76	1078	-5.28
0.03866	0.00500	0.00820	0.00155	0.725	0.815	1.67	658.2	-5.06
0.03831	0.01068	0.01107	0.00410	0.574	0.674	1.54	382.2	-4.83
0.03699	0.01787	0.01342	0.00805	0.455	0.545	1.44	247.1	-4.64
0.03777	0.02700	0.01609	0.01360	0.372	0.447	1.37	164.3	-4.46
0.03787	0.03882	0.01790	0.02109	0.298	0.360	1.33	121.1	-4.33
0.03687	0.05198	0.01992	0.03152	0.240	0.293	1.31	85.2	-4.18
0.03619	0.07020	0.02152	0.04541	0.192	0.228	1.25	59.4	-4.02
0.03607	0.09946	0.02407	0.06933	0.148	0.166	1.15	34.3	-3.78

X_{NO_3} and $\bar{X}_{NO_3}$ were the chloride mole fraction free and bound when overbarred.

Poly(vinylbenzyltripropylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03304		0.00092	0.00001					
0.03455	0.00237	0.00435	0.00066	0.741	0.900	3.15	2429	-5.51
0.03389	0.00481	0.00679	0.00190	0.626	0.837	3.07	12502	-5.22
0.03448	0.01084	0.00982	0.00577	0.451	0.710	2.97	667.8	-5.96
0.03305	0.01553	0.01155	0.01109	0.363	0.624	2.90	399.8	-4.81
0.03309	0.02326	0.01420	0.01648	0.296	0.548	2.88	314.8	-4.62
0.03292	0.03475	0.01612	0.02742	0.231	0.460	2.84	209.1	-4.46
0.03284	0.05056	0.01824	0.04099	0.185	0.387	2.77	138.5	-4.27
0.03134	0.06722	0.01952	0.05676	0.150	0.323	2.71	101.7	-4.12
0.03119	0.08938	0.02056	0.07923	0.120	0.267	2.67	71.7	-3.96

Poly(vinylbenzyltributylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03523		0.00074	0.00001					
0.03692	0.00250	0.00376	0.00066	0.768	0.898	2.67	1955	-5.58
0.03656	0.00483	0.00638	0.00180	0.653	0.819	2.40	998.3	-5.29
0.03570	0.01113	0.00948	0.00518	0.487	0.685	2.30	552.5	-5.02
0.03577	0.01806	0.01267	0.00844	0.406	0.602	2.21	389.8	-4.87
0.03447	0.02500	0.01384	0.01442	0.330	0.517	2.17	253.7	-4.69
0.03538	0.03851	0.01647	0.02309	0.259	0.419	2.06	173.0	-4.51
0.03437	0.05346	0.01864	0.03572	0.203	0.330	1.93	111.4	-4.33
0.03395	0.07144	0.01996	0.05000	0.161	0.261	1.84	78.7	-4.20
0.03394	0.09623	0.02158	0.06926	0.129	0.209	1.78	55.4	-4.05

Poly(vinylbenzyltripentylammonium nitrate)

Total nitrate (mol kg ⁻¹)	Total sulphate (mol kg ⁻¹)	Free nitrate (mol kg ⁻¹)	Free sulphate (mol kg ⁻¹)	$X_{NO_3^-}$	$\bar{X}_{NO_3}$	$\alpha_{SO_4^{2-}}^{NO_3^-}$	$K_{NO_3^-}^{SO_4^{2-}}$	SNS
0.03659		0.00057	0.00001					
0.03756	0.00236	0.00321	0.00005	0.969	0.881	4.27	66.1	-5.12
0.03724	0.00521	0.00620	0.00024	0.928	0.757	4.13	236.0	-5.78
0.03728	0.01026	0.00918	0.00078	0.854	0.597	3.96	148.6	-5.53
0.03744	0.01739	0.01183	0.00196	0.751	0.453	3.63	110.3	-5.34
0.03688	0.02536	0.01353	0.00360	0.652	0.349	3.50	89.1	-5.21
0.03659	0.03699	0.01636	0.00703	0.538	0.252	3.45	61.4	-5.01
0.03561	0.05028	0.01812	0.01207	0.429	0.189	3.22	49.3	-4.87
0.03553	0.06812	0.01990	0.01998	0.334	0.139	3.09	37.9	-4.72
0.03490	0.09356	0.02169	0.03362	0.244	0.099	2.93	27.8	-4.55

X_{NO_3} and $\bar{X}_{NO_3}$ were the chloride mole fraction free and bound when overbarred.

