SOLUTE - SOLVENT INTERACTIONS IN 2 - AND 3 - COMPONENT SYSTEMS

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A thesis presented for the degree of

Doctor of Philosophy at the

University of Adelaide.

June, 1967

Department of Physical and

Inorganic Chemistry.

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15th January, 1968

The Registrar,
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Dear Sir,

I hereby authorise the loan and/or photocopying of the copies of my doctoral thesis, "Solute-Solvent Interactions in 2- and 3-Component Systems", deposited in the Barr Smith Library, University of Adelaide.

Dennis E. Mulcahy

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SUMMARY

Solute-solvent interactions may be studied through their contribution to the viscosity B-coefficient of the solute. Values of the B-coefficient for seven alkali halides in aqueous solution, and in 20 percent sucrose solution as solvent, at 25°C., are presented. That the coefficients for the 3 - component systems are an additive property of the electrolyte ions, is demonstrated. On the basis of a criterion formerly applied to the 2 - component systems, these coefficients are divided into their ionic contributions. Correlations are drawn between ionic B-coefficients and the limiting equivalent conductances, in aqueous solution and in 20 percent sucrose solution, of the corresponding ions, and between ionic B-coefficients and the cubes of recent values of the crystal ionic radii.

Flared-capillary viscometers, in which the flow exhibited no apparent kinetic energy effect, were produced, and used for the necessary solution viscosity measurements. This represents the first recorded application of the technique proposed and developed by Caw and Wylie. The flow was photo-electrically timed. In the course of the calibration of these viscometers, certain interesting conclusions were reached, concerning the values, for the viscosity of sucrose solutions, normally

accepted as calibration standards.

Ancillary data, on the densities of the aqueous, and 20 percent sucrose, electrolyte solutions, are presented, and the corresponding limiting apparent molar volumes, at 25°C., derived. However, it was not possible, without extending some of the measurements to higher dilutions, to obtain reliable data for all the systems studied.

Since an examination of the basis for a correction made to viscosity data, recently reported in the literature, for two tetra-(n-propyl)-ammonium halides in aqueous solution at 25°C., failed to indicate the necessity of such a correction, a re-investigation of these systems was undertaken, the results of which are presented.

The effect of incomplete dissociation on the viscosity of electrolyte solutions is discussed, and illustrated by a treatment of data for magnesium sulphate in a 20 percent dioxan - water mixture at 35°C., which were drawn from the literature.

Another aspect of solute - solvent interactions, namely the interaction of a macro-ion (D.N.A.) with its solvent, as manifested in the value of the partial specific volume of that species in aqueous solution, was the subject of an independent study.

In order that a meaningful value of this partial specific

volume might be obtained from precise measurements of the density of dilute solutions of sodium deoxyribonucleate at 25°C., it was necessary to develop an effective method of weight analysis of the stock solutions from which these were prepared. A description of this method is given. The densities were measured by the Magnetic Float technique. Several aspects of this technique are discussed in detail, and in particular, a theoretical analysis of the extrapolation procedure employed, is presented. The process of denaturation is discussed briefly, and corroborative evidence for its occurrence, in the concentration range studied, is reported.

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

ACKNOWLEDGEMENT

I am glad of an opportunity to acknowledge my debt to Dr. B.J. Steel, my supervisor, whose guidance was an invaluable aid. The advice of Dr. P.J. Dunlop was also beneficial, particularly during Dr. Steel's study leave in 1965.

I should like to thank the other members of the Department of Physical and Inorganic Chemistry for their encouragement. In particular, thanks are due to H.D. Ellerton, K.R. Harris, C. Pepela and S. Phang, who were my fellows in a research group.

The co-operation of the glassblower, Mr. G. Duthie, and of Mr. K. Shepherdson of the electronics workshop, and Mr. A. Bowers and staff, of the mechanical workshop, was greatly appreciated.

Mr. R.M. Cooper of the Department of Computing Science, University of Adelaide, provided some valuable insights into the technique of computer programming.

The tenure of a Commonwealth Postgraduate Award for four years, and of a University Research Grant during the writing of this thesis, is gratefully acknowledged.

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ERRATA.

The author wishes to apologise for, and draw the attention of his examiners to, the following errors in, and omissions from, the thesis as presented.

In Contents - Part I, in the heading on p.8, on p.24 and p.173 (in the heading of Table 3.2),

read "Theoretical" for "Theorectical".

On p.18,

read "split perspex block, M"

for "split perspex block, P".

On p.111,

note the omission of a in "where a is (a) constant".

On p.126, in equation 6.14,

note that the Z_i are the valences of the ions concerned.

On p.141,

read "deoxyribonucleate" for "deoxyribouncleate".

On p.185,

read "apparently" for"apparantly".

PART I

SOLUTE-SOLVENT INTERACTIONS AND THE VISCOSITY OF ELECTROLYTES IN AQUEOUS SOLUTION AND IN AQUEOUS 20 PERCENT SUCROSE SOLUTION AT 25°C.

INTRODUCTION

Since 1956, there has been a steady accumulation of material, in the literature, on the viscosity and related properties of solutions of electrolytes in solvents, of which one component was water, and the other a non-electrolyte.

Data on the viscosity of potassium chloride in acetone-water[1] mixtures, were published by Das and co-workers, in 1956. Since that time they have published data on the viscosity and conductance of potassium chloride in methanol-water mixtures[3,10], and of sodium[4], potassium[2], magnesium[7,6], and barium[9,8] chlorides, barium bromide[9,8], magnesium[12,11] and barium[12,11] perchlorates, and potassium[7,6] and magnesium[13,5] sulphates in dioxan-water mixtures. They have also reported viscosity data for zinc sulphate[13], and apparent molal volume data[14] for sodium and potassium sulphates, in the latter solvents. All the measurements were conducted at 35°C. The B-coefficients derived from the viscosity data are summarised in Table 6.8 , on p.130 of this thesis.

Padova[15,16], in 1963, published viscosity and density data for sodium and magnesium sulphates, manganese chloride, and sodium, potassium, barium and magnesium acetates, in ethanol-water and acetone-water mixtures at 25°C.. The electrolyte concentration ranged from 0.125 to 1M in each case.

In all the above systems, the dielectric constant of the solvent was low, relative to that of pure water. Other viscosity measurements[17,18,19,20], on such systems, were reviewed by Padova[15].

One of the purposes of the research outlined in this section of the thesis, was the extension of such studies to 3-component systems, in which the solvent was an aqueous non-electrolyte solution with a dielectric constant little different from that of pure water. In particular, it was intended to ascertain whether, as had already been established for the corresponding aqueous solutions, the viscosity B-coefficients of the alkali halides were an additive property of the individual ions.

Evidence for the complete dissociation of these salts in aqueous 20 percent sucrose solution, at 25°C., was provided from the conductance measurements of Steel, Stokes and Stokes[21]. Hence it was not necessary, in the treatment of the corresponding viscosity data, to account for the effect of ion pairing. In 1958, these authors published[22] the individual mobilities of a wide range of ions in aqueous 10 percent mannitol, 10 and 20 percent sucrose, and 10 and 20 percent glycerol solutions. The cesium ion (Cs^+) was not studied.

It was with the possibility in view, of correlation between these data and data forthcoming from the proposed viscosity measurements, that one of the above solutions, aqueous 20 percent

sucrose, was selected as the solvent for the 3-component systems to be investigated in this research.

Viscosity data for the system sodium chloride-water - mannitol, at 25°C., appeared in the thesis of Kelly[23], in 1961. It was not his purpose however, in obtaining these data, to interpret them in terms of ion-solvent interaction. Relatively high sodium chloride concentractions (1.3 - 3.0 M) were studied, at a constant mannitol concentraction of 0.2 M.

In 1966, Tonomura and Okamoto[24] reported density, viscosity and conductance measurements for lithium chloride and potassium chloride respectively, at concentrations from 0.05 to 0.25 M, in aqueous urea solutions and in aqueous glycine solutions, at 15°, 25° and 35°C.. During that year, Phang[25] made a study of the same properties of potassium chloride and potassium iodide respectively in 1M aqueous solutions of the same non - electrolytes at 25°C..

With respect to the viscosities of 2-component aqueous electrolyte systems, the most interesting recent developments concern the behaviour of concentrated solutions[26,27]. Vaslow[27], in 1966, discussed evidence for salt-induced structure transitions, at high concentractions (0.8 - 1.0 M.) in aqueous alkali metal chloride solutions.

A comprehensive review of the best viscosity data for

electrolytes in both 2- and 3-component aqueous systems has recently been provided by Stokes and Mills[28].

In Chapters 3 and 6 of this section of the thesis, the results are reported, of the viscosity measurements on the chlorides and iodides of sodium, potassium and cesium respectively, and on potassium bromide, in aqueous solution and in 20 percent sucrose solution, at 25°C., and on aqueous solutions of tetra-(n-propyl)-ammonium iodide and bromide, respectively, at that temperature. In each instance the highest electrolyte concentration was 0.2 m. Corresponding density data were determined where necessary. These, and the derived apparent molar volume data, are also reported. On the basis of current theories of ion-solvent interaction, correlations were sought between parameters of the concentration dependence of the alkali halide viscosities (the B-coefficients) and other individual ionic properties.

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CHAPTER 1

VISCOMETRY AND ITS THEORETICAL BASIS

VISCOMETRY AND ITS THEORECTICAL BASIS

Viscosity

The viscosity of a fluid is its internal resistance to flow. More strictly, if x, y and z are the mutually perpendicular cartesian co-ordinate directions, viscosity may be defined as the transport of momentum in the x direction due to a velocity gradient, $\left(\frac{\partial v_x}{\partial z}\right)$, in the z direction. The flow of fluid is said to be laminar, if points fixed in the fluid move smoothly in layers, each layer moving with a certain velocity relative to its neighbours.

A coefficient of viscosity, η, may be defined by the equation, first postulated by Newton[1] in 1687,

$$f_x = \eta \left(\frac{\partial v_x}{\partial z} \right) \qquad 1.1$$

where f_x is the shearing force per unit area exerted in the direction of flow (x), on the element of fluid between two planes, at the plane of larger z[2]. Hence, a fluid is said to be Newtonian if its coefficient of viscosity is a constant, independent of the velocity gradient. The value of η depends upon temperature, pressure, and the composition of the fluid.

Despite Newton's fundamental work, it was not until 1823 that the first general differential equations of motion for real fluids were proposed by Navier. Similar equations were deduced by Poisson (1831), and by Stokes (1845), who integrated

them to give the velocity distribution in two cases of great importance in connection with the measurement of viscosity; namely flow through a cylindrical tube, and motion between co-axial cylinders[3].

Capillary Flow

Meanwhile, Hagen[3] (1839), investigating the flow of water, a Newtonian fluid, through brass tubes, found that the volume discharged per second was proportional to the pressure, to a power of the radius, and inversely proportional to the length of the tube. Hagen's work was completely overshadowed by the classical researches of Poiseuille (1846), who obtained the empirical equation,

$$Q = \frac{kPD^4}{L} \quad , \qquad 1.2$$

relating the quantity, Q, of water discharged per unit time from a glass capillary, to its diameter, D, and length, L, and to the pressure difference, P, between the ends of the capillary. The constant k is characteristic of the fluid.

Wiedemann[3], in 1856, was the first to publish a theoretical derivation of Poiseuille's law. He obtained the equation,

$$Q = \frac{\pi P r^4}{8\eta L} \quad , \qquad 1.3$$

where r is the radius of the capillary. Poiseuille's law was thus shown to be a direct consequence of Newton's postulate.

However, the assumption made in this derivation, that the pressure is entirely balanced by the viscous resistance, applies strictly only to those parts of the tube in which the fluid velocity is constant. Generally, only part of the pressure is used in overcoming frictional resistance, the remainder imparting kinetic energy to the fluid. Calculation of the latter quantity leads to a value of the pressure, effective in overcoming viscous forces, of,

$$P - m \cdot \frac{d\,Q^2}{\pi^2 r^4} \qquad 1.4$$

in which d is the fluid density and m is a number approximately equal to unity. Substitution in equation 1.3, yields,

$$\eta = \frac{\pi r^4 P}{8QL} - \frac{mdQ}{8\pi L} \qquad 1.5$$

Liquid entering a capillary from an upper reservoir, would flow in a converging stream from the wider vessel. Any difference in velocity, between adjacent flow lines in this stream, would require expenditure of energy in overcoming viscous forces. Couette suggested that an hypothetical increase, nr, in the length of the tube, would compensate for this effect. Equation 1.5 thus becomes,

$$\eta = \frac{\pi r^4 P}{8Q\,(L + nr)} - \frac{mdQ}{8\pi(L + nr)} \qquad 1.6$$

Viscometry

Until 1890, when Couette devised a new method based on a system of two concentric cylinders, capillary flow was the only widely used technique in the measurement of the flow properties of fluids. It remains one of the most popular methods.

Capillary viscometers may be divided into three main types; the cylindrical piston or plunger variety, glass capillary units and orifice viscometers[4]. Because its mechanical structure permits the use of high pressures, the former type is well suited to measurements on non-Newtonian fluids of high viscosity. It is used widely in measuring flow properties of materials such as high polymers, greases and soaps. Orifice viscometers which, because of their simplicity of operation, find wide application in limited industrial fields, are unsuitable for general investigations because of the difficulty of interpretation of the results.

Glass Capillary Viscometers

Glass capillary viscometers have been widely used in determining the viscosity of many fluids, mainly Newtonian, in which case the hydrostatic head of fluid is commonly utilised to drive the flow. However external pressure can also be applied, thereby increasing the range of measurement, or allowing

non-Newtonian behaviour to be studied[5].

For Newtonian fluids in the former case, i.e. the absence of external pressure; P, in equation 1.6, may be replaced by dgh, where h is the head of fluid and g is the gravitational acceleration, and Q by V/t, where t is the flow-time corresponding to the discharge of the reservoir volume, V.

$$\therefore \eta = \frac{\pi r^4 dght}{8V(L + nr)} - \frac{mdV}{8\pi t\,(L + nr)} \qquad 1.7$$

If two factors A and B, are defined by,

$$A = \frac{\pi r^4 gh}{8V(L + nr)} \quad \text{and} \quad B = \frac{m\,V}{8\pi(L + nr)}\ , \qquad 1.8$$

then,

$$\eta = Adt - Bd/t \qquad 1.9$$

η is often referred to as the absolute viscosity of a fluid. The viscosity of a fluid relative to another, accepted as standard, having an absolute viscosity, η_o, may be expressed by,

$$\eta_{rel} = \eta / \eta_o = \frac{Adt - Bd/t}{Ad_o t_o - Bd_o/t_o}\ , \qquad 1.10$$

where t_o is the flow-time for the standard fluid in the same viscometer. Defining the factor, K, by,

$$K = \frac{B}{A} = \frac{MV^2}{\pi^2 r^4 gh}\ , \qquad 1.11$$

and neglecting any correction terms involving the inverse fourth power of the time, equation 1.10 simplifies to,

$$\frac{\eta}{\eta_o} = \frac{d\,t}{d_o t_o}\left[1 + K\left\{\frac{1}{t_o^2} - \frac{1}{t^2}\right\}\right] \qquad 1.12$$

K is often referred to as the kinetic energy correction factor, and is theoretically determinable from the dimensions of the apparatus, and an assumed value of m. In practice, however, a calibration of the viscometer with liquids of known viscosity is usually undertaken.

Equation 1.9,

$$\eta = Adt - Bd/t \ ,$$

may be rearranged as,

$$\eta/dt = A - B/t^2. \qquad 1.13$$

Thus, if flow-times and densities are measured, of a series of standard liquids, and if K is regarded as a constant, its value should be obtainable from the slope and intercept of a linear graph of η/dt against $1/t^2$. However, for most conventional viscometers, K is apparently not a constant, and calibration becomes a matter of constructing a non-linear plot of these variables[6,7,8]. Measurement of the flow-time and density of a particular solution would then permit the determination of its viscosity, directly from the curve. The observed non-linearity may be a reflection of inadequacies in the theory, and in particular, of the approximate nature of the

correction made for end-effects.

Flared Capillary Viscometers

Caw and Wylie[9] have recently (1961) described viscometers in the design of which the concept of a uniform capillary with identifiable ends was abandoned. (See Figure 1.1.). Instead, the aim was to achieve a constant hydrodynamic resistance, through the absence of any marked curvature of the stream-lines in those regions of the flow-pattern where the contribution to the resistance is significant.

For such viscometers, a relationship of the form,

$$\eta/d = At - B'/t^n \qquad 1.14$$

or

$$\eta/dt = A - B'/t^{n+1}, \qquad 1.15$$

was found[9] between the viscosity of the test liquids, their density and flow-time. This relationship is analogous to that obtained for conventional viscometers (equation 1.9) except that B has been replaced by B'/t^{n-1}.

The more specific relationship[9],

$$\frac{\eta}{d} = \frac{Mh}{V} t - \frac{NV^n}{h^{\frac{1}{2}(n-1)}} \cdot \frac{1}{t^n} \qquad 1.16$$

is also implied, where M and N are constants associated with a particular capillary, and h is the mean head of liquid.

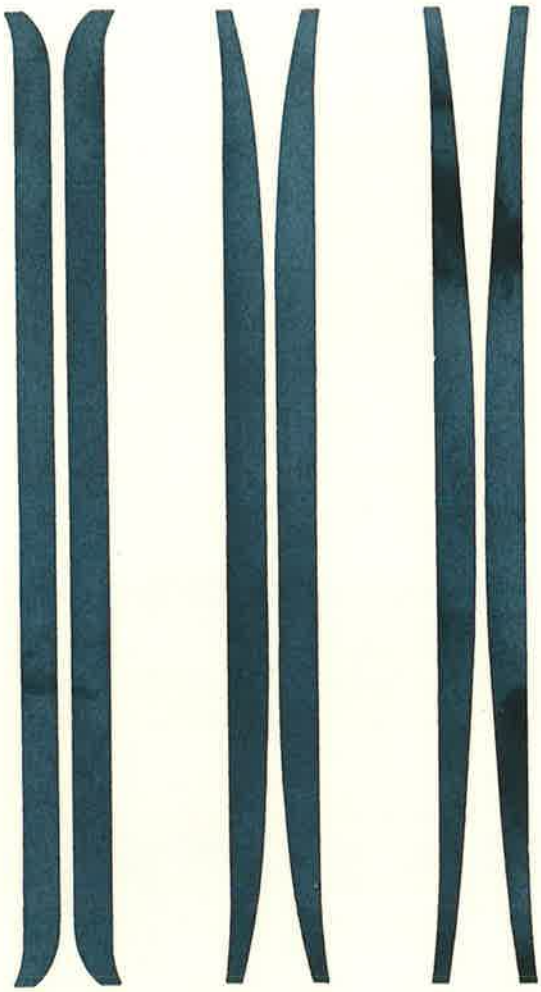

Figure 1.1. Conventional and long-flared capillaries. (a) conventional; (b) long-flared with parallel centre section; (c) with overlapping long flares.

(From reference 9)

For flared-capillary viscometers constructed with two timing bulbs above the capillary, if t_1 and t_2 are the flow-times for the upper and lower bulbs respectively, and α is the corresponding ratio, $V_2{}^{n}h_1{}^{\frac{1}{2}(n-1)} / V_1{}^{n}h_2{}^{\frac{1}{2}(n-1)}$,

$$\frac{\eta}{d} = A_1 t_1 - \frac{B_1'}{t_1{}^{n}} = A_2 t_2 - \frac{\alpha B_1'}{t_2{}^{n}} \qquad 1.17$$

Hence

$$\frac{A_1 t_1}{A_2 t_2} - 1 = B_1' \left[\frac{t_2{}^{n} t_1{}^{n} - \alpha}{A_2 t_2{}^{(n+1)}} \right] \qquad 1.18$$

When $n = 1$, and $V_1 = V_2$, as was the case for Caw and Wylie's test viscometer, this equation reduces to,

$$\frac{A_1 t_1}{A_2 t_2} - 1 = B_1' \left[\frac{t_2/t_1 - 1}{A_2 t_2{}^{2}} \right] \qquad 1.19$$

They plotted $\frac{A_1 t_1}{A_2 t_2} - 1$ against $\frac{t_2/t_1 - 1}{A_2 t_2{}^{2}}$, for a series of capillaries with progressively longer flares. A linear graph was obtained, as expected, for a conventional capillary, and curves with a progressively decreasing initial slope, for the flared capillaries. The curve for the capillary with the most extensive flare, rose slowly from an initial slope corresponding to a value of B_1' close to zero. In an analogous series of plots of the variables corresponding to $n = 4$, the graph for the latter capillary was linear.

On the basis of these observations, two capillaries were produced which had almost continuous flares; the aim, in this research, being the reduction of the constants, B', to zero. From equation 1.18,

$$\text{if } B' = 0, \text{ then } \frac{A_1 t_1}{A_2 t_2} - 1 = 0$$

and $\therefore \frac{t_1}{t_2}$ = a constant.