CONCLUSION

In order to determine the guidelines for the selectivity of some ion-exchange resins towards nitrates, the association of common ions such as chlorides, nitrates and sulphates, was first studied. The binding site of the monomer was a quaternary ammonium functional group on which three alkyl chains were attached. The alkyl chains varied from methyl to n-pentyl in order to compare the effects of the size of the alkyl group. The monomers were polymerised to form linear and cross-linked polymers. The association between the different polymers and the anions was studied to estimate the role of the resin matrix. Two differently cross-linked polymers were prepared to assess the influence of the cross-linking.

The monomers studies were actually carried out on monomer analogues, benzyltrialkylammonium chloride. Monomers, vinylbenzyltrialkylammonium chlorides, were synthesised as reported in the literature [23]. They were used to prepare linear and cross-linked polymers, with divinylbenzene as a cross-linker for the latter [23].

Investigations of ion-pair formation were done in aqueous solutions, which were prepared by weight. Densities were measured to convert molalities into molarities, and to obtain the relative viscosities. Apparent molar volumes were deduced from densities, using the Masson equation [31], for all salts considered. The cation contributions were identical when deduced from both salt results. The results obtained were in good agreement with a previous publication [4].

From viscosity B coefficients, the hydrodynamic volumes of the solute were calculated and compared to the apparent molar volumes obtained from density measurements. Salt hydrophobic hydration numbers were appraised. These values increased with the size of

the alkyl group, from 2 for the ethyl group up to 20 for the pentyl group and therefore displayed an increasing structure maker character of the long monomer analogues. Cation radii were computed. They increased steadily, from 403 pm for the methyl, up to 520 pm for the pentyl monomer analogue.

Viscosity corrected relaxation times, available from ^{14}N NMR spectroscopy, were used to estimate the extent of ion-pair associations. The method was initially tested using potassium nitrate as a control. Association constants obtained were in the order of the results calculated from the conductance data, (see table 3-8). The model implying a slow ion-pair exchange rate compared to the rotational correlation times, τ_c , for the end-over-end rotation of the C_3 axis of the anions was preferred; due to the fact that association constants were in closer agreement with the conductance results previously measured and the fact that this model fits the data better. It is logical that the rate of ion-exchange is slower than τ_c , equal to a few pico seconds and thus characteristic of electron transfer processes.

The nitrate monomer analogue solutions were measured at different concentrations. Association constants were small, but increased from methyl, $K_a = 0.5$, to butyl $K_a = 2.29$. They were in good agreement with constants published previously from conductance measurements [12], and the slow model was also preferred for the ion-exchange.

To understand the role of the matrix, monomers were linearly polymerised using a radical initiator. The number of monomer units, obtained from viscosity measurements and the Mark-Houwink relation [74], were estimated to be around 90000. ^{14}N nitrate relaxation times of solutions containing some soluble chloride linear polymers, from 2×10^{-4} to 9×10^{-3} equivalent mole per dm^{-3} , and a constant nitrate concentration of 5×10^{-2} M were measured. The nitrate fraction bound was found to be high and indicated up to twice as much nitrate bound as expected on the polymer from the known capacity or charge density. This amount increased as the length of the alkyl group increased. It was quite possible that a large proportion of nitrate was bound, especially when compared to the chloride co-ions. The excess of the measured bound species was probably due to

nitrates, not really bound, but probably trapped in the coil formed by the dissolved polymer in an electrolyte solution. It is known that the charge density of such a poly electrolyte is high and that ionic condensation takes place [93]. One can imagine that strong interactions occur with the anions.