Also, from equation 1.15,

$\eta/dt = A$ = a constant.

To test the achievement of this aim, the capillaries were subjected to two tests. One of the capillaries was incorporated into a double-bulb viscometer, and flow-times of water and of 20 percent sucrose solution measured for both bulbs. Constancy of the ratio of these times was observed (see p.51). Following this successful preliminary run, both capillaries were calibrated by measurement of the flow-time, from single bulbs of the respective viscometers, of water at various temperatures. In both cases, the function, η/dt, was found to be constant, within the uncertainty in the standard viscosities. (See Figure 3.1).

Details of the Apparatus Used

Production of the Flared Capillaries

The flares were produced by subjecting each end in turn, of a pyrex glass, precision-bore capillary, to internal pressure

from a controlled flow of gas, while applying a temperature gradient along half its length, with a broad-flamed glass-blowing torch. During the process, the capillary was held in a chuck-device and rotated steadily. In the production of the first capillary, which was later incorporated into the double-bulb viscometer, a 0.4 mm. capillary was used, and the chuck rotated by hand operation of a drive-belt. The other capillary used was selected from a large batch made later, from 0.5 mm. capillary, using a more refined apparatus in which the chuck was driven indirectly by a small electric motor.

The Viscometers

For convenience, viscometers of the suspended-level type introduced by Ubbelohde[10] were used. There has been a tendency to adhere to the use of the Ostwald viscometer for precise viscosity measurements, despite its inconvenience. However, from an examination of the results obtained, in a previous study[6], with an Ostwald and a Ubbelohde viscometer of almost identical flow times, no advantage could be found in the use of the former. Although Caw and Wylie[9] used an Ostwald viscometer for their tests of the relations pertaining to the flared capillary, they also showed that such capillaries, incorporated into viscometers of the suspended-level type, behaved identically. Thus it appeared that a suspended level

could be satisfactorily formed at the extremity of a long flare, provided that its union with the efflux bulb was shaped with the usual care.

The Timing of the Flow

The transit of the liquid meniscus, past reproducible positions in the tubes above and below the timing bulb, was detected photoelectrically, and the interval automatically recorded. The device used has recently been described by Steel[11]. Its advantages over its predecessors[12,13] were those of simplicity, and ease of operation.

The optical principle involved was similar to that used by Jones and Talley[12]. Narrow beams of light, focussed on the tubing above and below the timing bulb, were partially deflected, due to reflection at the glass-air interface, on the transit of the meniscus. The change in resistance thus caused, in light-dependent resistors illuminated by the upper and lower beams respectively, was used to actuate a trigger circuit, starting a crystal timer, in the first case, and to stop the timer in the second.

The photocells, lens system, L, and viscometer, were all rigidly mounted in a brass frame, the latter by means of a split perspex block, P, and a grooved perspex block, G, as shown in Figure 1.2. This frame was suspended in a water-bath, maintained

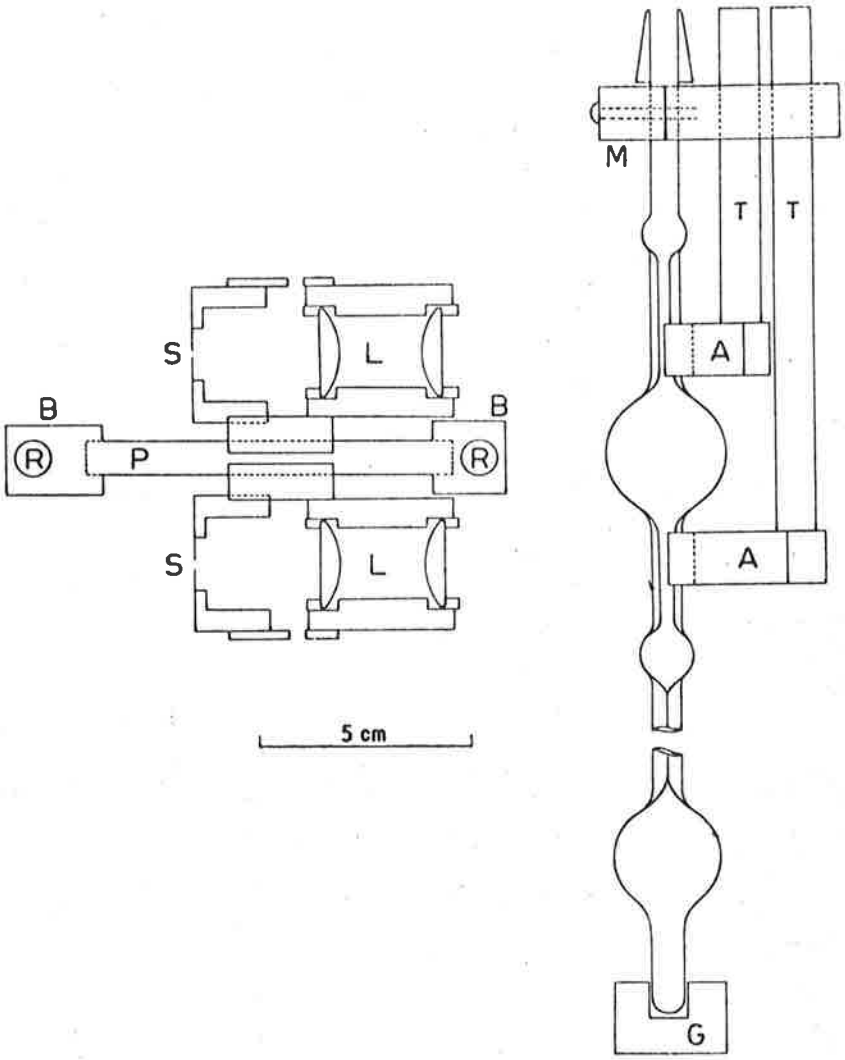

Figure 1.2. Drawing of those parts of the viscometer immersed in the water bath. The letters are referred to in the text.

(From reference 11)

at temperature within $\pm$ 0.002°C. Images of the horizontal filaments of the 6V., 24W., projector lamps used as light sources, were focussed on the slits, S, through the glass front of the bath. The two viscometers used were interchangeable in the frame, and were initially annealed in position.

Cylindrical channels, drilled in brass blocks, A, housed the light-dependent resistors, which were cemented in position with liquid araldite. Their leads were taken above water level through brass tubes, T, soldered to the blocks.

The timer was assembled from a 10 kc./s. crystal oscillator and gate, the output of which was counted using a series of decade counters. The gating circuit was opened by an applied voltage greater than 42V., and closed by one below 29V. Figure 1.3 shows the trigger circuit. Initially, the angle of the photocells to their respective reflected beams was simultaneously adjusted, until the above working voltages were attained on the transit of the first and second incident beams respectively. The corresponding changes in tube current were observed on the scale of a milliammeter. Fine current adjustments could be made by means of a rheostat.

Cleaning of the Viscometers

Before each series of runs on a particular salt, the viscometer was cleaned with chromic acid. Following each individual de-

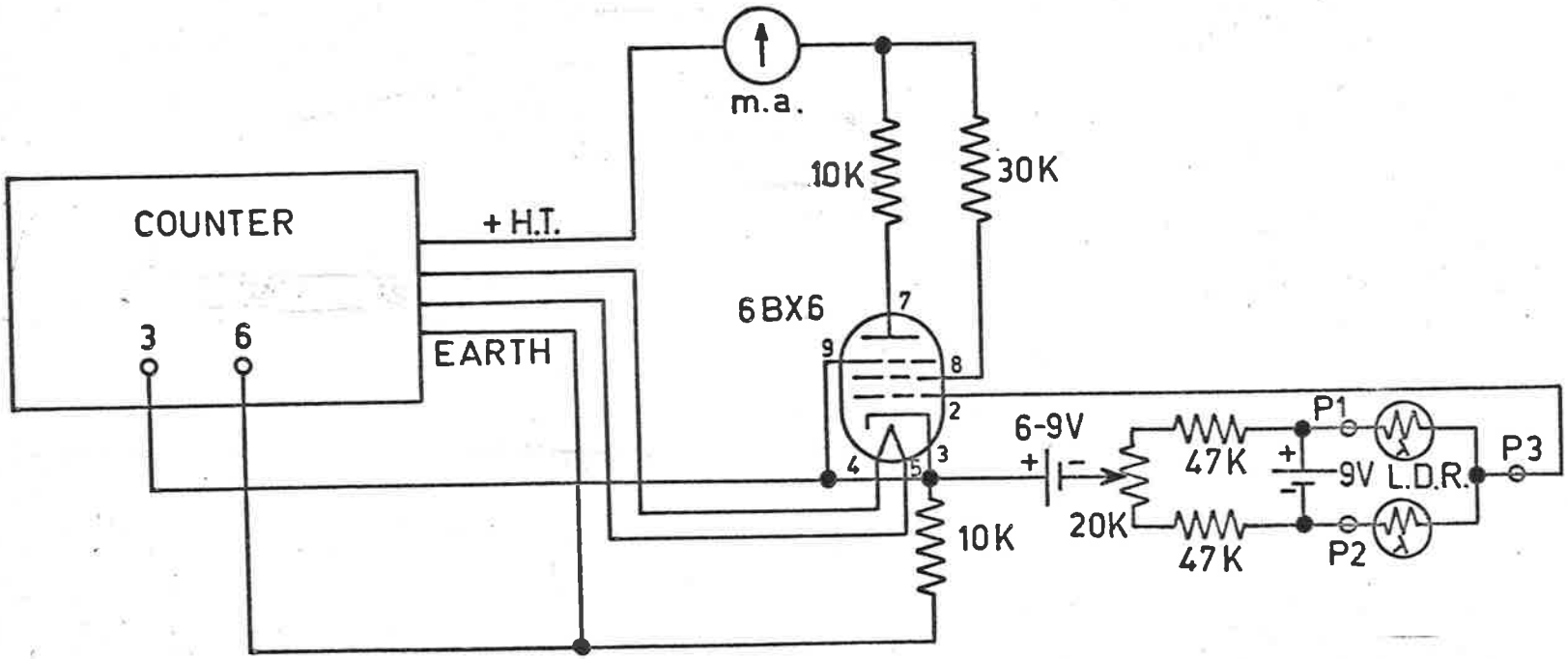

Figure 1.3. Viscometer Timing Circuit.

P_1, P_2 and P_3 represent a 3-pin connection to the light-dependent resistors (L.D.R.).

termination, it was washed four times with twice-distilled water, rinsed twice with Univar A.R. methanol, and dried by suction from an aspirator for at least half an hour. All liquids were introduced through a sintered-glass filter of porosity 2. The viscometer was seldom removed from the frame. It was never removed during a series of measurements.

Mode of Operation

After the introduction of the solution to be studied, into the clean, dry viscometer, through the same sintered-glass filter, without the use of suction, the instrument was placed in the water-bath. A gentle tapping of the frame on its support, sufficed to remove any air bubbles present in the space between the slits and the lenses, through a vent provided for this purpose. The frame was then clamped firmly in a reproducible position on its support, and levelled by means of adjustable screws on the latter. The circuit was completed and the counter switched on. After an equilibration period of at least half an hour, the solution was slowly forced into the timing bulb, by the application of controlled pneumatic pressure. Oxygen-free nitrogen, which passed through a desiccant and through a sintered-glass filter, was used for this purpose. Sufficient time was required for this process, to allow the illuminated photocells to attain stability. The counter was then set at zero, the voltage adjusted

if necessary, and the flow timed. The first reading was usually disregarded. Measurements were continued until three consecutive times were obtained which agreed within the experimental uncertainty of 0.01%. The reproducibility was, however, usually much better than this.

Solvent flow-times were measured at the beginning of each series of runs, and occasionally also at the conclusion of a series, or, where necessary, within it.

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CHAPTER 2

TECHNIQUES OTHER THAN VISCOMETRY

TECHNIQUES OTHER THAN VISCOMETRY

I. PYCNOMETRY AND ITS THEORETICAL BASIS

Pycnometry

The most common method of determination of the density of liquids consists in finding the weight of liquid occupying a known volume defined by the shape of a given vessel. Since it is obviously impracticable to determine this volume from the geometry of the vessel, it is calibrated instead in terms of the weight of pure water which it will contain.

Three single-stemmed bulb-pycnometers of approximately 30 ml. capacity, with closely-fitting ground-glass stoppers, were so constructed that their volumes agreed within 0.02 ml., and their dry weights within 0.002 gm. An accompanying tare of closely similar shape, had a weight, when empty, equally close to that of an empty pycnometer, and a weight when sealed, containing twice-distilled water, corresponding to that of a pycnometer filled to a scratch mark with the same liquid. The tolerances for this matching of weights are discussed on p. 33. The calibration of the pycnometers was checked twice during the course of measurements, once by a single determination, and once in triplicate. The results of these determinations are presented in Table. 2.1.

TABLE 2.1.

Calibration of Pycnometers

No.	m_1	V
A	0.03369	33.04450
	0.03372	33.04453
	0.03377	33.04463
B	0.02495	33.03767
	0.02537	33.03806
	0.02540	33.03806
D	0.04462	33.05586
	0.04455	33.05578
	0.04468	33.05589
	Average Values	
A	0.03373	33.04455
B	0.02538	33.03806
D	0.04462	33.05584
	Previous single determination	
A	0.03401	33.04519
B	0.02592	33.03930
D	0.04539	33.05731

Most densities were determined in a single pycnometer, three solutions of different concentrations being studied concurrently. However, occasionally duplicate or triplicate determinations were performed to check the reproducibility of the technique.

Prior to each determination, the solutions were equilibrated at 25 - 30°C. in a vacuum oven for several hours, and the pycnometers heated for a short period in a drying oven, and cooled to approximately the same temperature. The solutions were then introduced into the pycnometers from a glass syringe with a long stainless-steel capillary. Bubble formation was carefully avoided. The pycnometers were then clamped in a special frame suspended in a water bath maintained at 25.000 ± 0.002°C., and they were equilibrated for half an hour. The meniscii were then sheared, close to the scratch mark, with the same syringe, and the capillary above the liquid dried thoroughly with thin strips of extra-hard filter paper. With the ground-glass caps removed, the distances between meniscii and scratch marks were then measured in triplicate, with a cathetometer mounted outside the glass front of the bath. A light bulb protruding below the water surface provided the necessary illumination. The caps were then replaced, and the pycnometers removed from the bath, washed with distilled water, dried with a towel, and then polished, as was the

tare, with a fine cotton handkerchief.

After equilibration for 1 hour, the pycnometers and tare were weighed on a Mettler B6 balance. The weighing was repeated to check that equilibrium had been attained.

From the length and weight of a column of mercury in a sample of the 0.6 mm. precision bore capillary used in these pycnometers, Ellerton[1] had determined its cross sectional area. Volume corrections were calculated from this quantity and the measured meniscus-mark distances. Weight corrections could then be calculated, using an approximate density value for each solution.

From the calibrations, the pycnometer volumes, V, and the corrected differences, m_1, in weight between each pycnometer containing solvent, and the tare, were obtained. In combination with the corresponding differences, m_2, for the pycnometers containing solution, these quantities yield values of the density increments, Δd, according to the formula,

$$\Delta d = \frac{(m_2 - m_1)}{V} \left(1 - \frac{d_a}{d_m} \right) \qquad 2.1$$

which is derived and discussed on the following pages.

Theory of the Sealed Tare

Let

W_t = Weight of the tare in vacuum,

W_p = Weight of an empty pycnometer,

W_w = Weight of solvent to the mark in that pycnometer,

W_s = Weight of solution to the mark in that pycnometer,

m_1 = Difference in balance readings for tare and for pycnometer + solvent,

m_2 = Difference in balance readings for tare and for pycnometer + solution,

d_w = Density of solvent,

d_s = Density of solution,

d_t = Density of tare,

d_m = Density of balance masses,

d_p = Density of glass in the pycnometers,

d_a = Density of air,

W_t^g = Weight in vacuum of glass in the tare,

W_t^w = Weight in vacuum of water in the tare.

If the tare and then the pycnometer containing solvent are weighed at air density, d_a', the difference in readings = m_1 (tare lighter), and

$$W_t - W_t \frac{d_a'}{d_t} + m_1 - m_1 \frac{d_a'}{d_m} = W_p - W_p \frac{d_a'}{d_p} + W_w - W_w \frac{d_a'}{d_w} \qquad 2.2$$

If the tare and then the pycnometer containing solution are weighed at air density d''_a, the difference in readings $= m_2$ (tare lighter), and

$$W_t - W_t \frac{d''_a}{d_t} + m_2 - m_2 \frac{d''_a}{d_m} = W_p - W_p \frac{d''_a}{d_p} + W_s - W_s \frac{d''_a}{d_s} \qquad 2.3$$

Subtracting 2.2 from 2.3,

$$\frac{W_t}{d_t}(d'_a - d''_a) + m_2 - m_1 - m_2 \frac{d''_a}{d_m} + m_1 \frac{d'_a}{d_m}$$

$$= \frac{W_p}{d_p}(d'_a - d''_a) + W_s - W_w - \frac{W_s}{d_s} d''_a + \frac{W_w}{d_w} d'_a \qquad 2.4$$

Dividing throughout by the volume of the pycnometer, V,

$$\left(V = \frac{W_s}{d_s}, = \frac{W_w}{d_w} \right) \qquad 2.5$$

$$\frac{W_t}{Vd_t}(d'_a - d''_a) + \frac{(m_2 - m_1)}{V} - \frac{m_2}{V}\frac{d''_a}{d_m} + \frac{m_1}{V}\frac{d'_a}{d_m}$$

$$= \frac{W_p}{Vd_p}(d'_a - d''_a) + d_s - d_w + (d'_a - d''_a) \qquad 2.6$$

$$\therefore (d_s - d_w) = \frac{(m_2 - m_1)}{V} - \frac{m_2}{V}\frac{d''_a}{d_m} + \frac{m_1}{V}\frac{d'_a}{d_m} + (d'_a - d''_a)\left(\frac{W_t}{Vd_t} - \frac{W_p}{Vd_p} - 1\right) \qquad 2.7$$

$$= \frac{(m_2 - m_1)}{V} + \frac{m_2 d'_a}{Vd_m} - \frac{m_2 d'_a}{Vd_m} - \frac{m_2 d''_a}{Vd_m} + \frac{m_1 d'_a}{Vd_m} + (d'_a - d''_a)\left(\frac{W_t}{Vd_t} - \frac{W_p}{Vd_p} - 1\right) \qquad 2.8$$

$$= \frac{(m_2 - m_1)}{V}\left(1 - \frac{d'_a}{d_m}\right) + \frac{(d'_a - d''_a)}{V}\left(\frac{m_2}{d_m} + \frac{W_t}{d_t} - \frac{W_p}{d_p} - V\right) \qquad 2.9$$

$$\therefore\ d_s - d_w = \frac{(m_2 - m_1)}{V}\left(1 - \frac{d'_a}{d_m}\right)$$

$$+ \frac{(d'_a - d''_a)}{V}\left(\frac{m_2}{d_m} + \frac{W_t^{\,g}}{d_p} + \frac{W_t^{\,w}}{d_w} - \frac{W_p}{d_p} - V\right) \qquad 2.10$$

Now, if the weight of glass in the tare equals the weight of the empty pycnometer,

$$\underline{\text{i.e.}} \qquad W_t^{\,g} = W_p \quad , \qquad 2.11$$

and the weight of water in the tare equals the weight of water in the pycnometer,

$$\text{or} \qquad V = \frac{W_t^{\,w}}{d_w} \quad , \qquad 2.12$$

then,

$$d_s - d_w = \frac{(m_2 - m_1)}{V}\left(1 - \frac{d'_a}{d_m}\right) + \frac{(d'_a - d''_a)}{V}\frac{m_2}{d_m} \qquad 2.13$$

Expanding brackets,

$$d_s - d_w = \frac{(m_2 - m_1)}{V} - \frac{1}{d_m V}(m_2\, d''_a - m_1\, d'_a) \quad , \qquad 2.14$$

which reduces to,

$$\underline{d_s - d_w = \Delta d = \frac{(m_2 - m_1)}{V}\left(1 - \frac{d_a}{d_m}\right)} \quad , \qquad 2.15$$

when $d'_a = d''_a$.

Δd is known as the density increment, and d_a is a generalised air density.

It should be noted that, since the pycnometers were calibrated with water, the tare liquid, the density increments obtained for the mixed-solutions always represented the difference between the solution density and that of water as solvent, rather than of aqueous 20 percent sucrose.

Tolerances for Tare Pycnometry

Effect of Variation in Air Density

From an examination of the correction terms of equation 2.10, the range may be determined within which the approximate equation, 2.15, may be employed, without a possible reduction in precision below that attainable experimentally.

If a possible variation, in d_a, of $\pm$ 1 x 10^{-4} is assumed, which is greater than the maximum observed variation, then for a pycnometer of volume 30 ml.,

$$\frac{d'_a - d''_a}{V} = 3 \times 10^{-6} \qquad 2.16$$

For an overall precision in the determined densities of 1 in 10^6, the contribution to $d_s - d_w$ from the correction terms must be $< 1 \times 10^{-6}$. Thus,

$$\left[\frac{m_2}{7.6} + \frac{1}{2.4}(W_t^g - W_p) + \frac{1}{0.997}(W_t^w - W_w)\right] < 0.3 \qquad 2.17$$

And, if $W_t^g = W_p$, and $W_t^w = W_w$,

then, $m_1 = 0$

and $m_2 < 2$ gm.

Hence the maximum value of Δd to which this precision can extend,

$$\Delta d_{max.} = \frac{2}{30} = 0.07 \quad , \qquad 2.18$$

which corresponds to a density of 1.07, which is close to that of 20 percent sucrose solution. In practice, a lower precision is obtained, and the equation has a greater range.

The Matching of Pycnometers and Tare

If the remaining correction terms in equation 2.10 are also considered independently, it can be seen that,

$$W_t^g - W_p < 0.75 \text{ gm.} \qquad 2.19$$

and

$$W_t^w - W_w < 0.30 \text{ gm.} \qquad 2.20$$

These inequalities define the limits for divergence between the weights of glass, and of water respectively, in a given pycnometer and in the tare. Above these limits the use of equation 2.15, could result in a reduction, in excess of the experimental uncertainty, in the precision of the measured densities.

Cleaning of Pycnometers

The pycnometers were cleaned with chromic acid after each series of determinations on a particular salt. Between individual determinations they were mounted on an apparatus

whereby they could be washed internally with demineralised water sprayed through stainless-steel capillaries, and partially dried by suction. After heating at over 100°C., in a drying-oven, for 1 hour, they were again dried by suction until cool.

II. CONDUCTANCE MEASUREMENT: BASIC CONCEPTS AND THE EXPERIMENTAL TECHNIQUE

Basic Concepts[2]

The resistance, R, of a uniform conductor, at a particular temperature, is directly proportional to its length, L, and inversely to its cross-sectional area, A. Thus,

$$R = sL/A \quad , \qquad 2.21$$

where the constant of proportionality, s, is called the specific resistance of the material at that temperature. Its reciprocal is the specific conductance, denoted by $K_{sp.}$

$$K_{sp.} = 1/s = L/AR \qquad 2.22$$

In electrolyte solutions, another variable, the concentration, must be considered. Thus it is necessary to define another quantity, the equivalent conductance, Λ, by,

$$\Lambda = \frac{1{,}000\ K_{sp.}}{c} \qquad 2.23$$

where the concentraction, c, is expressed in gram equivalents per litre. Since current flow is the result of motion, in opposite directions, of oppositively charged ions, the equivalent conductance can be considered as a sum of ionic conductances. In the simplest case this can be expressed by,

$$\Lambda = \lambda_1 + \lambda_2 \qquad 2.24$$

At infinite dilution,

$$\Lambda^{o} = \lambda_1^{o} + \lambda_2^{o} \qquad 2.25$$

Kohlrausch's Law of Independent Migration of Ions concerns the independence of the limiting equivalent conductances, λ_1^{o}, and, λ_2^{o}, of the two ions. The partitioning of the total conductance, into the individual ionic contributions, requires a knowledge of the relevant transport numbers.

Resistance Measurements

Resistance measurements were made with a Leeds-Northrup A.C. bridge, CAT. No. 4666, of the type designed by Dike[3]. This incorporated a Wagner earth. The bridge was used in conjunction with a variable frequency audio-oscillator, tuned amplifier, and C.R.O. detector. Resistances measured over a range of frequencies, ω, were plotted as a function of $1/\omega$ and extrapolated to infinite frequency[4].

Cells of conventional design were used. Platinum-tungsten-platinum seals linked the electrodes with the internal leads, through the cell wall. With the exception of those in the cell reserved for determinations of the specific conductance of water, all the electrodes were "platinised"[5]. The resistance of the external leads was measured, and that of the internal leads, which had identical dimensions in all the cells, was calculated from the specific resistivity of platinum.

Before filling, the cells were repeatedly rinsed with solution. Occasionally the platinised electrodes were electrolytically "stripped", and re-plated with fresh material.

During each conductance measurement, the bath of light petroleum oil (Shell Diala B), in which the appropriate filled cell was suspended and had previously been equilibrated for half an hour, was maintained at a temperature of 25.000 $\pm$ 0.002°C. For this purpose a mercury-toluene regulator was employed, in conjunction with a thyratron relay which activated a heating coil.

The Cell Constant

Since measured values of solution resistance depend, not only on the electrode dimensions and separation, neither of which can be determined accurately, but also on the cell geometry, it is the invariable practice to calibrate the cell by means of solutions of known specific conductance. A cell constant, a, may be defined by,

$$K_{sp.} = a/R$$

Standard values of the specific conductance of potassium chloride solutions have been provided by the painstaking researches of Jones and Bradshaw[6,7]. The standard compositions are expressed on the demal (D) concentration scale, which is not in general use.

Cell constants determined using the 0.01 D., and 0.10 D. standards respectively, were identical within the experimental error.

Extrapolation of Equivalent Conductance Data for 1 : 1 Electrolytes

For this purpose an approximation proposed by Robinson and Stokes[8],

$$\Lambda = \Lambda^{o} - \frac{B_1\Lambda^{o} + B_2}{1 + \kappa a^{o}} \cdot \sqrt{C}, \qquad 2.26$$

was used, which may be rearranged as,

$$\Lambda^{o} = \Lambda + \frac{B_1\Lambda + B_2}{1 + (Ba^{o} - B_1)\sqrt{C}}\sqrt{C} \qquad 2.27$$

where κ has been replaced by $B\sqrt{C}$. The parameter, a^{o}, is the "distance of closest approach" of the ions, and the parameters B, B_1 and B_2 may be evaluated from the appropriate Debye - Hückel - Onsager expressions. Tabulated values are available[9].

Extrapolation to infinite dilution of a plot of Λ^{o} values obtained from equation 2.27, against the corresponding concentrations, should yield the true limiting equivalent conductance.

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CHAPTER 3

EXPERIMENTAL

EXPERIMENTAL

I. MATERIALS

Sodium Chloride

A.R. sodium chloride was used which had been once recrystallised, and fused in a platinum crucible. Prior to use, the sample was dried by heating above 100°C., and cooled in a desiccator over silica-gel. In the fusing of salts, a frequently encountered problem is the hydrolysis of the salt by reaction with atmospheric water vapour[1].

$$NaCl + H_2O \rightleftharpoons NaOH + HCl. \qquad 3.1$$

However, no visible colouration was produced by the addition of phenolphthalien to a 0.05 molal aqueous solution of this salt.

Potassium Chloride

The potassium chloride used was a once recrystallised sample which had been fused. Once and twice recrystallised samples had been shown to be identical according to the isopiestic method[2]. A preliminary drying was undertaken as for sodium chloride.

Cesium Chloride

B.D.H. Laboratory reagent Cesium Chloride (1 Kg.) was recrystallised three times from twice-distilled water. The product was first dried by suction on a Buchner sintered-glass filter plate, and then transferred to a vacuum oven where it was

dried at above 100°C., by continuous pumping, until constant weight was attained. It was stored over silica-gel in an evacuated desiccator.

Conductance measurements at 25°C. on a 0.009379 M. solution of the recrystallised material yielded an equivalent conductance of 144.66, which may be compared with the value 144.21 interpolated graphically from the uncorrected data of Treiner, Justice and Fuoss[3]. The difference between these two values is identical to the difference between the limiting equivalent ionic conductances of the cesium ion, as determined by Treiner, Justice and Fuoss, op.cit., and by Lind and Fuoss[4] from the conductance of aqueous cesium iodide solutions. The same discrepancy was found between the measured and graphically interpolated values for a solution of concentration 0.006729 M., prepared from B.D.H. Analar cesium chloride, which had been once recrystallised from A.R. acetone.

Analysis*, by flame photometry, of a sample of the latter material, indicated that it was of high purity. The presence of trace impurities in the following weight proportions (parts per million), Li (less than 1), Na (18), K (1), Rb (40), was detected.

*By A.M.D.L. (Australian Mineral Development Laboratories), Adelaide.

Hydriodic Acid

B.D.H. hydriodic acid, 55 weight per cent (1 litre), was decolourised at its boiling point by adding dropwise a 30 per-cent solution of hypophosphorous acid. Distillation under nitrogen at a constant temperature of 124°C., yielded approximately 800 mls. of a perfectly clear liquid (57 weight percent[5]). Upon standing overnight in the ground-glass-stoppered receiving flask sealed with Parafilm, the liquid developed a slight yellow colouration. Freshly distilled hydriodic acid was necessary for the following preparations of both sodium and potassium iodide.

Sodium Iodide

Sodium iodide was freshly prepared by neutralising once-recrystallised B.D.H. sodium carbonate (anhydrous) with hydriodic acid. After all effervescence had ceased, a slight excess of acid was added. It is advisable to add as little excess acid as possible, since acid solutions of iodide are oxidised by oxygen from the air.

$$4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O \qquad 3.2$$

The solution was then filtered, concentrated by evaporation, and cooled slowly. A crop of yellow-white crystals was collected and dried by suction on a sintered-glass Buchner filter, the filtrate having a red colouration.

The product was recrystallised three times from twice-distilled water until a final sample of quick-draining white crystals was obtained. These were first dried by suction, and then under vacuum, the temperature being gradually raised to over 100°C. Vacuum drying was continued for 24 hours, after which the crystals were stored over phosphorous pentoxide in an evacuated desiccator, which was shielded from intense light.

Crystals of sodium iodide appear to be slightly deliquescent, and will decompose on standing according to equation 3.2, leaving their surface moisture alkaline by hydrolysis. Thus sodium hydroxide or carbonate impurities may be introduced. Hence the suction drying of the crystals, unless rapid, should be replaced by pressure-filtration using nitrogen. Strong light catalyses[6] the reaction 3.2, and hence should be excluded when handling the material in air.

Potassium Iodide

Potassium iodide was prepared by an analogous method from anhydrous potassium carbonate. The only differences in detail were that heating was carried out in the final stages of the neutralisation, that the product was only recrystallised twice, and that the suction drying of the crystals was accomplished more rapidly.

Cesium Iodide

Stoichiometric quantities of barium iodide and cesium sulphate, of B.D.H. Laboratory Reagent grade, were independently dissolved in similar amounts of twice-distilled water. Cesium iodide was then prepared by double decomposition, the latter solution being added to the former. At first a thick gelatinous precipitate formed, but only in small quantity. Further addition produced a fine white precipitate capable of passing through a sintered-glass Buchner filter. The suspension was centrifuged at 3,000 to 3,500 r.p.m. in a Hettich Roto-Silenta centrifuge for half an hour at first, and then for varying periods after further additions of reagent from a Pasteur pipette. Co-precipitation was counteracted by disturbing the residues after one of the later additions. When no further precipitation was apparent, the centrifugates were gravity filtered through the Buchner sinter. Several drops of both reagents were added in turn to the filtrate without effect. After standing to remove any further trace of barium sulphate, and re-filtration, the solution was concentrated by boiling and cooled slowly. The product obtained was recrystallised three times, and dried and stored as described for sodium iodide.

Potassium Bromide

Univar* A.R. potassium bromide (700 gm.) was recrystallised

*Ajax Chemical Company

three times from twice-distilled water. The final product was first dried by suction, then transferred to a vacuum oven where it was pumped dry at approximately 110°C. for two days. It was removed hot and placed over phosphorous pentoxide in a desiccator which was then evacuated.

Tetra n-Propyl Ammonium Bromide

A sample was kindly supplied by C. Pepela*, of material which had been once recrystallised from A.R. acetone, dried under vacuum, and stored over calcium chloride in an evacuated desiccator.

His analysis of this sample, by potentiometric titration against silver nitrate solutions, using the previously described fused sodium chloride as the primary standard, yielded a percentage purity value of 99.93 $\pm$ 0.05 %.

Tetra n-Propyl Ammonium Iodide

B.D.H. Laboratory reagent tetra n-propyl ammonium iodide (75 gm.) was twice recrystallised from B.D.H. Analar ethanol (95%). After drying by suction, the final crop was quickly transferred to a vacuum oven where it was pumped dry at 70° - 80°C. for a total of 24 hours. Finally the material was stored over phosphorous pentoxide in an evacuated desiccator.

Conductance measurements at 25°C. on a 0.004990 M. solution of the recrystallised material yielded an equivalent conductance

*C. Pepela, Dept. of Physical and Inorganic Chemistry, University of Adelaide.

TABLE 3.1.

Molecular Weights and Solid Densities

Salt	M.W.*	Density**
NaCl	58.4428	2.165 [a] $25^{o}C.$
KCl	74.555	1.984 [a]
CsCl	168.358	3.97 (3.988)[a]
NaI	149.8942	3.667 [a] $25^{o}C.$
KI	166.0064	3.13 [a]
CsI	259.8094	4.510 [a] $25^{o}C.$
KBr	119.011	2.75 [a] $25^{o}C.$
$(nPr)_4NI$	313.2681	1.3138 [a] $25^{o}C.$
$(nPr)_4NBr$	266.2727	1.17 [b]

* Calculated from atomic weights[8].

** gm/cc.

a Reference 9.

b Measured by displacement by C.N. Pepela.

of 93.24, which is in good agreement with the value 93.41 interpolated graphically from the data of Evans and Kay[7].

Sucrose

The majority of the sucrose solutions were prepared from B.D.H. Microanalytical grade material, but a B.D.H. Analar grade sample was used to prepare the solvent for the potassium iodide mixed solutions. In each case the sucrose was vacuum dried at 30°C. in kilogram or half-kilogram quantities, and stored over silica-gel in a desiccator.

Distilled Water

Demineralised water from a bulk supply was distilled from glass and stored in a 20l. carboy with a ground-glass stopper. For simplicity, this water may be described as twice-distilled. Its average specific conductivity was 1.3×10^{-6} ohms^{-1} cm.$^{-1}$.

Another sample of water which had been distilled twice from glass, and stored in polypropylene containers, was used specifically for the cesium chloride conductance measurements discussed on p. 43. The specific conductivity of this sample was 1.1×10^{-6} ohms^{-1} cm.$^{-1}$.

Preparation of the Solutions

All solutions were prepared by weight, and vacuum corrections[10] were applied in the calculation of their concentrations. To avoid decomposition, the iodides were weighed from

cones with close fitting ground-glass caps. For each run on a particular salt, a series of solutions was prepared by successive dilutions, from that of highest concentration. A sucrose stock solution, of approximately 2 litres, was prepared for each of the three-component runs. A Stanton, type H.D.2, beam balance was used for this purpose.

"Quickfit" flasks, which had previously been steam cleaned, were used. These were sealed with Parafilm, following the final weighing. The sucrose solutions and the aqueous iodide solutions were stored in a refrigerator, and the tetraalkylammonium salt solutions in a dark cupboard.

II. RESULTS

The Testing and Calibration of the Flared Capillaries

Preliminary Investigation

The first of the flared-capillaries produced in this research was incorporated into a double-bulb test viscometer. Prior to the alignment of the optical system and photocells, a preliminary test of the effectiveness of the flaring procedure was undertaken. Thin strips of coloured adhesive tape provided effective temporary timing marks on the tubing above and below the bulbs. The time of efflux from each of these, of water, and of two sucrose solutions, at 25°C., was determined manually. The crystal oscillator-timer, and a Heuer stopwatch, were used for the upper and lower bulb respectively. The results of this investigation are presented in Table 3.2.

TABLE 3.2

Preliminary Test on the Flared-Capillary in the Double Bulb Test Viscometer. (PE.1)

Flow times at 25°C. (sec.)

Liquid	Upper Bulb	Lower Bulb	Ratio $\frac{(\text{Lower})}{(\text{Upper})}$
Water	794.94	1154.14	1.4519
10% Sucrose	1015.41	1474.52	1.4521
20% Sucrose	1403.93	2039.35	1.4526

Although a slight trend was noted, the ratio of the average flow times from the upper and lower bulbs was regarded as constant. Thus the indication was that a flared capillary had been successfully produced which had a "kinetic energy correction factor" very close to zero.

Calibration of the Viscometers

Both the flared-capillary viscometers were calibrated with water at various temperatures. The results of these calibrations are presented in Table 3.3 and illustrated in Figure 3.1, in the form of plots of η/dt against $1/t^2$. Within the precision of the standard viscosities, each of these plots was found to be horizontal, verifying the indication of the preliminary test, on the one viscometer, that the kinetic energy correction factor was negligible.

Standard Values of the Viscosity of Water

The standard values for the viscosity of water, used in the above calibrations, were obtained from a tabulation by Robinson and Stokes[11]. From an examination of the sources of this tabulation, it appeared that the values for 0° and 5°C. were averages based on a large number of experimental and calculated data quoted by Weber[12], while the 25°C. value was based on the identical data of Weber[12] and Coe and Godfrey[13], and that for 35°C. on the average of the data determined by Bingham and White[14] and

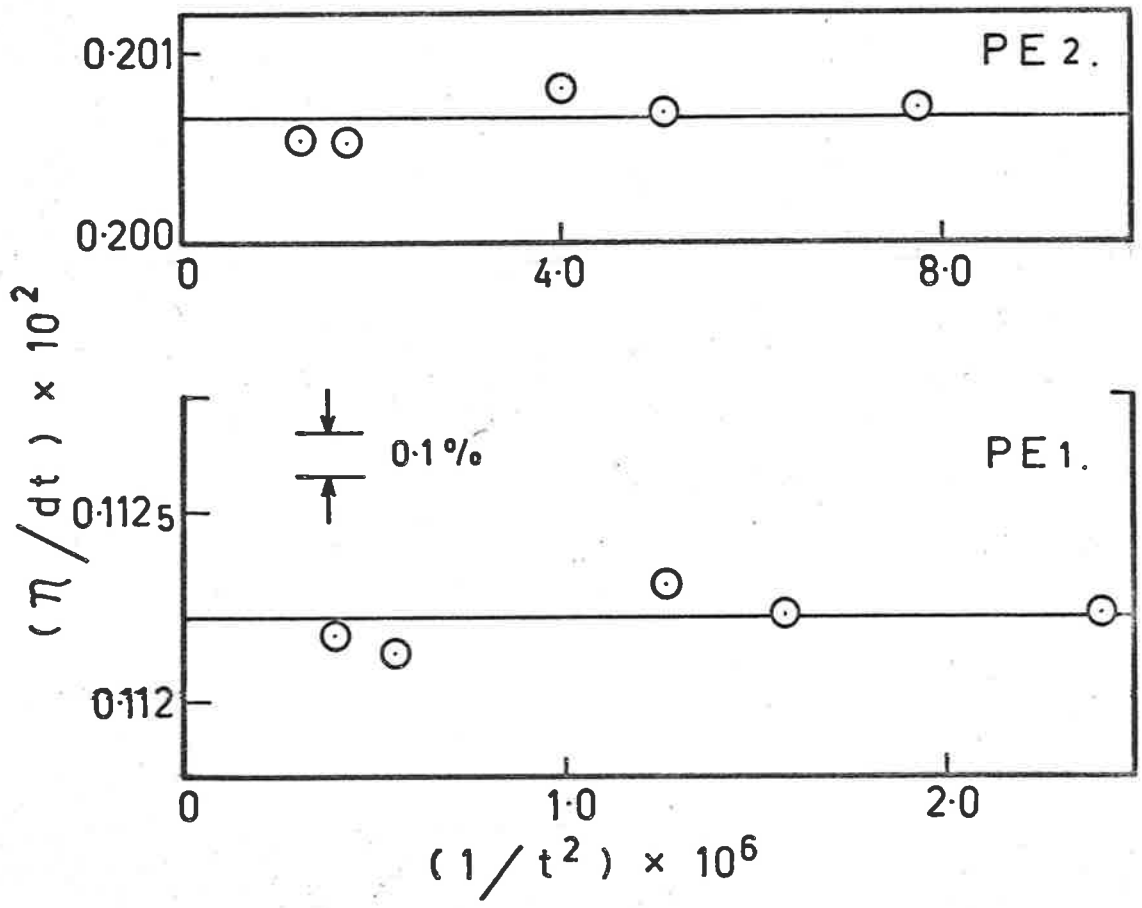

Figure 3.1. Viscometer Calibration Graphs.

TABLE 3.3

Calibration of Two Flared-Capillary Photo-Electric Viscometers using Viscosity Data for Water at Various Temperatures as the Standard

I Double - Bulb Model (P E.1.)