More problems emerged because of a low signal/noise ratio. Due to its solubility, the polymer concentration was at the most $0.01 \text{ eq mol dm}^{-3}$. On the other hand, a nitrate concentration of $5 \times 10^{-2} \text{ M}$ was required in order to detect an acceptable signal. Therefore, there was always an excess of nitrates. A different experiment was designed to study the nitrate binding in a low nitrate/polymer concentration range.

Ion selective electrodes, I.S.E., were used to measure quantitatively the amount of free species in solution. Equilibrium constants were obtained by measuring the free species in permanently stirred solutions. The concentration of bound anions were deduced from the total known concentration and the measured free concentration. The equilibrium constants showed that polyelectrolyte had a higher affinity towards nitrates than either the chlorides or sulphates. When they were compared to the nitrate/monomer analogues association constants, they displayed a common increase with the size of the alkyl group. A loose tridimensional structure improved nitrate associations. It was surprising that the nitrate affinity was higher when the co-ion was sulphate rather than chloride since the electrostatic laws state that the binding force between charged particles is proportional to the product of the charge of both the anion and the cation. Sulphates were not measured directly, but were deduced from the measurements of the free chlorides released. As already shown in the cross-linked polymer survey, the equality assumed one sulphate bound for every two chlorides released, was not always verified.

The degree of cross-linking in the two sorts of polymers synthesised was satisfactorily determined using microanalysis of five samples each. Water retention proved that the structure was homogeneous among the polymers having the same cross-linking.

Using chloride-, nitrate- and lead-I.S.E., the free anion species were measured, the amount of bound ones deduced, and results were expressed using several different

conventional ways such as separation factors, equilibrium constants, selectivity and isotherms.

Cross-linked polymers were nitrate selective against chlorides, a phenomena usually observed, and sulphates. Previously observed with monomer analogues and linear polymers, nitrate affinity was enhanced by the cross-linked structure. Among the cross-linked polymers, higher nitrate selectivity was recorded when long alkyl chains such as butyl or pentyl were attached to the quaternary ammonium functional group. A long alkyl group cluttered up the binding site and diminished the potential effect of the charged quaternary ammonium sites. Nitrates had a charge density smaller than chlorides and were therefore less affected by a more hydrophobic environment, produced by long alkyl chains. Larger sulphate anions needed a larger binding site than either chlorides or nitrates.

A high cross-linked degree also favoured nitrate adsorption. It was responsible for a more rigid structure polymer, and a consequently smaller binding site, which reduced the rate of exchange with larger ions such as sulphates.

Both, the large size of the alkyl chain and the high cross-linking degree contributed to the increasing nitrate affinity of the polymer over the small affinity of the monomer analogues. A parallel could be established if one compares the properties of the amino acids, considered to be monomers, and the specific functions carried out by proteins which depend so much on the tertiary structure of the polypeptide.

The small extent of the nitrate selectivity recorded was also interesting. A very strong ion-pair formation would handicap the second function expected from an ion-exchange resin, which would be the regeneration. Then, high concentration solutions would have to be employed, which represent a high cost and a polluting factor. At that time, the use of bacteria, capable of degrading nitrates, to regenerate the resins could be an interesting solution. Nitrates would be present at a high concentration, and a necessary amount of regenerant material would provide a certain flexibility in the regeneration step.

This study shows that the initial association characteristic of the monomer unit improves when polymerised and that nitrate affinity was recorded against chlorides and sulphates

for the cross-linked polymers, which have a binding site formed by a quaternary ammonium function. The larger the size of the alkyl group, the easier was the adsorption of relative low charged density anions. Long alkyl chains could be seen as charge buffers which would hinder the adsorption of highly charged ions. The cross-linking degree determines the size of the binding sites, and a highly cross-linked polymer favours the adsorption of smaller ions. From our study, the effect on the equilibrium constant of the size of the alkyl group attached on the binding site was as important as the cross-linking degree. The low charged and medium sized nitrate had a selectivity enhance by these two criteria which should be valid with other binding sites including in other resins and for other anions of the same type. On the contrary sulphates association was favoured by low cross-linked degree and short alkyl group fixed on the binding sites. These results could start a trend in the affinity property which might include other species.

References

- [1] P. Fritsch, G. de Saint Blanquat, *La Recherche* **1985**, 169, 1106.
- [2] L. Zilliox, C. Schenck, H. Kobus, B. Huwe, *La Recherche* **1990**, 227, 18.
- [3] M. Saull, *New Scientist* **1990**, 37, 1.
- [4] G. Solt, *Chem. Eng.* **1987**, 436, 33.
- [5] W. A. G. Ten Brink, J. H. A. Wiezzer, A. F. M. G. Luilpen, A. N. P. Van Heijst, S. A. Pikkar, R. Seldenrijk, *J. Toxicol. Clin. Toxicol.* **1982**, 2, 139.
F. Faivre, *Annales de la Nutrition de L'Alimentation* **1976**, 30, 831.
- [6] C. J. Johnson, B. C. Kross, *Am. J. Ind. Med.* **1990**, 18, 449.
- [7] S. S. Mirvish, *Tox. Appl. Pharm.* **1977**, 31, 235.
- [8] D. Klein, *Cahier du Nutrition et de Dietetique* **1981**, 16, 89.
- [9] *Off. J. Eur. Com.* **1980**, 23, 11.
- [10] M. P. Tassin, *Que Choisir* **1993**, 297, 40.
- [11] R. B. Mellor, J. Ronnenberg, W. H. Campbell, S. Dieckmann, *Nature* **1992**, 355, 717.
- [12] B. J. Steel, A. S. Kayaalp, T. Kurucsev, A. D. Ward, M. B. Jackson, *Aust. J. Chem.* **1990**, 43, 1983.
- [13] B. A. Bolto, M. B. Jackson, R. V. Siudak, *Isr. J. Chem.* **1985**, 26, 17.
- [14] D. Clifford, W. Weber Jr., *Reactive Polymers* **1983**, 1, 77.
- [15] M. B. Jackson, B. A. Bolto, *Reactive Polymers* **1990**, 12, 277.
- [16] P. J. Flory, *Statistical Mechanics of Chain Molecules*, John Wiley & Sons, New York, **1969**.
- [17] R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworths 2nd ed., London, **1959**, a406, b31, c230, dcp14, e408, f457, g125.
- [18] G. A. Guter, Report 4 479 877, U. S. Environment Protection Agency, Cincinnati, OH, **1984**.
- [19] S. Charache, *N. Engl. J. Med.* **1986**, 20, 776.
- [20] T. R. Owen, S. Juergens-Geschwind, *Fertilizer Research* **1986**, 10, 3.
- [21] R. P. Lauch, G. A. Guter, *J. AWWA* **1986**, 83.
- [22] M. Makosza, B. Serefin, *Rocz. Chem.* **1965**, 39, 1223,
Chem. Abstr. **1966**, 64, 12595.
- [23] T. Ikeda, S. Tazure, Y. Suzuki, *Makromol. Chem.* **1984**, 185, 869.
- [24] L. Savidan, *Les Resines Echangeuses d'Ions*, ed. Dunod, Paris, **1963**, a11, b25, c34.