T	η [11] (centipoise)	d [11] (gm./cc.)	flow time,[a] t (sec.)	flow time,[b] t (sec.)	flow time,[c] $t_{corr.}$ (sec.)	$\frac{\eta}{dt} \times 10^2$	$\frac{1}{t^2} \times 10^6$
0°C.	1.787	0.99984	1593.81		1593.33	0.11217	0.3939
5°	1.516	0.99996	1352.45		1352.04	0.11213	0.5470
20°	1.002	0.99820		893.78		0.11231	1.2518
25°	0.8903	0.99704_7	795.75*	795.51		0.11225	1.5802
30°	0.7194	0.99403		644.58		0.11228	2.4068

a $t_{25°}$ = 795.75 in this series

b $t_{25°}$ = 795.51 in this series

c corrected to $t_{25°}$ = 795.51

* Measured before the 0° and 5° runs, after which the value 795.77 was obtained.

TABLE 3.3 Continued

II Single - Bulb Model (P E.2.)

T	η^{11} (centipoise)	d^{11} (gm./cc.)	flow time, t (sec.)		$\frac{\eta}{dt} \times 10^2$	$\frac{1}{t^2} \times 10^6$
0°C.	1.787	0.99984	891.28		0.20053	1.2588
5°	1.516	0.99996	756.08		0.20052	1.7493
20°	1.002	0.99820	499.87		0.20081	4.0021
25°	0.8903	0.997047	444.96[d]	444.93[e]	0.20068	5.0508
30°	0.7194	0.99403	360.58		0.20071	7.6912

d Before runs at other temperatures.

e After runs at other temperatures.

Weber[12]. The 20°C. value was that of the absolute viscosity of water (1.002 centipoise), determined by Swindells, Coe and Godfrey[15], to which standard all the other tabulated values were referred. Support for the acceptance of this standard has been provided by Roscoe and Bainbridge[16] who obtained, using an oscillating disc technique, a value of 1.0025 ± 0.0005 centipoise, at 20°C.

Standard Values of the Viscosity of Sucrose Solutions

Sucrose solutions, the standard viscosities of which have been determined, and recently recalculated on the basis of the new reference value of the absolute viscosity of water at 20°C., by the U.S.A. National Bureau of Standards[17,18], have been recommended as calibrating liquids for capillary viscometry.

If these standards are effective, they should provide results complementary to those obtained using the water standards based on the same reference value. However, it was found, for the viscometer PE.1., that plotted values of η/dt, calculated from the revised N.B.S. standard viscosities for 20, 30 and 40 percent sucrose solutions, fell significantly (0.4% - 0.6%) below the water calibration graph. A discrepancy between the two series of standards, in their common range, was thus apparent.

Previously, in this research, in connection with the calibration of several conventional capillary viscometers, it was noted that the 20 percent sucrose point always lay below a smoothed curve through points for 30 percent sucrose at 25°C., and for water at 20°, 25° and 30°C. Hence the revised data of the N.B.S. were re-examined, and it was noted that the value of the viscosity of 20 percent sucrose solution at 25°C. had not only been corrected to the new reference value, but had been subjected to a further correction. This was apparently that which applied to most of the other tabulated values as a consequence of the re-calculation of the constants of the viscometers used for their determination. However, the value for 20 percent sucrose solution at 25°C. had apparently originated in a paper of Jones and Stauffer[19], and the latter correction was inapplicable. Communications were exchanged with the N.B.S. on this subject.

A survey of the values available in the literature, of the viscosity of 20 and 40 percent sucrose solutions, is presented in Table 3.4.

TABLE 3.4

Literature Values (in centipoise) of the Viscosity of 20 and 40 Percent Sucrose Solutions at 25°C.

	Source	20 Percent Sucrose	40 Percent Sucrose
(1)	Bingham & Jackson[20] (interpolated values). Corrected from $\eta_{H_2O}(25^\circ C.) = 0.894$, to $\eta_{H_2O}(25^\circ C.) = 0.8903$.	1.697	5.166
(2)	Quoted by Jones & Stauffer[19] as a relative viscosity. Multiplied by $\eta_{H_2O}(25^\circ C.) = 0.8903$.	1.701	5.179
(3)	Original Tables N.B.S. (1942). $\eta_{H_2O}(20^\circ C.) = 1.005$	1.706	5.200
(4)	Revised Tables N.B.S. (1958).	1.695	5.164

From the constant value of η/dt (0.11224×10^{-2}) obtained from the water calibration graph for the double-bulb, flared-capillary viscometer, PE.1, values were calculated of the viscosity of 20, 30 and 40 percent sucrose solutions. These data, and the corresponding flow times and densities, are presented in Table 3.5. The sucrose solutions were all prepared from the same batch of Microanalytical grade material.

TABLE 3.5

Values (in centipoise) of the Viscosity of Sucrose Solutions at 25°C., Calculated from the Calibration Graph of the Viscometer PE.1

Weight Percent Sucrose	Flow time* (sec.)	Density (gm./cc.)	Calculated η
20	1407.33	1.07937^{21}	1.705
30	2173.46	1.12524	2.744
40	3934.48	1.17458^{22}	5.188

*All the flow times were corrected to the same standard, namely a flow time for water at 25°C. of 795.51 sec.

By substitution of these viscosity data, for 20 and 40 percent sucrose, for those from the N.B.S. revised tables, it was found that the curvature of a calibration graph presented by Kelly[22] could be greatly reduced. Similarly, by substitution of the 20 and 30 percent sucrose values, satisfactory calibration graphs were obtained for the conventional capillary viscometers in use in this laboratory.

Phang[23], using water at 0°, 5°, 20°, 25° and 35°C. as standards, obtained a linear calibration graph for a conventional capillary viscometer. From this graph, values of η/dt, corresponding to the flow times of 20 and 30 percent sucrose solutions, were obtained, which yielded viscosity values for these solutions of 1.706 and 2.745 cp. respectively. He also obtained a value of 2.744 cp. for the viscosity of the 30 percent sucrose solution, by extrapolation of the corresponding graph for a flared-capillary viscometer identical in design with the viscometer, PE.2, used in the present research.

It therefore appears that if the viscosity values presented in Table 3.5 are adopted, a general complementarity of the calibration procedures, with water at various temperatures, and with sucrose solutions, may be achieved. In accordance with the theory, linear calibration graphs of zero slope would be expected for continuously-flared capillaries, and graphs of slight

or no curvature, and finite negative slope, for conventional capillaries.

The Viscosity of Aqueous Solutions and 20 Percent Sucrose Solutions of Electrolytes at 25°C.

In Appendix A are presented the results of viscosity measurements made on aqueous solutions of electrolytes, and on solutions of electrolytes in 20 percent sucrose solution, at 25°C. The following table lists the salts studied, the particular viscometer used, and the respective page numbers of this Appendix.

TABLE 3.6

Contents of Appendices A and B

Salt	In Aqueous Solution Page	In 20 Percent Sucrose Solution Page	Viscometer
NaCl	A 2	A 15 , B 8	PE.1.
KCl	A 4	A 17 , B 8	PE.1.
CsCl	A 6 , B 2	A 18 , B 9	PE.1.
NaI	A 8 , B 2	A 19 , B 9	PE.1.
KI	A 9 , B 6	A 20 , B 7	PE.1.
CsI	A 10 , B 3	A 21 , B 10	PE.1.
KBr	A 11 , B 4	A 22 , B 11	PE.1.
$(n\text{-}Pr)_4NI$	A 12 , B 5		PE.2.
$(n\text{-}Pr)_4NBr$	A 13		PE.2.

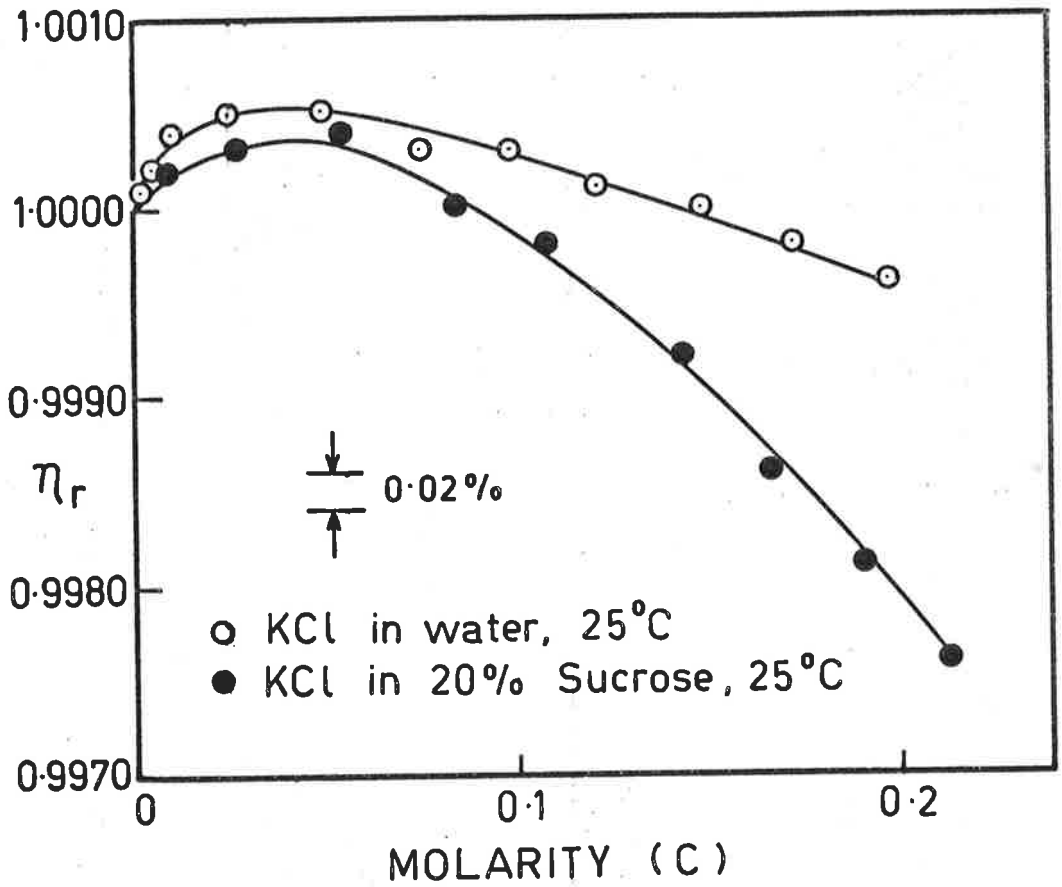

Figure 3.2. The Concentration Dependence of the Relative Viscosity of Potassium Chloride Solutions in Water and in 20 Percent Sucrose at 25°C.

The relative viscosity data for each system was treated according to the method of least squares using a C.D.C. 6400 computer. The computer programs used are presented in Appendix C. In the tables of Appendix A are listed the experimentally determined relative viscosities, η_r(EXPT.), those calculated from the least-squared equation, η_r(CALC.), and the difference, Δ, between the latter and former quantities. The values and corresponding standard errors of the parameters of the least-squared equations are presented in Tables 6.1 and 6.2, of Chapter 6. Where it was found helpful, in the course of the examination of the data, to construct a plot, against $\sqrt{C}$, of the function $(\eta_r - 1)/\sqrt{C}$, values of this function are also listed.

In Figure 3.2, the concentration dependence of the relative viscosity of aqueous solutions and aqueous 20 percent sucrose solutions respectively, of potassium chloride at 25°C., is illustrated.

The Density of Aqueous Solutions and 20 Percent Sucrose Solutions of Electrolytes at 25°C.

In Appendix B are presented the results of pycnometric measurements on aqueous solutions of electrolytes, and on solutions of electrolytes in 20 percent sucrose solution, at 25°C. The respective page numbers of this Appendix, for the

salts studied, are listed in the foregoing text table. In general both the viscometric and pycnometric determinations were conducted on the same solution. The availability of the excellent data of Jones and Christian[24], and of Jones and Talley[25], made a re-determination of the densities of aqueous solutions of sodium chloride and potassium chloride respectively, at 25°C., unnecessary. Determinations of the density of single solutions of each of these salts at 25°C. were performed, and the values shown to lie, within the experimental error, on graphs of the corresponding data of the above authors.

The density data for each system were fitted to the Root equation[26] by the method of least squares, using a C.D.C. 6400 computer. The relevant program, which was tested with the data of Jones and Christian, is presented in Appendix C. Values thus obtained, of the coefficients of this equation, are presented, with their standard errors, in Table 3.7. In the tables of Appendix B are listed the experimentally determined densities, d (EXPT.), those calculated from the least-squared equation, d (CALC.), and the difference, Δ, between the latter and former quantities.

TABLE 3.7.

Coefficients of the Root Equation (Eqn. 3.17)

Electrolytes in Aqueous Solution at 25°C.

Salt	COEFF.1	COEFF.2
CsCl	0.1285 ± 0.0003	0.0003 ± 0.0007
NaI	0.1146 ± 0.0001	0.0007 ± 0.0003
KI	0.1207 ± 0.0001	0.0011 ± 0.0003
CsI	0.2019 ± 0.0002	0.0005 ± 0.0005
KBr	0.08526 ± 0.00007	0.0018 ± 0.0002
$(n\text{-}Pr)_4NI$	0.06230 ± 0.00008	− 0.0027 ± 0.0002*
$(n\text{-}Pr)_4NBr$	0.0265 ± 0.0003[a]	− 0.0050 ± 0.0008*

Electrolytes in 20 Percent Sucrose Solution at 25°C.

Salt	COEFF.1	COEFF.2
NaCl	0.0393 ± 0.0004	0.0027 ± 0.0012
KCl	0.0457 ± 0.0002	0.0056 ± 0.0005
CsCl	0.1262 ± 0.0004	0.0053 ± 0.0010
NaI	0.1119 ± 0.0007	0.0031 ± 0.0016
KI	0.1126 ± 0.0004	− 0.0051 ± 0.0009*
CsI	0.1926 ± 0.0004	− 0.0087 ± 0.0011*
KBr	0.0830 ± 0.0007	0.0052 ± 0.0018

a From the density data of C.N. Pepela.

* Theory precludes a negative sign for this coefficient.

Limiting Apparent Molar Volumes of Electrolytes in Aqueous Solution and in 20 Percent Sucrose Solution at 25°C.

The equivalence of the limiting partial and apparent molar volumes of a solute component, for both two-component systems, and three-component systems in which the ratio of numbers of moles of the other two components is held constant, may be demonstrated as follows.

Partial Molar Volume

The partial molar volume, $\bar{V}_i$, of a component, i, in a solution containing n_i moles of that component, may be defined by

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \quad (j \neq i) \,, \tag{3.3}$$

where V is the volume of the solution and the n_j are the moles of the other components present.

(1) 2 - component systems.

For a 2-component system, where the subscripts o and 1 denote solvent and solute respectively, the apparent molar volume of the latter may be defined by,

$$\phi_1 = \frac{V - V_o}{n_1} \tag{3.4}$$

where V_o is the volume of pure solvent used in making a solution of volume, V, containing n_1 moles of component 1. Differentiation of equation 3.4 with respect to n_1 yields,

$$\frac{\partial \phi_1}{\partial n_1} = \frac{1}{n_1}\left(\frac{\partial V}{\partial n_1}\right) - \frac{(V - V_o)}{n_1^2} \qquad 3.5$$

$$= \frac{1}{n_1}\left[\left(\frac{\partial V}{\partial n_1}\right) - \frac{(V - V_o)}{n_1}\right] \qquad 3.6$$

$$= \frac{1}{n_1}(\bar{V}_1 - \phi_1) \qquad 3.7$$

$$\therefore \quad \bar{V}_1 = \phi_1 + n_1\left(\frac{\partial \phi_1}{\partial n_1}\right) \qquad 3.8$$

and, at infinite dilution of component 1, provided that $(\partial \phi_1 / \partial n_1)_{n_1 = 0}$ is finite,

$$\underline{\bar{V}_1^{\,o} = \phi_1^{\,o}} \qquad 3.9$$

(2) 3 - component systems.

For a 3-component system, where the subscripts 0, 1 and 2 denote solvent and the two solute components respectively, the apparent molar volume of a component, 2, may be defined by,

$$\phi_2 = \frac{V - n_o \bar{V}_o^{\,*} - n_1 \bar{V}_1^{\,*}}{n_2}, \qquad 3.10$$

and $\therefore \quad V = n_2\phi_2 + n_o \bar{V}_o^{\,*} + n_1 \bar{V}_1^{\,*}$ 3.11

where $\bar{V}_o^{\,*}$ and $\bar{V}_1^{\,*}$ are the respective partial molar volumes of the components of the pure <u>mixed</u> solvent of constant composition.

$$\therefore \quad \bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_o, n_1} = \phi_2 + n_2 \left(\frac{\partial \phi_2}{\partial n_2}\right)_{n_o, n_1} \qquad 3.12$$

and, at infinite dilution of component 2, provided that $(\partial \phi_2 / \partial n_2)_{n_2} = 0$ is finite,

$$\underline{\bar{V}_2^{\,o} = \phi_2^{\,o}}. \qquad 3.13$$

The latter two equations correspond to those which may be derived if the mixed solvent is treated as one component of a 2-component system.

It may be shown that if Masson's relation[27,28],

$$\underline{\text{i.e.}} \quad \phi_2 = \phi_2^{\,o} + S\sqrt{C} \qquad 3.14$$

(where S is a constant), which has been shown to apply to dilute 2 - component solutions, and often to extend to higher concentrations[27], applies to the 3 - component systems considered, then the Root equation is also applicable to these systems.

Derivation of the Root Equation

It is possible to define a general apparent molar volume, for a component, 2, in either a 2 - component system or a 3 - component system in which two components can collectively be regarded as a mixed solvent.

$$\phi_2 = \frac{V - V_{solvent}}{n_2} \qquad 3.15$$

Since when V = 1,000 cc's., $n_2 = C$,

$$\phi_2 = \frac{1,000}{Cd_o}(d_o - d) + \frac{M_2}{d_o} \qquad 3.16$$

Thus, if Masson's relation applies,

$$d = d_o + \frac{(M_2 - d_o\phi_2^o)}{1,000} C - \frac{(Sd_o)}{1,000} C^{3/2} . \qquad 3.17$$

This equation is identical with that first derived by Root[26]. According to theory[29], the coefficient, $Sd_o/1,000$, should have a positive value, common to all strong electrolytes of the same valence type, in a given solvent, and the coefficient of the C term should be an additive property of the ions[30]. The experimental values of the former, however, show considerable individuality within a series of similar electrolytes (see for example the values of COEFF.2 in Table 3.7) and are only of the order of magnitude of the theoretical value[30]. Root reported that the experimental coefficients were both additive.

Discussion of the Results

In Table 3.8 are presented values of the limiting apparent molar volume, ϕ_v^o, derived from those values of the coefficients (COEFF.1), of the C term of the Root Equation, which appear in Table 3.7.

For the 2-component systems, a comparison with literature values is possible, and the agreement is seen to be very good. The discrepancy in the case of the cesium chloride value may be

TABLE 3.8

Limiting Apparent Molar Volumes at 25°C.

Salt	Aqueous Solution ϕ_v^o c.c./mole	ϕ_v^o (LIT.)[31] ml./mole	20% Sucrose Solution ϕ_v^o c.c./mole
NaCl		16.40 16.61 [a]	17.7 ± 0.4
KCl		26.52 26.81 [a]	26.7 ± 0.2
CsCl	40.0 ± 0.3	39.15 [a]	39.1 ± 0.4
NaI	35.4 ± 0.1	35.10	35.2 ± 0.7
KI	45.4 ± 0.1	45.36	49.5 ± 0.4
CsI	58.0 ± 0.2	57.74	62.2 ± 0.4
KBr	33.8 ± 0.1	33.73	33.3 ± 0.7
$(n\text{-}Pr)_4NI$	251.71		
$(n\text{-}Pr)_4NBr$	240.45*		

* Density data of C.N. Pepela[32]

[a] Values of 16.628, 26.886 and 39.15 have more recently been determined, by Vaslow[33], for NaCl, KCl and CsCl respectively.

attributed to the fact that this was based upon a smaller number (5) of density measurements.

Values of the apparent molar volume were calculated for potassium iodide in aqueous solution, and in aqueous 20 percent sucrose solution, at 25°C. The results of these calculations are presented with the corresponding density data in Table B.2 of Appendix B.

When extrapolated, against $\sqrt{C}$, to infinite dilution, the apparent molar volumes for the aqueous solutions yielded a limiting value of 45.3, in good agreement with the value calculated from the appropriate coefficient of the Root equation. The plot of the apparent molar volumes for the solutions in 20 percent sucrose, however, had a negative slope in the concentration range in which the density measurements were made (between $\sqrt{C}$ = 0.22 and $\sqrt{C}$ = 0.5). The negative value, obtained for this system, of the coefficient (COEFF.2) of the $C^{3/2}$ term of the Root equation, is a consequence of this concentration dependence, which is not in accordance with Masson's relation. However, according to recent work by Stokes and Dunn[34], following the studies of Wen and Saito[35], on the apparent molal volumes of tetra-alkyl-ammonium bromides in aqueous solution at 25°C., Masson's relation, which apparently does not hold, in a similar

concentration range to the above, for some such systems, may be expected to apply at lower concentrations. It seems reasonable to conclude that this should also be the case for those solutions of an alkali halide in 20 percent sucrose for which negative values of COEFF.2 are recorded in this thesis. Hence, for these systems, meaningful limiting apparent molar volumes, obeying the additivity rule (see later) could only be obtained if the density measurements were extended by some more accurate technique, such as dilatometry[36], to higher dilutions. However, since the measurements of density, in the present study, were essentially subsidiary to those of viscosity, it was not decided to undertake this extension for the systems in question.