- [25] R. Kunin, *Ion Exchange Resins*, John Wiley & Sons, 2nd ed., New York, 1958, ^a24,45, ^b337, ^c338, ^d99.
- [26] G. E. Boyd, B. A. Soldano, *Z. Elektrochem.* 1953, 57, 162.
- [27] W. C. Bauman, Abstracts, *Division of Colloid Chemistry, Am. Chem. Soc.* 1953, 49.
- [28] K. W. Pepper, *J. Chem. Soc.* 1952, 3124.
- [29] D. E. Mulcahy, Ph. D. Thesis, Department of Chemistry, University of Adelaide, 1967.
- [30] A. Weissberger, B. W. Rossiter, *Physical Methods of Chemistry*, vol. 1, part 4, Wiley Interscience, New York, 1972.
- [31] D. O. Masson, *Phil. Mag.* 1929, 8, 218.
- [32] R. A. Horne, *Water and Aqueous Solution*, Wiley Interscience, New York, 1972, ^a523, ^bcp13, ^c457.
- [33] O. Redlich, D.M. Meyer, *Chem. Rev.* 1964, 64, 221.
- [34] W. C. Root, *J. Am. Chem. Soc.* 1933, 55, 850.
- [35] H. S. Harned, B. B. Owen, *Physical Chemistry of Electrolytic Solutions*, 2nd. ed., Reinhold Publishing Corp., New York, 1950, ^a253.
- [36] J. Poiseuille, *Mem. Savants Etrangers* 1841, 7, 105; *ibid.* 1846, 9, 433.
- [37] A. Einstein, *Ann. Phys.* 1906, 19, 289; *ibid.* 1911, 34, 591.
- [38] G. Jones, M. Dole, *J. Am. Chem. Soc.* 1929, 51, 2950.
- [39] R. H. Stokes, R. Mills, *The International Encyclopedia of Physical Chemistry and Chemical Physics*, vol. 3, Pergamon Press, Oxford, 1965, ^a22.
- [40] J. E. Desnoyers, G. Perron, *J. Sol. Chem.* 1972, 1, 199.
- [41] C. W. Davies, V. E. Malpass, *Trans. Far. Soc.* 1964, 60, 2075.
- [42] P. W. Atkins, *Physical Chemistry*, 4th ed. Oxford University Press, Oxford, 1990, ^a556, ^b558.
- [43] A. Abragam, *The Principal of Nuclear Magnetism*, Oxford University Press, Oxford, 1961.
- [44] M. Gourdji, L. Guibe, A. Peneau, *J. Phys.* 1974, 35, 497.
- [45] W. T. Huntress, *Adv. Magn. Reson.* 1970, 4, 1.
- [46] D. D. McIntyre, A. W. Apblett, P. Lundberg, K. J. Schmidt, H. J. Vogel, *J. Magn. Res.* 1989, 83, 377.
- [47] A. M. de P. Nicholas, R. E. Wasylshen, ^a*J. Can. Chem.* 1987, 65, 951, ^bA. M. de P. Nicholas, R. E. Wasylshen, *J. Phys. Chem.* 1985, 89, 5446.
- [48] M. L. Martin, J. Delpuech, G. J. Martin, *Practical NMR Spectroscopy*, Heyden, London, 1980.