In accordance with the comments above, on the apparent molal volumes of the tetra-alkyl-ammonium bromides, a negative value of COEFF.2, of the Root equation was obtained from the tetra-(n-propyl)-ammonium bromide density data of Pepela[32]. The value of this coefficient was also found to be negative for the corresponding iodide. For the bromide, a value of the limiting apparent molar volume at 25°C. was obtained, which was identical, within the experimental error, with that determined by Wen and Saito[35].

Additivity of the Limiting Apparent Molar Volumes

If the prediction of the theory is correct, that the limiting apparent molar volume of an electrolyte in a particular solvent is an additive property of the ions, then the differences between values for pairs of electrolytes with a different common cation, but the same pair of anions, should be constant. The agreement between differences which can be formed from the experimental data for electrolytes in aqueous solution and those formed from the corresponding literature values of Table 3.8, is shown in Table 3.9.

It is interesting to note, that the difference between the ϕ_v^o values determined for tetra-(n-propyl)-ammonium iodide and bromide, and that between the values for the corresponding potassium salts, are identical within the experimental error, despite the fact that the former cannot be taken to be the true limiting values.

For the electrolytes in 20 percent sucrose solution, if additivity is assumed, the difference between the ϕ_v^o values for sodium iodide and chloride may be regarded as the most reliable value of the difference $\phi_v^o\ (I^-) - \phi_v^o\ (Cl^-)$, since the other differences presented are derived from the ϕ_v^o values for potassium iodide and cesium iodide respectively, neither of which can be regarded as a true limiting value. From those values

TABLE 3.9.

Additivity of Limiting Apparent Molar Volumes

Electrolytes in Aqueous Solution

Experimental Differences			Literature
$\phi_v^o(NaI) - \phi_v^o(NaCl)$			18.49
$\phi_v^o(KI) - \phi_v^o(KCl)$			18.55
$\phi_v^o(CsI) - \phi_v^o(CsCl)$	$= 18.0 \pm 0.5$		18.59
$\phi_v^o(KI) - \phi_v^o(KBr)$	$= 11.6 \pm 0.2$		11.63
$\phi_v^o(Pr_4NI) - \phi_v^o(Pr_4NBr)^*$	$= 11.26 \pm 0.4$		

Electrolytes in 20 Percent Sucrose Solution

Experimental Differences		
$\phi_v^o(NaI) - \phi_v^o(NaCl)$	$= 17.5 \pm 1.1$	
$\phi_v^o(KI) - \phi_v^o(KCl)$	$= 22.8 \pm 0.6$	
$\phi_v^o(CsI) - \phi_v^o(CsCl)$	$= 23.1 \pm 0.8$	

* From the density data of C.N. Pepela[32] .

TABLE 3.10.

Ionic Limiting Apparent Molar Volumes at 25°C.

Ion	ϕ_v^o * (In 20% Sucrose Solution) cc./mole	ϕ_v^o ** (In Aqueous Solution) ml./mole	B_{ION} (In 20% Sucrose Solution)
Na^+	- 1.9	- 2.95	0.107
K^+	7.1	7.29	- 0.013_5
Cs^+	19.6	19.68	- 0.055
Cl^-	19.6	19.56	- 0.013_5
Br^-	26.2	26.50	- 0.053
I^-	37.1[a]	38.06	- 0.090

* Calculated on the basis of the assumption, by analogy with the aqueous solution values, that $\phi_v^o (Cs^+) = \phi_v^o (Cl^-)$.

** Noyes'[37] values; computed relative to a value of ϕ_v^o for the H^+ ion = -1.49 ml./mole, from limiting apparent molar volume data tabulated by Harned and Owen[31] (see Table 3.8).

[a] In NaI.

thought to be reliable, ionic contributions were derived, on the basis of the assumption, by analogy with the aqueous solution values of Noyes[37], that the ionic limiting apparent molar volumes for the Cs^+ and Cl^- ions were equal. Values of these ionic contributions are presented, with Noyes' values, in Table 3.10. The B-coefficients for the corresponding ions in aqueous 20 percent sucrose solution are presented for comparison. As might be expected (from the manner in which ions may influence the structure of water - see Chapter 5) only a broad correlation between the latter quantities and the corresponding ϕ_v^o values is apparent. It is between their respective temperature coefficients that a more exact correlation is likely to exist (see Chapter 6).

<u>The Limiting Equivalent Conductance of Cesium Chloride in 20 Percent Sucrose Solution at 25°C.</u>

In Table 3.11 are presented the results of conductance measurements on solutions of cesium chloride in aqueous 20 percent sucrose at 25°C. Values of the limiting equivalent conductance, $\Lambda^o_{calc.}$, calculated from equation 2.27,

$$\Lambda^o_{calc.} = \Lambda + \frac{(B_1 \Lambda + B_2)\sqrt{C}}{1 + (B_a^o - B_1)\sqrt{C}} \quad , \qquad 2.27$$

TABLE 3.11

Conductance Data for Solutions of Cesium Chloride in Aqueous 20 Percent Sucrose at 25°C.

C	$\sqrt{C}$	Λ *	$\Lambda^{o}_{calc.}$ $\mathring{a} = 4.0$	$\Lambda^{o}_{calc.}$ $\mathring{a} = 3.0$	$\Lambda^{o}_{calc.}$ $\mathring{a} = 2.5$
0.0023138	0.048102	92.579	95.141	95.181	95.202
0.010528	0.10261	89.865	94.971	95.135	95.222
0.016607	0.12886	88.587	94.800	95.047	95.178
0.020629	0.14362	87.918	94.724	95.023	95.183
0.040881	0.20219	85.446	94.418	94.951	95.242
0.054490	0.23343	84.313	94.333	95.006	95.378

* Units of Λ:- $cm.^{2}.ohm^{-1}.gm.equiv.^{-1}$

in the numerical form,

$$\Lambda^{o}_{calc.} = \Lambda + \frac{(0.2529\,\Lambda + 32.67)\sqrt{C}}{1 + (0.3393\,\mathring{a} - 0.2529)\sqrt{C}} \qquad 3.18$$

with values of $\mathring{a}$ of 2.5, 3.0 and 4.0 $\mathring{A}$ respectively, are included in this tabulation. Each of these series extrapolated against C to the common Λ^{o} value of 95.22 at infinite dilution. Subtraction of the limiting equivalent conductance, 48.2, of the chloride ion in aqueous 20 percent sucrose at 25°C.[38], yielded a value for the cesium (Cs^{+}) ion of 47.0 $cm.^{2}$ ohm^{-1} $gm.\ equiv.^{-1}$.

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CHAPTER 4

THE STRUCTURE OF LIQUID WATER

THE STRUCTURE OF LIQUID WATER

Review

The anomalous nature of liquid water is revealed by a comparison of its properties with those of the hydrides of elements close to oxygen in the periodic table. Liquid water has a high boiling point suggesting the presence of strong intermolecular forces. Its high melting point suggests that there is a quasi-crystalline structure already present, so that the solid state can be formed with ease, despite the comparitively high thermal energy[1].

Developmentsteward a theory of the structure of liquid water began with Bernal and Fowler's[2] interpretation of the first reliable data on its X-ray diffraction (1933). The radial distribution function is the frequency distribution of the distances between an arbitrarily chosen central molecule and the molecules surrounding it, averaged over all directions in space. In a more recent experimental study (1962) Danford and Levy[3] found that, at 25°C., the maximum in this function corresponding to the smallest average distance between adjacent molecules, was remarkably sharp, and occurred at 2.88 Å. This was followed, according to the radial distribution curve, by a broad region of scattering density rising to a barely resolvable maximum at

4.9 Å. This region was indicative of considerable numbers of mole cules at separations intermediate between these limits, and hence between the first and second nearest-neighbour distances of ice. Bernal and Fowler concluded that the H_2O molecules in liquid water were four co-ordinate. They proposed a structure which was invoked to explain the high and very similar values of the static dielectric constant of water and ice, and the density maximum at $4^{\circ}C$. for liquid water.

It was Morgan and Warren[4] however, in a discussion of the results of their X-ray diffraction study (1938) who drew attention to the previously disregarded region between 3 and 4 Å on the radial distribution curve. Since no corresponding distribution could be found for any ice-like structures, they concluded that only part of the H_2O molecules in liquid water could be four co-ordinate.

On this basis both "cluster" and "cage" theories for liquid water have been proposed. In the former, the four co-ordinate water molecules are grouped in "clusters", which are in a continual state of flux, being built-up and broken-down in a rapid interchange with single water molecules. Hence the description, "flickering clusters". The first of these models was proposed by Hasted et.al.[5] in conjunction with dielectric relaxation measurements, and used to explain the occurrence of a single, uniform,

and remarkably fast relaxation process in water[6].

In an attempt to give a quantitative significance to the model proposed by Frank and Wen[7] (1957), Nemethy and Scheraga[8] (1962) applied the methods of statistical thermodynamics to the dissipation of the clusters with rising temperature. However, their theory failed to predict the temperature dependence of the specific heat of water. A further deficiency was the lack of correlation of the concentrations of the various species postulated, with the experimental findings of Buij's and Choppin[9], using infra-red techniques. Therefore Vand and Senior[10] (1965) were led to propose a theory which overcame this and the previously mentioned weakness. However, both this theory and its predecessor involve the assignment of a large number of adjustable parameters (12 in the more recent case). It should be noted that the first quantitative treatment of "ice like molecules" was that of Eucken in 1946[6].

In cell or cage type theories, only two components are proposed, one of which, in keeping with the views of Bernal and Fowler, is a bulky framework of tetrahedrally co-ordinated water molecules. Single water molecules occupy cavities in this framework where they rotate without restraint. The first model of this type was proposed in 1946 by Samoilov[11]. Difficulties arise with cage models due to their rigidity and insufficient

adaptability to dissolved particles[6].

Frank and Quist[12] (1961) have suggested that it is necessary to consider a "third state" of molecules in liquid water in addition to such tetrahedrally co-ordinated networks and freely rotating molecules. Wall and Hornig[13] (1965), as a result of a Raman spectral study, held that models in which ordered lattice regions are the only structural units apart from monomeric water were unrealistic.

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CHAPTER 5

THE EFFECT OF IONS AND OF NON-ELECTROLYTES ON THE STRUCTURE AND PROPERTIES OF LIQUID WATER

THE EFFECT OF IONS AND OF NON-ELECTROLYTES ON THE STRUCTURE AND PROPERTIES OF LIQUID WATER

Introduction

Studies using X-ray and Raman methods have also been made on the structure of water in the presence of ionic solutes[1]. Brady,[2,3] for example, studied concentrated solutions of KOH, KCl and LiCl by X-ray diffraction, and found that KOH produced an enhancement of the sharp peak in the radial distribution function of liquid water. For the KCl solution, presumably due to the presence of the Cl^- ion, a diminution of the peak was observed, and it was absent from the curve for the LiCl solution. Walrafen[4] observed that certain intensities in the Raman spectrum of water, which were increased by lowering its temperature, were also increased by the addition of alkali metal bromides and chlorides. These, and the majority of other recent observations on the properties of aqueous electrolyte solutions, have either been explained in terms of features of the model proposed by Frank and Evans[5] in 1945, or in terms of the more sophisticated "flickering cluster" theory of Frank and Wen,[6] derived from it.

The concept of the immobilisation of the nearest neighbour water molecules, by the strong field ($\sim 10^6$ volts/cm) at the surface

of the ions, provided an explanation of the small or negative values which salt solutions display of the solute partial molal volumes, heat capacities and compressibilities[6,7]. It also led to a simple explanation of the viscosity increase produced on the addition of certain electrolytes to water.

However, that this was not necessarily the principal effect of ions on water became clear from the fact that the addition of other electrolytes could lower the viscosity of water. Bernal and Fowler[8] and Cox and Wolfenden[9] interpreted this phenomenon as meaning that ions were somehow "breaking" the water structure.

The Model of Frank and Evans

Frank and Evans[5] showed that for the alkali metal cations other than Li^+ and Na^+, and for all the halide anions except F^-, the sum of the estimated entropy losses arising from immobilisation of the first layer water and from dielectric polarisation of more distant water, was insufficient to allow for the observed entropy of hydration, even after correction for restriction of the ions in "free volume" cells in the condensed phase[6].

Thus it is possible to conceive of an ion as surrounded by three regions, one of immobilisation, one in which the water is usually more random in organisation than normal, and a third containing water molecules polarised normally by the weakened ionic field. Either the first or the second of the regions might

be absent from the model in a particular case, depending on the value of the surface charge[10]. The inner immobilisation region could thus disappear if the value of the ionic radius was sufficiently high. On the other hand, for ions of high surface charge, additional structuring might extend past the region of immobilisation.

Interpretations of both the structure-making and structure-breaking properties of particular ions can be framed in terms of Frank and Wen's "flickering cluster" model for the structure of water, simply by recognising the statistical significance of the regions proposed by Frank and Evans. However, before attempting to interpret any observation in terms of this model it is essential to decide whether the property concerned is one which relates to the overall structure of the solution, to the structure in the close vicinity of the ion, or to that of the remaining solvent. The terms "structure-making" and "structure breaking" are only meaningful in a clear context.

Recently Ben-Naim and Egel-Thal[11] made a study of the solubility of argon, at various temperatures, in pure water and in 1 m. aqueous solutions of electrolytes. From these data, ΔS_t^*, the static entropy of transfer of argon, at constant molarity, from water to each electrolyte solution, was calculated.

This static term excludes the entropy changes arising from the re-orientation of both solvents in the presence of the argon. For each of the electrolytes studied (LiCl, NH_4Cl, NaCl, KCl, KBr, NaI and KI) ΔS_t^* was found to be negative, indicating some disruptive influence on the water structure.

The Effect of Non-electrolytes on the Structure of Water

In a similar study by Ben-Naim[12] on the solubility of argon in aqueous solutions of non-electrolytes, ΔS_t^* was found to be positive for methanol, ethanol, 1 - propanol and 1 - butanol solutions, while negative for glycerol, glucose and (0.5m) sucrose solutions, thus indicating some structure-breaking influence of the latter group on the solvent. The inference from the concentration dependence of the viscosity[13] of sucrose solutions, however, is that the overall effect is one of structure-making.

It should be noted that the total number of "cavities" available to the argon in the non-electrolyte solution would have been reduced, simply due to the presence of the solute. In studies of transport properties such as viscosity and conductance, in aqueous solutions of large non-electrolytes, an "obstruction effect"[14] may be an important consideration, in addition to the effect of the non-electrolyte on the structure of the water. The latter depends largely on the nature of the groups present in the non-electrolyte[12].

The Effect of Non-Polar Groups on the Structure of Water

Structure formation in the vicinity of non-polar groups was first proposed by Frank and Evans[5] as an explanation of the fact that non-polar gases, such as hydrocarbons, dissolve exothermically in water with a simultaneous large decrease in the entropy of the system. Ben-Naim[15,16] has shown that a preference for larger clusters in the vicinity of a non-polar group can be expected as a result of the energetic interaction, without the assumption, as in the treatments of Frank and Evans and, later, Némethy and Scheraga[17], that the clusters incorporate the non-polar groups. Penetration of the non-polar groups into the clusters was not however, excluded.

The explanation of the effect of non-polar molecules and groups in terms of Frank and Wen's "flickering cluster" model of water structure, is supported by the observation that aqueous solutions of non-polar solutes have a longer dielectric relaxation time[6].

The Interaction of Urea with the Water Structure

Abu-Hamdiyyah[18] has suggested that the physico-chemical properties of aqueous urea solutions indicate that urea actively participates in, and enhances the formation of clusters. However, his conclusion, on the basis of the small positive viscosity B-coefficient of urea[13], that it is a weak overall structure maker, is not valid. The overall effect on the solvent structure should

be assessed in terms of the difference between the observed B - coefficient and the contribution due to the Einstein effect.

Reviews

Recently, two excellent reviews of the subject of Solute-Water Interactions have been compiled. That of Kavanau[19] is extremely comprehensive, and that of Wicke[20] has influenced the approach adopted in this and the preceding chapter.

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CHAPTER 6

DISCUSSION

ION-SOLVENT INTERACTIONS AND THE VISCOSITY OF ELECTROLYTE SOLUTIONS

ION-SOLVENT INTERACTIONS AND THE VISCOSITY OF ELECTROLYTE SOLUTIONS

Introduction

In 1929, Jones and Dole[1] reported measurements of the viscosity of aqueous solutions of barium chloride, which showed that the Gruneisen effect[2] was magnified at great dilution. They proposed the equation,

$$\eta_r = 1 + A\sqrt{C} + BC \qquad 6.1$$

for the molar concentration dependence of the relative viscosity, η_r (actually a fluidity equation was proposed). This equation fitted both their data over the range 0.005 to 1 molal, and the best data on other strong electrolytes, available in the literature. Falkenhagen[3] was able to derive a limiting equation with an explicit expression for the coefficient, A, in terms of the limiting equivalent conductances λ, and valences of the ions of a general electrolyte, the temperature, and universal constants commonly appearing in Debye-Hückel theory expressions. Falkenhagen and Vernon computed the value of A for a number of salts from this equation, which reduces to,

$$A = \frac{1.45}{\eta_o\sqrt{2D_oT}}\left[\frac{\lambda_1 + \lambda_2}{4\lambda_1\lambda_2} - \frac{(\lambda_1 - \lambda_2)^2}{(3+\sqrt{2})\lambda_1\lambda_2(\lambda_1+\lambda_2)}\right] \qquad 6.2$$

for a 1 : 1 electrolyte. Thus the A - coefficient of equation 6.1, is clearly due to ionic interactions. If the influence of

incomplete dissociation or ion association, and the consequences of an approximation made in Falkenhagen's theory[4] are neglected, then the B-coefficient may be regarded as a measure of the interaction of the solute and solvent[5].

From the theory, it can be seen that the value of the A - coefficient should be positive for all salts, and zero for non-electrolytes. The B - coefficient may however be either positive or negative in aqueous solutions, so that in addition to the positive contribution, which would be expected from Einstein's equation[6], related to the size of the solute, there is evidently a further effect which can reduce the viscosity; namely the influence of the solute on the structure of water.

In Tables 6.1 and 6.2 are presented the values obtained in this research, of the coefficients of the Jones-Dole equation, for salts in aqueous solution and in aqueous 20 percent sucrose solution respectively, at 25°C. The standard errors[7] (S.E.) of both coefficients are presented in each case, as are the corresponding values of A, calculated from equation 6.2, using literature data for the equivalent ion conductances[8,9] in, and dielectric constants[10,11] and viscosity[12,13] of, the respective solvents. No explanation can at present be offered for the discrepancy observed, for several of the systems with aqueous 20 percent sucrose as solvent, and for both the aqueous tetra-(n-propyl)-ammonium halide systems, between the theoretical

TABLE 6.1

Coefficients of the Jones-Dole Equation (Eqn. 6.1)

and the Extended Jones-Dole Equation (Eqn. 6.4)

Electrolytes in Aqueous Solution at 25°C.

Salt	A	S.E.A.	A(Theory)	B	S.E.B.	B(Lit.)	C	S.E.C.
NaCl	0.0060	± 0.0005	0.0060	0.081	± 0.001	0.079[15]		
						0.079[16]		
KCl	0.0050	± 0.0003	0.0050	- 0.013	± 0.001	- 0.014[2]		
						- 0.014[17]		
CsCl	0.0052	± 0.0006	0.0049	- 0.050	± 0.002			
NaI	0.0053	± 0.0004	0.0060	0.010	± 0.001			
KI	0.0052	± 0.0004	0.0050	- 0.084	± 0.001	- 0.076[18]		
						- 0.088[19]		
CsI	0.0038	± 0.0008	0.0049	- 0.116	± 0.002	- 0.118[20]		
KBr	0.0054	± 0.0006	0.0050	- 0.046	± 0.002	- 0.049[21]		
$(n\text{-}Pr)_4NI$	0.0435	± 0.0036	0.0078	0.588	± 0.016		0.77	± 0.05
$(n\text{-}Pr)_4NBr$	0.0319	± 0.0036	0.0077	0.687	± 0.017		0.64	± 0.06

TABLE 6.2

Coefficients of the Jones-Dole Equation (Eqn. 6.1)

Electrolytes in 20 Percent Sucrose Solution at 25°C.

Salt	A	S.E.A.	A(Theory)	B	S.E.B.
NaCl	0.0082	± 0.0005	0.0052	0.093	± 0.001
KCl	0.0075	± 0.0009	0.0043	- 0.027	± 0.002
CsCl	0.0056	± 0.0005	0.0043	- 0.068	± 0.001
NaI	0.0057	± 0.0009	0.0053	0.017	± 0.002
KI	0.0035	± 0.0007	0.0044	- 0.099	± 0.002
CsI	0.0033	± 0.0007	0.0044	- 0.143	± 0.002
KBr	0.0077	± 0.0012	0.0043	- 0.066	± 0.003

A - coefficient value, and that determined experimentally.

The Additivity of B - Coefficients

The additivity of B - coefficients for aqueous solutions of electrolytes has been demonstrated by Cox and Wolfenden[14] and by Kaminsky[5]. When differences between B - coefficients of different salts were formed in such a manner that the cation pair was kept the same, and only the common anion varied, the constancy of these differences allowed the conclusion that there was a specific contribution to the B - coefficient from the cation. Unfortunately, the absence of an analogue to the transport number prevents the partition of B - coefficients into ionic contributions in like manner to equivalent conductances. However, division may be conducted on the basis of certain reasonable assumptions. Cox and Wolfenden assumed that the ionic B values of Li^+ and IO_3^- in $LiIO_3$ were proportional to the ionic volumes, and that these in turn were inversely proportional to the third power of the ionic mobilities. Kaminsky, following Gurney[22], assigned ionic B values on the basis of the equality of the values for the K^+ and Cl^- ions ($B_{K^+} = B_{Cl^-}$). This criterion was chosen since, over the range of temperatures covered by the viscosity studies, the ionic mobilities of the K^+ and Cl^- ions were known not to differ by more than 3%. Values calculated on the basis of the two different criteria agreed well.

That the B - coefficients for 1 : 1 electrolytes in aqueous 20 percent sucrose solution at 25°C. are an additive property of their constituent ions is indicated by the results presented in Table 6.3. Differences formed in a manner analogous to that of Kaminsky, between the B - coefficients for the chloride and iodide of sodium, potassium and cesium respectively, are shown to be constant within the experimental error. The constancy of the corresponding differences for aqueous solutions of these electrolytes is also confirmed.

Excellent agreement is shown, of the difference obtained in this research, between the B - coefficients for aqueous solutions of sodium chloride and potassium chloride respectively, at 25°C., with that obtained by Kaminsky.

Since the electrical mobilities of the K^+ and Cl^- ions, at 25°C. in aqueous 20 percent sucrose solution, were known to differ by only 4%[9], it seemed reasonable to assign individual ionic contributions to the B - coefficients of electrolytes in that solvent, at that temperature, on the basis of the criterion adopted by Kaminsky for the assignment of such contributions to the B - coefficients of electrolytes in aqueous solution. Hence the ionic B - coefficients presented in Table 6.4 have their basis in the assumed equality of the values for the K^+ and Cl^-

TABLE 6.3

Additivity of B - Coefficients

Electrolytes in Aqueous Solution

	Experimental Differences	Literature
$B_{NaCl} - B_{KCl}$	$= 0.094 \pm 0.002$	0.093^{5}
$B_{NaCl} - B_{NaI}$	$= 0.071 \pm 0.002$	
$B_{KCl} - B_{KI}$	$= 0.071 \pm 0.002$	
$B_{CsCl} - B_{CsI}$	$= 0.066 \pm 0.004$	
$B_{KBr} - B_{KI}$	$= 0.038 \pm 0.003$	
$B_{Pr_4NB_r} - B_{Pr_4NI}$	$= 0.099 \pm 0.04$	

Electrolytes in 20 Percent Sucrose Solution

	Experimental Differences
$B_{NaCl} - B_{NaI}$	$= 0.076 \pm 0.003$
$B_{KCl} - B_{KI}$	$= 0.072 \pm 0.004$
$B_{CsCl} - B_{CsI}$	$= 0.075 \pm 0.003$

TABLE 6.4

Ionic B - Coefficients

Electrolytes in Aqueous Solution at 25°C.

$$B_{K^+} = B_{Cl^-} = -0.0065 \pm 0.0005$$

Ion	B - Coefficients		Literature
Na^+	0.088 ± 0.0015		0.086[5]
K^+	- 0.0065 ± 0.0005		- 0.007[5]
Cs^+	- 0.044 ± 0.0025		- 0.045[23]
Cl^-	- 0.0065 ± 0.0005		- 0.007[5]
Br^-	- 0.040 ± 0.0025		- 0.042[24] - 0.032[23]
I^-	- 0.078 ± 0.0015	(KI)	- 0.069[5] - 0.081[19]*
	- 0.078 ± 0.0025	(NaI)	
	- 0.073 ± 0.0045	(CsI)	- 0.073[20]*
$(n\text{-}Pr)_4N^+$	0.67 ± 0.02	($(n\text{-}Pr)_4NI$)	
	0.73 ± 0.02	($(n\text{-}Pr)_4NBr$)	

* The references in these cases refer to the source of the data for the appropriate salt.

TABLE 6.4 (Continued)

Electrolytes in 20 Percent Sucrose Solution at 25°C.

$$B_{K^+} = B_{Cl^-} = -0.0135 \pm 0.001$$

Ion	B - Coefficient	
Na^+	0.107 ± 0.002	
K^+	-0.0135 ± 0.001	
Cs^+	-0.055 ± 0.002	
Cl^-	-0.0135 ± 0.001	
Br^-	-0.053 ± 0.004	
I^-	-0.086 ± 0.003	(KI)
	-0.090 ± 0.004	(NaI)
	-0.089 ± 0.004	(CsI)

ions in each of the solvents studied. The data presented, for ions in aqueous solution, compare favourably with the available literature values.

The Effect of Temperature on the B-Coefficient[5]

An overall disruption of the structure of water would be expected as its temperature increased. The higher thermal energy would hinder the formation of clusters, and in fact, any ordering except possibly the immobilisation of water molecules at the surface of the ions. This could be enhanced, since, although the statistical average time spent by a given molecule in a state of immobilisation might be reduced, the concentration of single water molecules which could participate, would be increased.

Such an overall disruption would imply a consequent decrease in the disruptive contribution made by certain ions. Conversely, a less rapid decrease, of the solution viscosity with increasing temperature, might be expected, than of the solvent viscosity, if the presence of ions had already caused some disruption. Hence, those ions with the strongest structure breaking influence (e.g. I^-) have the largest positive temperature coefficients of their B values[5].

Correlations with Other Properties

Kaminsky[5] demonstrated graphically that the ionic B - coefficients exhibit a temperature dependence very similar to that of the apparent molal heat capacities (C_p^o) and the apparent molal volumes (ϕ^o) of the same ions. His interpretation of the observed dependence for the B - coefficients accorded with that proposed by Eigen and Wicke[25] for the other quantities.

A correlation may also be drawn between the sign of the B - coefficient of an ion and the temperature dependence of its electrical mobility[14]. Gurney[26] plotted values of the ratio, $(\lambda^o_{18}\eta_{18}) / (\lambda^o_0\eta_0)$ of the limiting Walden products at 18°C. and 0°C. respectively, of various ions, against their B - coefficients and limiting equivalent conductances respectively. In each case, apparently continuous linear relationships were observed for both the atomic (alkali metal and halide), and the molecular ions studied. It is important to note, for comparison with results obtained in this research, that the above plots incorporated no bromide or iodide ion values.

Nightingale[27] plotted ionic B - coefficients, at 25°C., against corresponding values of the hydrated ionic radius, calculated from Stokes' Law or the Stokes - Einstein equation[28], with an empirical correction proposed by Robinson and Stokes[29].

Simple linear plots were obtained for two groups of molecular ions, and a linear plot, discontinuous at $B_{ion} = 0$, for the combined alkali-metal and halide ions, including bromide and iodide. It was concluded from the diagram that the hydrated radius measured the region about an ion in which the solvent was more or less ordered than in the bulk water. The section of the discontinuous graph in the region of negative B-coefficients lay parallel to the B-coefficient axis, thus indicating an effective constancy of the hydrated radius for the ions concerned.

Gurney[30] also demonstrated the correlation between the B-coefficients of ions in aqueous solution and their partial molal entropies (on a scale relative to-5.5 for H^+). A linear relationship, indicating an increase in entropy for a decrease in the B-coefficient, was obtained for the combined alkali metal and halide ions including iodide and bromide. The graph was strikingly similar, in regard to the order of the various points, to that of the ionic Walden product ratio against the ionic limiting conductances. The presence, on a separate line, of several points for molecular ions, may be explained in terms of the difference in rotational entropy between these and the atomic ions[27].

In Figure 6.1, the ionic B-coefficient values determined in the present research, for electrolytes in aqueous solution at

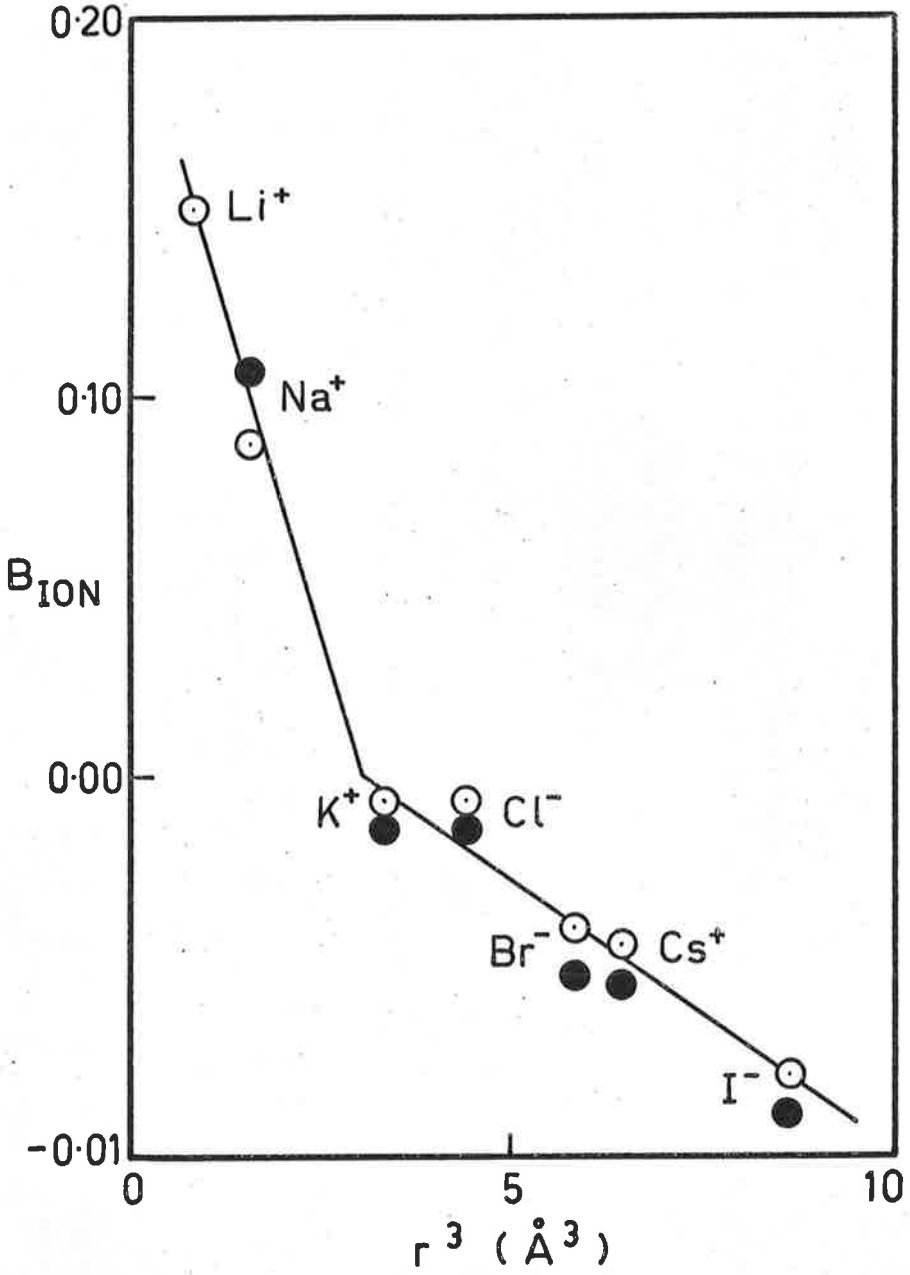

Figure 6.1. Ionic B - Coefficients at 25°C. plotted as a function of the Cube of the Ionic Radius.

⊙ Aqueous Solutions.

● Aqueous 20 Percent Sucrose Solutions.

TABLE 6.5

Correlation of Ionic B - Coefficients with Crystallographic Ionic Radii, and with Walden Product Data

Ion	Radius[a] (r) (Å)	B_{ion} (H_2O)	B_{ion}[c] (20% Sucrose)	r^3 $(Å)^3$	$\frac{(\lambda^o\eta)_s}{(\lambda^o\eta)_o}$ d, e
Na^+	1.17	0.088	0.107	1.60	1.181
K^+	1.49	- 0.0065	- 0.0135	3.31	1.194
Cs^+	1.86	- 0.044	- 0.055	6.43	1.167
Cl^-	1.64	- 0.0065	- 0.0135	4.41	1.201
Br^-	1.80	- 0.040	- 0.053	5.83	1.178
I^-	2.05	- 0.078	- 0.088	8.62	1.149
Li^+	0.94	0.1495[b]	-	0.83	-

a Gourary and Adrian[31], as quoted by Blandamer and Symonds[32].

b Kaminsky[5].

c B - coefficients of ions in 20% sucrose solution.

d Conductance data for all ions except Cs^+, from references 9 and 8. Conductance data for Cs^+ ion, from the present research and reference 33. The subscript, s, refers to 20% sucrose solution, and o to water, as solvent. The λ^o are ionic values.

e The values 0.8903 and 1.695 were used for the absolute viscosity of water and of 20% sucrose solution respectively, at 25°C.

25^{o}C., and the Li^{+} ion value determined by Kaminsky[5], are plotted as a function of the corresponding values of the crystal ionic radius, recently proposed by Gourary and Adrian[31]. The co-ordinates of the apparent discontinuity in the straight line to which the points conform, are $B_{ion} = 0$, and $r^{3} = 3$ cubic Angstrom units. The latter value corresponds to a crystal ionic radius of 1.44 Å, which is equal to half the smallest average distance of separation between the molecules in liquid water at 25^{o}C., as determined by Danford and Levy[34].

It appears likely that a similar graph could be drawn through the corresponding points shown for electrolytes in aqueous 20 percent sucrose solution at 25^{o}C., if another point in the positive B-coefficient range was available. That section, of the discontinuous line, lying in the negative B-coefficient range, would in this instance have a greater negative slope.

The observed decrease of the ionic B - values with increaseing crystal ionic radius, may be explained in terms of a decrease in the contribution to this coefficient due to the Einstein effect[35], and an accompanying increase in the disruptive effect of the ions on the structure of water, as this radius increases.

The contribution, due to the Einstein effect, to the B-coefficient of a solvated ion in solution may be expressed as,

$$B'_{ion} = a\,\bar{V}_{ion} \qquad 6.3$$

where a is constant, the value of which depends on the shape of the solvated ion, and $\bar{V}_{ion}$ is the molar volume of the ion including its electrostricted solvent. For species of spherical shape, a has the value of 2,5, and for those of other shapes, a higher value[35].

A decrease in the degree of electrostictive solvation with increasing ionic radius (see p.90 , Chapter 5) could thus result in a decrease in the Einstein effect contribution.

Disruption of the water structure, due to the presence of ions, may be invoked to explain the negative values which were obtained for the B - coefficients of ions whose crystal ionic radius lay beyond the suggested limiting value of 1.44 Å. In such terms, Kaminsky[5] was able to explain the positive temperature coefficients which he obtained, of the B - values of several of these ions (K^+, Cl^-, I^-) in aqueous solutions.

It appears therefore, that for an hypothetical ion, the crystal ionic radius of which corresponds to half the distance of closest approach of the molecules in pure water, there is an exact balance between the disruptive effects on the water structure and those ion - solvent interaction effects which tend to increase the viscosity, and that at greater radii the disruptive effects take precedence.

An increase in magnitude of the ionic B - coefficients, regardless of their sign, was brought about by the addition of sucrose molecules (20 weight percent) to aqueous solutions of the relevant electrolytes at 25°C. According to the results presented by Kaminsky[5], the same effect was produced, for the ions with negative B - coefficients, by a lowering of the temperature of these aqueous solutions. Thus the sucrose may be regarded as "lowering the structural temperature of the water". In Table 6.6 are presented for comparison, B - coefficient values tabulated by Kaminsky, for several ions in aqueous solution at 25°C. and at a lower temperature, and the B - coefficients obtained in the present research, for these ions in aqueous solution and in aqueous 20 percent sucrose solution, at 25°C..

It is therefore suggested that in aqueous solutions of sucrose and a 1 : 1 electrolyte, the hydration of the electrolyte ions or of the sucrose molecules, or of both, is enhanced due to the presence of the other, and the disruptive effects of the ions on the water structure are increased due to its enhancement by the sucrose molecules. This latter enhancement may be analogous to that produced by a decrease in the temperature of pure liquid water. An explanation of the observed changes in the B - coefficients of the ions studied, is possible in terms of the simultaneous operation of the above effects. It was not possible

TABLE 6.6

A Comparison of Ionic B - Coefficient Data

Ion	Kaminsky[5]		This Research		Das et.al.
	$B_{25^\circ C.}$	$B_{T<25^\circ C.}$	$B_{25^\circ C.}$	$B_{20\%\ Sucrose}$	$B_{20\%\ Dioxan}$
		$15^\circ C.$			$35^\circ C.$
Na^+	0.0863	0.0860	0.088	0.107	0.0923
K^+	- 0.0070	- 0.0200	- 0.0065	- 0.0135	0.0199
Cl^-	- 0.0070	- 0.0200	- 0.0065	- 0.0135	0.0199
		$18^\circ C.$			
I^-	- 0.0685	- 0.0880	- 0.078	- 0.088	

in terms of the current models of the structure of water, to establish a basis for the postulated enhancement of hydration effects in the mixed solutions. However, the analogy with the effect on the ionic B - coefficient values, of a decrease in the temperature of the appropriate aqueous solutions, is apparently still tenable for ions with positive B - coefficients. Kaminsky[5] found that the B - coefficient of the Li^+ ion was increased from 0.1495 at 25°C. to 0.1615 at 15°C.. Although for the same temperature change, the B - coefficient of the Na^+ ion was unaltered, the former case lends support to the overall parallelism between the effect on the value of ionic B - coefficients, of the addition of sucrose to aqueous alkali halide solutions at 25°C., and that of a decrease in the temperature of such solutions. That the effect of sucrose on the water structure is the same as that of a temperature decrease, however, does not necessarily follow.

Values, which are presented in Table 6.6, of the B - coefficient of the K^+, Cl^- and Na^+ ions respectively, in aqueous 20 percent dioxan at 35°C., were derived from the data of Das et.al. (see Table 6,8), on the basis of the assumption that the K^+ and Cl^- ion values were equal. Kaminsky[5] obtained the values -0.0070, +0.0049 and +0.0121, for the B - coefficient of the K^+ (and Cl^-) ion in aqueous solution at 25°, 35° and 42.5°C.

respectively. It appears that the B - coefficients of these ions are made more positive by the addition of dioxan to aqueous solutions of potassium chloride at 35°C., which behaviour is analagous to that produced by an increase in the temperature of these solutions. Such behaviour may be general for those alkali-halide ions which have negative B - coefficients at 25°C., but,on the basis of the Na^+ ion values,it appears that the analogy cannot be extended to those of these ions whose B - coefficients are positive at this temperature.