- [49] T. Kurucsev, E. H. Williams, *J. Cryst. Spectr. Res.* **1982**, *12*, 397.
- [50] E. Fukushima, S. B. W. Poeder, *Experimental Pulse NMR*, Addison-Wesley Publishing Company, Reading, U. S. A., **1981**, a165.
- [51] Handbook of Electrode Technology, Orion Research, **1982**.
- [52] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York, **1980**.
- [53] Ion Exchange Resins, BDH, Product 57020 4 G, **1988**.
- [54] J. E. Salmon, D. K. Hale, *Ion Exchange, a Laboratory Manual*, Butterworths Publications, London, **1959**.
- [55] H. W. Kerr, *J. Am. Soc. Agron.* **1928**, *20*, 309.
- [56] A. P. Vanselow, *J. Am. Chem. Soc.* **1932**, *54*, 1307; *ibid.*, *Soil Sci. Soc. Amer. Proc.* **1932**, *33*, 195.
- [57] Handbook of Chemistry and Physics, 55th ed., C.R.C. Press, **1974**.
- [58] T. Kurucsev, *J. Chem. Educ.* **1978**, *55*, 128.
- [59] G. Owens, Ph. D. Thesis, Department of Chemistry, University of Adelaide, **1994**.
- [60] C. Yatome, Y. Takase, *Sen-I Gakkaishi* **1974**, *30*, 54; *ibid.* **1976**, *32*, 69.
- [61] T. Kurucsev, A. M. Sargeson, B. O. West, *J. Phys. Chem.* **1957**, *61*, 1567.
- [62] W. Zielenkiewicz, O.V. Kulikov, I. Kulis-Cwikla, *J. Sol. Chem.* **1993**, *22*, 968.
- [63] H. Falkenhagen, E. L. Vernon, *Z. Phys.* **1932**, *33*, 140.
- [64] A. F. Scott, *J. Phys. Chem.* **1931**, *35*, 2315.
- [65] D. Fu-Tai-Tuan, R. M. Fuoss, *J. Phys. Chem.* **1943**, *67*, 1343.
- [66] H. S. Frank, W.-Y. Wen, *Far. Soc. Disc.* **1957**, *24*, 133.
- [67] M. Nakahara, A. Adachi, H. Kiyoyama, A. Shimizu, Y. Taniguchi, Y. Masuda, *J. Phys. Chem.* **1990**, *94*, 6179.
- [68] Kaye & Laby, *Tables of Physical and Chemical Constants*, Longman, London, **1986**, a255.
- [69] Handbook of Electrolyte Solutions, U.M.M. Lobo, Elsevier, **1989**, a1050.
- [70] M.-C. Justice, R. Bury, J.-C. Justice, *Electrochim. Acta* **1971**, *16*, 687.
- [71] I. D. McKenzie, R. M. Fuoss, *J. Phys. Chem.* **1961**, *65*, 999.
- [72] T. Shedlovsky, *J. Am. Chem. Soc.* **1932**, *54*, 1411.
- [73] W. H. Lee, R. J. Wheaton, *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 743; *ibid.* **1978**, *74*, 1456; *ibid.* **1979**, *75*, 1128.
- [74] I. N. Levine, *Physical Chemistry*, 3rd ed., Mc Graw-Hill, New York, **1988**.
- [75] Y. Higo, Y. Kato, M. Itoh, N. Kozuka, I. Noda, M. Nagasawa, *Polymer J.* **1982**, *14*, 809.
- [76] G. Allen, *Comprehensive Polymer Science*, vol. 2, Pergamon Press, Oxford, **1989**.

- [77] R. L. Darskus, D. O. Jordan, T. Kurucsev, M. L. Martin, *J. Polym. Sci.* **1965**, 3, 1941.
- [78] F. E. Harris, S. A. Rice, *J. Phys. Chem.* **1954**, 58, 725 and 733; P. J. Flory, *J. Phys. Chem.* **1953**, 21, 162.
- [79] J. M. G. Cowie, *Polymers: Chemistry and Physics of Modern Materials*, Intertext Books, London, **1973**, ^a213,283.
- [80] F. G. Helfferich, *Ion Exchange*, Mc Gra- Hill, New York, **1962**.
- [81] Chemical & Micro Analytical Services Pty ltd, P.O.Box 139, Essendon North, 3041.
- [82] A. D. Mc Laren, B. J. Katchman, *J. Am. Chem. Soc.* **1951**, 73, 2124.
- [83] A. Hulanicki, R. Lewandowski, A. Lewnstam, *Analyst* **1976**, 101, 939.
- [84] J. O. Goertzen, J. D. Oster, *Soil Sci. Soc. Amer. Proc.* **1972**, 36, 691.
- [85] J. W. Ross Jr., M. S. Frant, *Anal. Chem.* **1969**, 41, 967.
- [86] E. P. Scheide, R. A. Durst, *Anal. Lett.* **1977**, 10, 55.
- [87] R. Delmas, *Mikrochim. Acta [Wien]* **1978**, 219.
- [88] D. J. G. Ives, G. J. Janz, *Reference Electrodes*, Academic Press, New york, **1961**.
- [89] J. D. F. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, **1970**.
- [90] R. T. Boere, G. G. Kidd, *Annual Report on Spectroscopy*, 14, 320, Academic Press, London, **1982**.
- [91] T. Itaya, K. Ueda, H. Ochiai, A. Imamura, *Polym. J.* **1993**, 25, 545.
- [92] J. W. Lyons, L. Kotin, *J. Am. Chem. Soc.* **1965**, 87, 1670.
- [93] F. Vosawa, *Polyelectrolytes*, Marcel Dekker, New York, **1971**.