In Figure 6.2 the ratio of the limiting Walden products for aqueous 20 percent sucrose solutions and for aqueous solutions respectively, at 25°C., of the alkali metal and halide ions studied, are plotted against their aqueous solution B - coefficients. From the position of the point for the Na^+ ion,relative to the straight line to which the points for the other ions conform, it may be presumed that a discontinuous linear relationship also exists between these parameters. Since the ratio of the viscosity at 25°C. of aqueous 20 percent sucrose,to that of water at that temperature,is 1.904 (calculated on the basis of the N.B.S. revised value for the former), each of the values, presented in Table 6.5, of the ratio $(\lambda^o\eta)_s/(\lambda^o\eta)_o$, indicates a reduction of the limiting equivalent conductance of the ion concerned,in aqueous 20 percent sucrose,relative to its value for the corresponding aqueous solution. Apparently, if the discontinuous

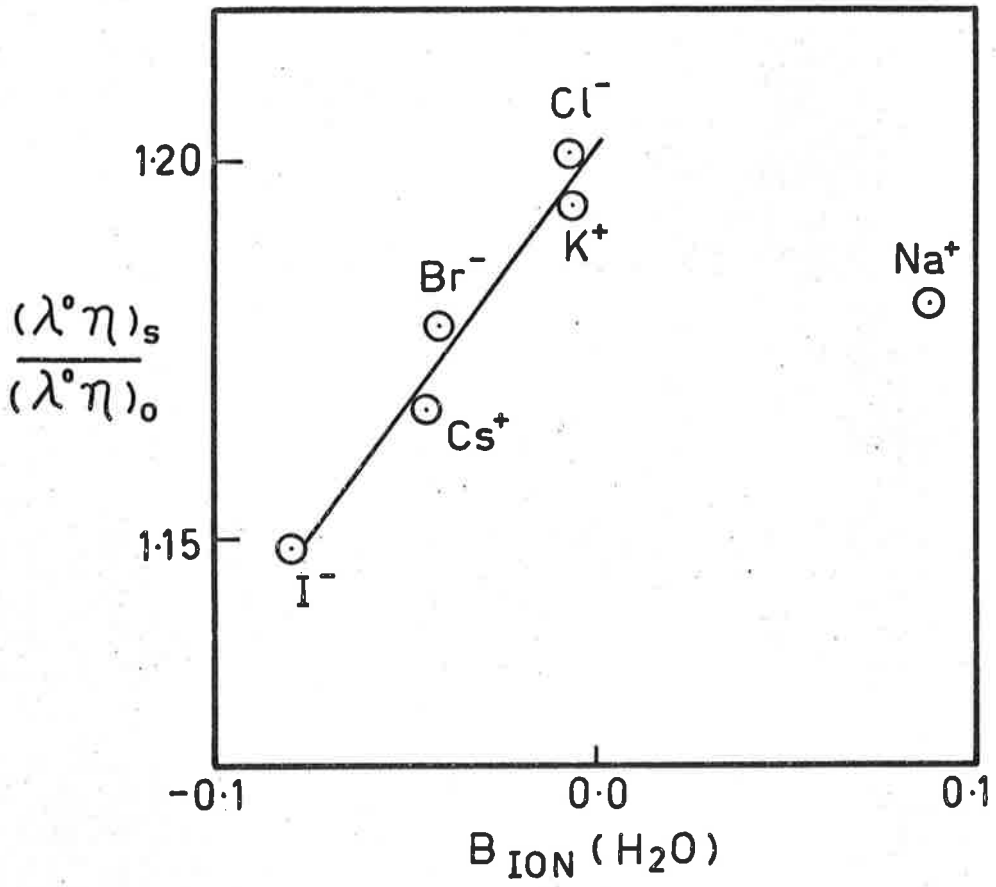

Figure 6.2. The Ratio of the Limiting Walden Products, for Aqueous 20 Percent Sucrose Solutions and Aqueous Solutions respectively, at 25°C., of Various Alkali Halide Ions, plotted against the Corresponding Ionic B - coefficients for the Aqueous Solutions.

linear relationship predicted from the figure, is correct, this reduction is least for those ions whose interactions with either solvent affect its viscosity least, (see Table 6.5). It is suggested that, in fact, the discontinuity occurs at the value $B_{ion} = 0$, which corresponds to the hypothetical situation in which an ion makes no nett contribution due to its interactions with the solvent, to the viscosity of electrolyte solutions in which it occurs. Earlier in this discussion it was proposed that, for aqueous solutions at 25°C., this situation occurs at the limiting value of the crystal ionic radius which corresponds to the smallest average distance between the molecules in liquid water at that temperature. It is perhaps surprising that the least reduction is not observed for those ions whose interactions with the solvent produce a greater reduction in the viscosity of aqueous 20 percent sucrose, than they do in that of water, at 25°C. (that is, whose B - coefficients are lower for the former than for the latter solvent).

Values (0.946 and 0.941) of the ratio, $(\lambda^{o}\eta)_{18^{o}C.}/(\lambda^{o}\eta)_{0^{o}C.}$, of the limiting Walden products, calculated from the relevant limiting equivalent conductance[8] and viscosity[12] data tabulated by Robinson and Stokes, for the iodide and bromide ions respectively, in aqueous solution, were plotted on the graph, presented by Gurney[26], of this ratio against the corresponding ionic

B - coefficients, tabulated[23] by this author, for aqueous solutions at 25°C. A more comprehensive graph was thus obtained which was, in form, an inverted mirror-image of Figure 6.2, except for the position of the Cs^+ ion point. If the exception can be disregarded, this observation may be invoked in support of the view that an analogy exists between the effects of the addition of sucrose and of a decrease in temperature, on the values of the B - coefficients (or limiting equivalent conductances) of ions in aqueous solution.

Recently, McCall and Douglass[36] have shown that a close correlation exists between the electrolyte concentration dependence of the relative self diffusion coefficient of water at 23°C., and the concentration dependence of the corresponding solution fluidity (the reciprocal of the relative viscosity). It therefore appears that both interionic and ion-solvent interactions may have similar, but inverse, effects on the self diffusion of water in, and the viscosity of, aqueous electrolyte solutions. Hence, interpretations, of the solution B - coefficients, in terms of particular ion-solvent interactions, are likely to apply also to the concentration dependence of the relative self diffusion coefficient of water.

The Extended Jones-Dole Equation

In connection with measurements of the relative viscosity of potassium bromide solutions, Jones and Talley[20] found it necessary to extend the Jones-Dole equation by adding a c^2 term, in order to fit their data over the concentration range from 0.001 M. to 2 M.. This term is intended to account for higher order interactions which may become appreciable at higher concentrations (above 0.2 M.). Thus,

$$\eta_r = 1 + A\sqrt{c} + Bc + Cc^2 \quad , \qquad 6.4$$

where the molarity has been represented by a lower case c, in this instance, simply to avoid confusion . The notation, for the coefficients, used in the relevant computer program (Appendix C), has been retained.

Kay et.al. recently reported[37] viscosity measurements at concentrations up to 0.2 M for the tetramethyl - , tetraethyl - , tetrapropyl - , and tetrabutyl - ammonium bromides and iodides in water, deuterium oxide, methyl alcohol, and acetonitrile, at various temperatures between 0° and 65°C. B - coefficients were determined by fitting the data to the Jones-Dole equation. These authors considered that the validity of this relationship could be established for each of the solvent systems investigated, at the relevant temperature, by obtaining a number of points over the above concentration range for at least one of the salts

containing the larger ions. It would then remain only to measure one or two points in each case, in order to obtain the corresponding B - coefficients for other salts under identical conditions.

However, they found it necessary to apply to the measured flow times for three of the salts studied in aqueous solutions, a correction, Δt, to compensate for the fact that values of the function $(\eta-\eta_0)/\eta_0$, based on the uncorrected flow times, did not extrapolate to zero at infinite dilution, for these systems. The magnitude of Δt was determined by measuring the viscosity of solutions so dilute ($C < 10^{-6}$ M) that their flow time would normally have been indistinguishable from that of the pure solvent. A maximum correction of 2 seconds was detected; the flow time of water at 25°C., being 500 sec. The existence of this significant correction was attributed to a surface-tension effect due to the presence of a trace of surface-active impurity in the samples of the salts in question, namely tetrabutylammonium iodide and tetrapropylammonium iodide and bromide.

It had been intended, in the present research, to extend the studies of the additivity of B-coefficients in aqueous solution at 25°C., to coefficients obtained for tetraalkylammonium halides, and, in fact, tetra-(n-propyl)-ammonium iodide and bromide had been selected as a suitable trial pair. Hence it was decided to measure the flow times of extremely dilute solutions of these salts, to

ascertain whether the effect observed by the above authors, namely the significant deviation of such times from the corresponding pure solvent value, was reproduced. No such effect was observed, at 25°C., for 10^{-6}M and 2 x 10^{-5}M solutions of the bromide, or an 8 x 10^{-5}M solution of the iodide, which were prepared from samples described in Chapter 3. Hence, it was considered worthwhile to make a complete series of measurements of the relative viscosities of each of these salts in aqueous solution at 25°C., at concentrations up to 0.2M. The data obtained are presented in Tables A.9 and A.8 respectively, of Appendix A, and represented graphically in the form of plots of $(\eta)_r - 1)/\sqrt{C}$ against $\sqrt{C}$, in Figures 6.3 and 6.4, in each of which the corresponding data of Kay et.al. are plotted for comparison. In each of these figures, also, the theoretical intercepts calculated from the Falkenhagen equation (equation 6.2), are indicated by a triangle. The limiting equivalent ionic conductance data, required for these calculations, were drawn from a tabulation by Robinson and Stokes[8]. The point indexed, 1, in Figure 6.4 was ignored in drawing the smoothed curve. Between the corresponding experimental relative viscosity value and that calculated from the least-squared equation, the discrepancy was such (0.0008) that little confidence could be had in the former (as confirmed by the application of Chauvenet's Criterion[38]). Accordingly, the least-squares analysis of the

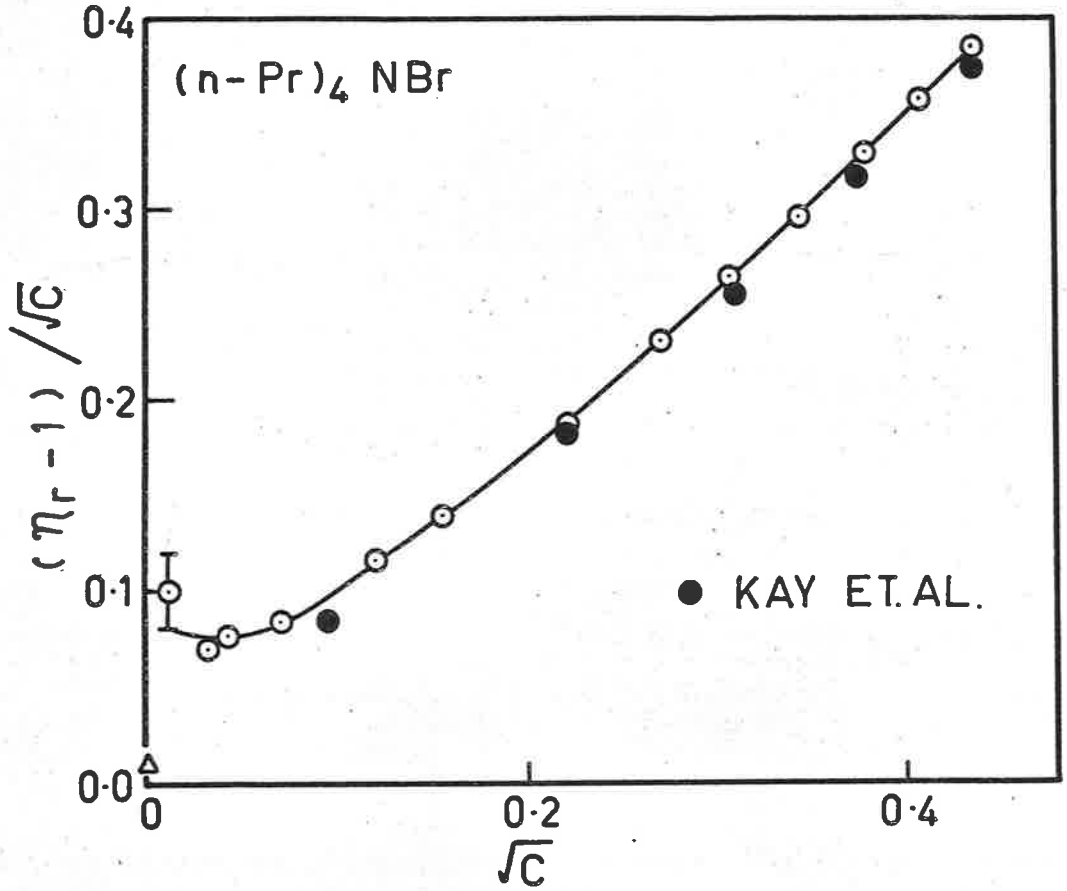

Figure 6.3. The Dependence of the Function $(\eta_r - 1)/\sqrt{C}$ on $\sqrt{C}$, for Aqueous Tetra (n-Propyl) Ammonium Bromide Solutions at 25°C. The Theoretical Intercept is indicated by a triangle.

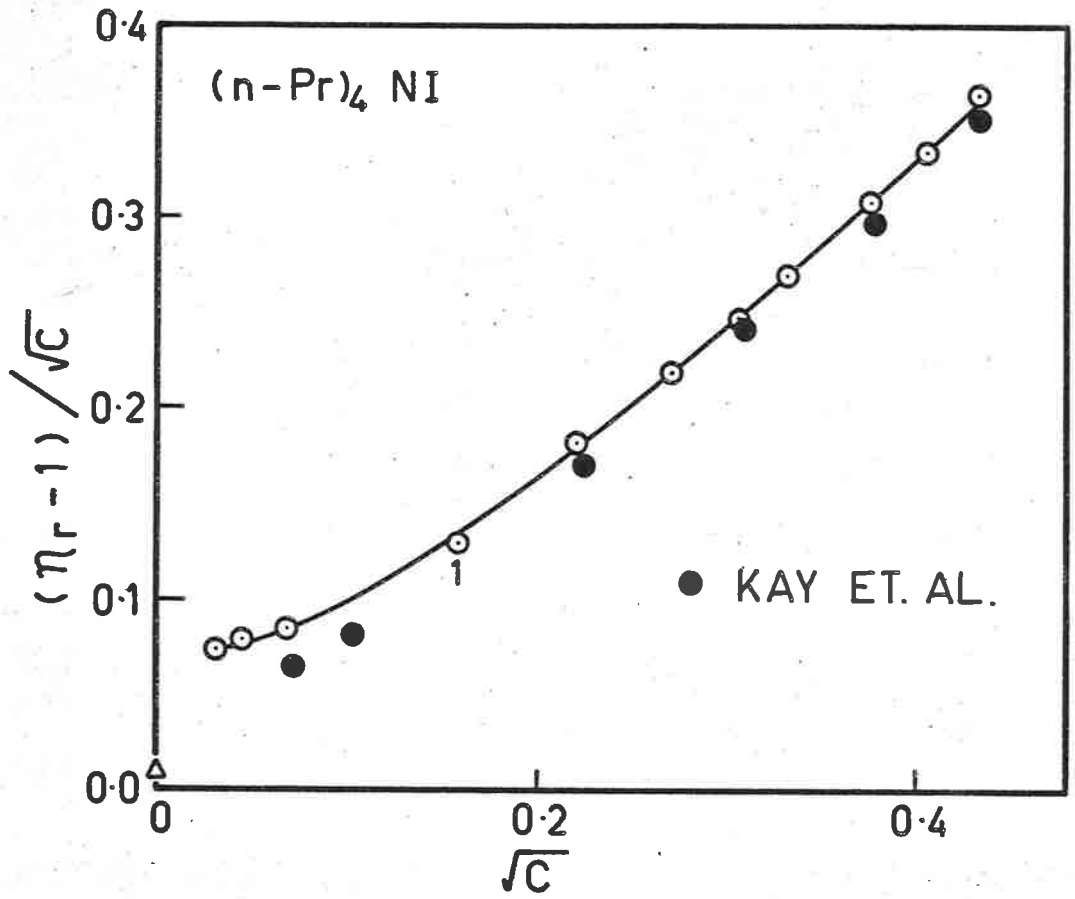

Figure 6.4. Dependence of the Function $(\eta)_r - 1)/\sqrt{C}$ on $\sqrt{C}$, for Aqueous Tetra (n-Propyl) Ammonium Iodide Solutions at 25°C. The Theoretical Intercept is indicated by a triangle.

tetra-(n-propyl)-ammonium iodide data was repeated, with the omission of this datum.

The relative viscosity data for both systems were found to conform to the Jones-Dole equation only in its extended form. Values of the coefficients A, B and C, of the latter, are presented in Table 6.1, with the theoretical values of A.

Evans and Kay[39] found that if their conductance data, for tetra-alkyl-ammonium halides in aqueous solution at 25°C., were processed in order to allow for ion association effects, the association constants determined were either negative, or smaller than the standard deviation, except in the cases of tetrapropyl-ammonium iodide at 25°C. and tetra-butylammonium iodide at 25°C. and 10°C., for which a definite but exceedingly small amount of association was indicated. Hence, no allowance for ion-association effects was considered necessary in the treatment of the tetra-(n-propyl)-ammonium iodide and bromide viscosity data obtained in the present research.

As shown in Table 6.3, the difference between the B - coefficients of these salts varied by more than the sum of the appropriate standard errors, from the difference between the B - coefficients of the corresponding potassium salts. Subtraction of the B - coefficient of the Br^- ion and I^- ion respectively from the appropriate tetra-(n-propyl)-ammonium salt coefficient yielded values of 0.73 and 0.67 for the B - coefficient of the

tetra-(n-propyl)-ammonium ion. The average, 0.70, of these values may be compared with the value 0.86 obtained by Kay et.al., who also obtained for the difference between the B - coefficients of tetrapropylammonium bromide and iodide in aqueous solution at 25°C., a value of 0.05, which compares favourably with that, 0.038, of the corresponding potassium salt difference.

However, the tetrapropylammonium salt viscosity data determined in the present research, exhibited a normal concentration dependence; that is, a plot of the relative viscosity against c, extrapolated in characteristic fashion to the value of unity at zero concentration. Thus it was unnecessary to correct the data, prior to its analysis in order to obtain B - coefficients. Had a correction been required, the fact may have been obscured that the data could be more satisfactorily fitted to the extension of the Jones-Dole equation, than to the equation itself. It is therefore considered that the values obtained of these coefficients, for tetrapropylammonium bromide and iodide, are more reliable than those obtained by Kay et.al.

No explanation can at present be offered, either for the apparent curvature exhibited at low concentrations by the plots shown in Figure 6.3 and 6.4, or for the fact that these plots do not appear to approach the theore tical intercept.

The Effect of Ion-Association

Davies and Malpass[4] have recently proposed a modification of the Jones-Dole equation,

$$\eta_r = 1 + A\sqrt{C} + BC \quad , \qquad 6.1$$

to account for the effect of ion-association or incomplete dissociation.

(1) For symmetrical electrolytes of degree of dissociation α, equation 6.1 may be written,

$$\eta_r = 1 + A\sqrt{C} + B_i \alpha C + B_{ip} (1 - \alpha)C \quad , \qquad 6.5$$

where B_i and B_{ip} are the B - coefficients for the dissociated solute, and for the ion pair respectively.

$\therefore$

$$\eta_r = 1 + A\sqrt{C} + \alpha B_i C + B_{ip} C - \alpha B_{ip} C \quad . \qquad 6.6$$

Hence

$$(\eta_r - 1 - A\sqrt{C})/C = \alpha (B_i - B_{ip}) + B_{ip} \quad . \qquad 6.7$$

Therefore, a plot of $(\eta_r - 1 - A\sqrt{C})/C$ against α should have a slope of $(B_i - B_{ip})$, and an intercept, at $\alpha = 0$, of B_{ip}. However, it is unnecessary to determine the slope, since the value of B_i may be found directly, as the intercept at $\alpha = 1$.

(2) For unsymmetrical electrolytes which dissociate in two stages,

e.g. $$M_2A \longrightarrow M^+ + MA^- \qquad 6.8$$

$$MA^- \rightleftharpoons M^+ + A^= \quad , \qquad 6.9$$

if α is the degree of dissociation of the ion pair, MA^- ,

$$\eta_r = 1 + A\sqrt{C} + B_{M^+}(1 + \alpha)C + B_{A^-}\alpha C + B_{MA^-}(1 - \alpha)C \quad . \qquad 6.10$$

$$\eta_r = 1 + A\sqrt{C} + B_i \alpha C + \left[B_{M^+} + B_{ip}\right](1 - \alpha)C \quad . \qquad 6.11$$

Hence, by analogy with equation 6.5, the intercept of the function $(\eta_r - 1 - A\sqrt{C})/C$, at $\alpha = 0$, would in this case yield the sum of the B - coefficients of the ion pair and the dissociated M^+ ion.

As expected, since the dielectric constant of aqueous 20 percent sucrose at 25°C. (73.6) is little different from that (78.30) of water at that temperature, no indication of incomplete dissociation was obtained from the results of the conductance studies[9] of alkali halides in aqueous 20 percent sucrose solution at 25°C. It was therefore unnecessary, in the treatment of the viscosity data obtained for such systems, to account for this effect.

Das et.al.[40] proposed a modified Jones-Dole equation,

$$\eta_r = 1 + A\sqrt{C} + BC^x \quad , \qquad 6.12$$

to which the relative viscosity data for many of the electrolytes which they studied at 35°C, in dioxan-water mixtures, were found to conform, within the experimental error. The value of x was always close to 1 (0.92 and 1.05 were its lowest and highest value respectively).

The dielectric constants of dioxan-water mixtures are considerably lower than that of water. For the 20 percent mixture, the dielectric constant at 35°C. has the value 57.73[41]. Nevertheless, from the conductance studies conducted by these authors, on sodium chloride and potassium chloride solutions in these mixtures, at 35°C., no evidence for ion-pair formation was obtained. However, their conductance study of solutions in dioxan-water mixtures at 35°C., of magnesium sulphate, which is a weak electrolyte in aqueous solution, did provide such evidence. Consequently, it was decided, in the present research, to apply the Davies-Malpass treatment to the corresponding viscosity data for the 20 percent mixture. For these data a value of the index, x, in equation 6.12, had been obtained[42], of 1.03.

The values of α, the degree of dissociation, were determined by successive approximations. Values of the activity coefficients, f, of the Mg^{++} and $SO_4^{=}$ ions, were calculated by means of the extended Debye-Hückel expression, and α obtained by solving the equation,

$$K = \frac{\alpha^2 C}{(1 - \alpha)} \cdot f^2 \qquad 6.13$$

where C is the molar concentration of magnesium sulphate, and K its dissociation constant, the value (4.24×10^{-3}) of which was obtained by Das et.al.[43] from the functional table compiled by

Fuoss[44]. The activity coefficient of the undissociated salt was assumed to have the value of unity.

Substitution of the value 57.73, of the dielectric constant, D, calculated from the equation of Akerlöf and Short, and the value 9.12 Å, of the distance of closest approach $\overset{o}{a}$, evaluated by Bjerrum's method[45] by Das et.al., in the extended Debye-Hückel expression,

$$\ln f = - Z_i^2 \left[\frac{\pi N e^6}{1{,}000(DkT)^3}\right]^{\frac{1}{2}} \sqrt{\Gamma} \cdot \frac{1}{1 + \kappa \overset{o}{a}} \quad , \qquad 6.14$$

$$\text{where} \quad \kappa = \left[\frac{4\pi N e^2}{1{,}000\ DkT}\right]^{\frac{1}{2}} \sqrt{\Gamma} \quad , \qquad 6.15$$

and e is the electronic charge, T the absolute temperature and Γ the ional strength, yields the numerical form,

$$\ln f = - 5.0166 \sqrt{\Gamma} \cdot \frac{1}{1 + 2.43276 \sqrt{\Gamma}} \qquad 6.16$$

In the first approximation, the value of Γ was computed on the basis of the assumption that α had the value of unity. Successive approximations were made until constant values of α were obtained.

From the relative viscosity data of Das et.al., a plot of $(\eta)_r - 1)/\sqrt{C}$ against $\sqrt{C}$ was constructed, which yielded, on extrapolation to $\sqrt{C} = 0$, a value of 0.0280 for A. On the basis

TABLE 6.7

Ion Association

Degree of Dissociation and Viscosity Functions for $MgSO_4$ in 20 Percent Dioxane-Water Solutions at 35°C., from the Data of Das. et.al.[42]

C	$\sqrt{C}$	f	α	η_r	$(\eta_r - 1)/\sqrt{C}$	$(\eta_r - 1 - A\sqrt{C})/C$ *
0.0025	0.0500	0.6094	0.844	1.0032	0.06400	0.68 ± 0.08
0.0050	0.0707	0.5368	0.789	1.0064	0.09051	
0.0075	0.0866	0.4950	0.754	1.0076	0.08776	0.69 ± 0.03
0.0100	0.1000	0.4663	0.728	1.0098	0.09800	0.70 ± 0.02
0.0250	0.1581	0.3824	0.643	1.0218	0.13788	0.702 ± 0.008
0.0500	0.2236	0.3291	0.576	1.0411	0.18380	0.710 ± 0.004
0.0750	0.2739	0.3024	0.536	1.0614	0.22420	0.716 ± 0.003
0.1000	0.3162	0.2855	0.507	1.0807	0.25519	0.719 ± 0.002

* Compiled from η_r values obtained from a smoothed curve of $(\eta_r - 1)/\sqrt{C}$ against $\sqrt{C}$.

A = 0.028 from this graph, by extrapolation.

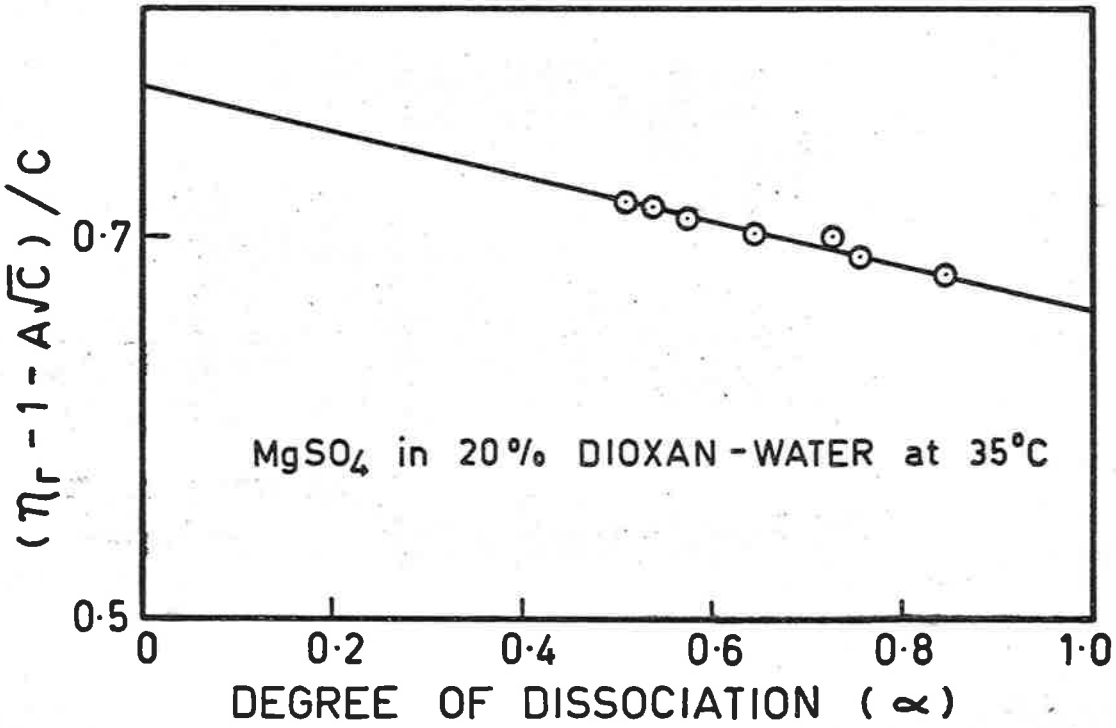

Figure 6.5. A Treatment of the Data of Das, Das and Patnaik according to the method suggested by Davies and Malpass.

of the relative viscosity values derived from this smoothed curve, the values of the function $(\eta_r - 1 - A\sqrt{C})/C$, which are presented in Table 6.7, were calculated. The linear plot obtained, of these values as a function of the degree of dissociation, α, is shown in Figure 6.5. Extrapolation of this plot to $\alpha = 0$, and $\alpha = 1$, yielded a value for B_{ip} of 0.77_9, and a value for B_i of 0.66_3. This latter value may be compared with that of 0.76 obtained by Das et.al.[42] for the B - coefficient of the modified Jones-Dole equation (equation 6.12). In this instance, the corresponding value of A was 0.0313. From their treatment of the data of Kaminsky[17] for the relative viscosity of aqueous solutions of magnesium sulphate at 25°C., Davies and Malpass[4] obtained values for B_{ip} and B_i of 0.576 and 0.702 respectively. The latter of these may be compared with Kaminsky's B - coefficient value of 0.5937, obtained by treatment of the same data according to the Jones-Dole equation (equation 6.1).

It should be emphasised that, within the small experimental error, several alternative treatments of the above relative viscosity data of Das et.al. are possible, namely the modified Jones-Dole treatment employed by these authors, that proposed by Davies and Malpass, as outlined above, or that according to the simple Jones-Dole equation. Each of these methods may be effective in fitting the data, but yields a different value for the B - coefficient of the dissociated electrolyte. A logical

basis for the employment of one of the modified forms of the Jones-Dole equation, is provided in the indication, from the conductance measurements[43], that the dissociation of magnesium sulphate, in 20 percent dioxan-water mixture at 35°C., is incomplete. Of these modifications, the Davies-Malpass treatment should be the more suitable, since it was formulated specifically to account for the effect of ion-association.

In Table 6.8 a summary is presented, of the B - coefficient data determined by Das et.al. for various electrolytes in dioxan-water mixtures at 35°C. Where these had not been obtained by fitting the corresponding relative viscosity data to the simple Jones-Dole equation, the modified form proposed by these authors had been employed. The additivity of the coefficients presented, is indicated by the equality of the values, included in this table, of the differences, $B_{MgSO_4} - B_{K_2SO_4}$, and $B_{MgCl_2} - 2B_{KCl}$, for these electrolytes in 10 and 20 percent dioxan-water mixtures respectively. This equality is noteworthy. The electrolytes concerned are dissociated to different extents. The values of the ion-pair dissociation constant, K, on the molar concentration scale, are 4.24×10^{-3} for magnesium sulphate[43], 4.96×10^{-2} for magnesium chloride[50], and 9.44×10^{-2} for potassium sulphate[50], in 20 percent dioxan-water mixture at 35°C.. Potassium chloride[47] is apparently

TABLE 6.8

Summary of B – Coefficient Data for Electrolytes in Dioxan–Water Mixtures at 35° C. (Das et.al.)

% Dioxan	10	20	30
B_{NaCl} [46]	0.091	0.1122	0.1662
B_{KCl} [47]	0.020	0.0398	0.0525
B_{MgCl_2} [48]	0.43	0.54	0.84
B_{BaCl_2} [49]	0.230	0.405	0.648
B_{BaBr_2} [49]	0.284	0.440	0.675
$B_{K_2SO_4}$ [48]	0.28	0.30	0.38
B_{MgSO_4} [42]	0.69	0.76	
$B_{MgSO_4} - B_{K_2SO_4}$	0.41	0.46	
$B_{MgCl_2} - 2B_{KCl}$	0.39	0.46	

completely dissociated in this solvent at this temperature. Thus, it is perhaps surprising, when it is considered that each of the coefficients involved in the above differences is essentially a weighted sum of contributions due to the dissociated ions, and the corresponding ion-pair, respectively, that the equality of these differences was observed. However, analogous behaviour was observed, and invoked as evidence of the additivity of the individual ionic contributions to the B - coefficients of the electrolytes concerned, by Kaminsky[5] in his aqueous solution study. Insufficient information is available to allow the calculation, for potassium sulphate and for magnesium chloride in dioxan-water mixtures at 35°C., of the coefficients, B_i, in order to test the additivity of such coefficients separately. The analogous case for aqueous solutions at 25°C. is worthy of consideration in this regard also. It was found for these solutions, that the values of the differences, $B_{MgCl_2} - 2B_{KCl}$, and $B_{MgSO_4} - B_{K_2SO_4}$, were identical (0.399 and 0.400 respectively) when calculated on the basis of the B - coefficients determined by Kaminsky[17], but failed to agree (0.412 and 0.478 respectively) when calculated on the basis of coefficients, B_i, determined by Davies and Malpass[4] from the same data. These authors made allowance for the incomplete dissociation of magnesium sulphate and potassium sulphate, but magnesium chloride and potassium

chloride were regarded as completely dissociated in aqueous solution at 25°C.. (Note that allowance was made in Davies and Malpass' treatment, for the effect of ionic strength on the A - coefficient, the limiting value for each electrolyte being calculated from equation 6.2. Thus, for the completely dissociated electrolytes also, the B - coefficients determined by these authors differed from those determined by Kaminsky. The respective values of the difference $B_{MgCl_2} - 2B_{KCl}$ also differed.)

In their discussion of the B - coefficient data presented, Das et.al. concerned themselves with the effect of change of the percentage composition of the mixed solvent on such differences between the coefficients of electrolytes with a common anion. Thus Das[46], for example, presented the following table, and on the basis of the disagreement between the value of the difference, $B_{NaCl} - B_{KCl}$, obtained at the solvent composition of 30 percent dioxan, and that obtained at the other two solvent compositions, concluded that, in the former case,a "departure from the additive nature of B" had occurred. This conclusion is invalid. It is not in the constancy, from medium to medium, of the difference between the B - coefficients of pairs of electrolytes with a common ion, that additivity of the individual ionic contributions to electrolyte B - coefficients is reflected. It is in the equality, for

a given medium, of the appropriate differences between the B - coefficients of corresponding pairs of electrolytes with a common ion which varies from pair to pair (e.g. $B_{MgSO_4} - B_{K_2SO_4}$ and $B_{MgCl_2} - 2B_{KCl}$).

TABLE 6.9

B - Coefficient Differences Presented by Das[46]

Solvent Composition (Percent Dioxan)	$B_{NaCl} - B_{KCl}$ ($\Delta B \times 10^2$)
10	7.1
20	7.24
30	11.37

As Das explained, constancy from medium to medium, of the differences between the B - coefficients of pairs of electrolytes with a common ion, can be expected only when the nett effect, of the changes of medium, on the values for both electrolytes considered in forming such differences, is the same. Hence it is unlikely that such constancy should be a general rule.

However, with respect to the results of the present research, an approximate constancy of this nature was in fact observed. (See Table 6.3). For each of the three alkali metals of which halide salts were studied, the differences between the B - coefficients of their chloride and iodide, in aqueous solution at

25°C., and in aqueous 20 percent sucrose solution at 25°C., respectively, varied by little more than the sum of the probable errors in each, although on the average the differences for the 3-component systems were slightly higher (by 0.005).

Das[46] noted such an approximate equality between the differences quoted in Table 6.9, for 10 and 20 percent dioxan-water mixtures respectively, at 35°C.. That the equality did not extend to the value for the 30 percent mixture is not surprising.

General additivity of the individual ionic contributions to the B - coefficients might, however, be expected, regardless of both the solvent and temperature. In the present research, such additivity was verified experimentally for several alkali halides in aqueous 20 percent sucrose at 25°C., and confirmed for these salts in the corresponding aqueous solutions. From the data of Das. et.al., it was also verified (see before) for several electrolytes in 10 and 20 percent dioxan-water mixtures at 35°C.

For each of the salts studied in dioxan-water mixtures by Das et.al., an increase in the B - coefficient was observed with increasing dioxan content of the solvent. The increase was considered to result from changes in the constitution of the solvation spheres of the ions concerned[42]. This would be determined by the character of the ions, that is, their size and charge,

and by the differences in nature between, and relative proportions in the mixture of, the two solvent components. The effect of added sucrose on the B - coefficient of electrolytes in aqueous solution, however, cannot be interpreted in such terms, since, on the basis of the evidence of the conductance study[9] of aqueous 20 percent sucrose solutions of electrolytes, it can be concluded that sucrose molecules do not form a hydrodynamic entity with the electrolyte ions.

Whereas the presence of dioxan appeared to increase the B - coefficient relative to that for the corresponding aqueous solution, the effect of the presence of sucrose, like that of an increase in temperature, was, as previously discussed, an increase in the modulus of the coefficient. Steel, Stokes and Stokes[9] suggested, on the basis of the value of the limiting apparent molar volume of sucrose in aqueous solution at 25°C., that approximately 8 water molecules could be considered as immobilised at the surface of the sucrose molecule. This figure was consistent with the known presence of 8 free hydroxyl groups in the molecule. In relation to the ion-solvent interactions occurring in electrolyte solutions in aqueous 20 percent sucrose at the above temperature, this hydration of the sucrose molecules is likely to be an important consideration. It could, for instance, play a major role in the production of the postulated (p. 112) overall enhancement in this solvent, of the water structure.

Interactions between the electrolyte ions and sucrose molecules might be considered to occur indirectly, through solvated water molecules common to both. The probability of such interactions would be higher for those ions known to be strongly hydrated in the corresponding aqueous solutions. An explanation, alternative or complementary to that proposed on p. 112, is thus afforded, of the increase in the positive B - coefficients of such ions in aqueous solution, at 25°C., due to the presence therein of sucrose molecules.

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PART II

THE PARTIAL SPECIFIC VOLUME OF SODIUM DEOXYRIBONUCLEATE (D.N.A.) IN AQUEOUS SOLUTION AT 25°C.

INTRODUCTION

To quote Hearst (1962), "The partial specific volume of the salts of D.N.A. has long been in question. Conventional methods of measuring specific volumes have not been accurate because of difficulties in measuring either D.N.A. weight concentrations or the small solution density changes caused by the presence of the D.N.A."[1].

It was the purpose of this research to obtain a meaningful value of the partial specific volume of sodium deoxyribouncleate at high dilution in aqueous solution at 25°C. Hence it was necessary to develop a reliable method for weight analysis of D.N.A. solutions, and to adopt a high precision method of density measurement which would be suitable for viscous solutions, and the mechanics of which would be unlikely, of itself, to bring about any structural changes in the D.N.A. The Magnetic float method was adopted, which had been previously used by MacInnes et.al.[2] and by Charlwood[3] for the determination of the partial specific volume of proteins.

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CHAPTER 1

THE NUCLEIC ACIDS: SOME ASPECTS OF THE BEHAVIOUR OF D.N.A. IN SOLUTION

THE NUCLEIC ACIDS: SOME ASPECTS OF THE BEHAVIOUR OF D.N.A. IN SOLUTION

The Nucleic Acids

The nucleic acids are copolymers of nucleotides, which consist of a purine or pyrimidine base, linked to a sugar phosphate. Degradative studies have suggested the existence of two distinct types of nucleic acids. On hydrolysis, one type yielded the purines adenine and guanine, the pyrimidines cytosine and uracil, and a pentose sugar. The other yielded adenine, guanine, cytosine and thymine (5 - methyl uracil), and a deoxypentose sugar. The two types are referred to as pentose - and deoxypentose - nucleic acids respectively[1].

Of the latter class, the particular species first isolated from thymus gland was shown to contain the sugar deoxyribose, and became known as deoxyribo-nucleic acid. It is commonly obtained and studied as the sodium salt.

The Watson and Crick[2] structure, proposed in 1953, for deoxypentose nucleic acids, consists of two polynucleotide chains, which run in opposite directions, are coiled around each other to form a double helix, and are bound to each other by specific hydrogen bonds between the purines and pyrimidines.

Denaturation

Denaturation is the decomposition process whereby such bonds are broken, usually without change in the molecular weight[3].

Native or double-helical D.N.A. is believed to exist only above a certain "critical" concentration in aqueous solution. Above this point the concentration of counter ions is sufficient to preclude denaturation. At lower D.N.A. concentrations, however, the dissociation of these counter ions occurs, leaving free phosphate groups. Denaturation follows, resulting in a more flexible structure[4].

The Partial Specific Volume: Its Importance, and a Correlation with other Solution Properties of D.N.A.

Because it is considered that they play a fundamental role in the control of the metabolism, reproduction, and growth of living systems[1], the nucleic acids have been the subject of much research.

Molecular weights calculated from sedimentation equilibrium and sedimentation velocity measurements[5] on D.N.A. solutions, in the ultracentrifuge, depend upon an independent determination of the partial specific volume.

The absorption of ultra-violet radiation at 259 mμ., by solutions of D.N.A., is very sensitive to changes in (chemical) structure. The process of dilution denaturation is accompanied

by a large increase in the optical density of the D.N.A. solution, at this wavelength[6].

The structural changes involved are also reflected in a decrease of the solution viscosity[7], and of the transforming activity[7] for virus D.N.A's, on thermal denaturation. This fall in viscosity is not accompanied by a change in molecular weight. Changes such as the above, in the properties of D.N.A. solutions, often exhibit hysteresis effects.

It is therefore conceivable that, on dilution, a change in the structural properties of D.N.A. in solution, might result, which would be reflected in a change in its partial specific volume, and that this change might only be partially reversible. Therefore a discontinuity might be expected in the concentration dependence of the density of aqueous D.N.A. solutions. A preliminary study[8] indicated that such a discontinuity did, in fact, occur.

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CHAPTER 2

THE EXPERIMENTAL TECHNIQUES AND THEIR THEORETICAL BASES

THE EXPERIMENTAL TECHNIQUES AND THEIR THEORETICAL BASES

Summary

From the basic definition of the partial specific volume, its relationship to the apparent specific volume may be established. Thus it can be seen that the determination of partial specific volume requires precise measurement of solution densities.

One of the most accurate techniques available for this purpose is the Magnetic Float Method, which is discussed in detail. Attention is concentrated upon the technical details peculiar to this research.

The laws which are fundamental to Absorption Spectroscopy are outlined, and discussed with particular reference to spectrophotometer design. A description of the instrument used is appended.

Partial Specific Volume

The partial specific volume, $\bar{v}_i$, of a component, i, in a solution containing g_i grams of that component, may be defined by,

$$\bar{v}_i = \left(\frac{\partial V}{\partial g_i}\right)_{T,P,g_j} \qquad (j \neq i) \qquad 2.1$$

where V is the volume of the solution and the g_j are the weights of the other components present.

For a 2-component system, where the subscripts 1 and o denote solute and solvent respectively, the apparent specific volume of the former may be defined by,

$$\phi_1 = \frac{V - V_o}{g_1} \quad , \qquad 2.2$$

where V_o is the volume of pure solvent used in making a solution of volume, V, containing g_1 grams of component 1.

Differentiation of equation 2.2 with respect to g_1, yields, by analogy with equation 3.8, p.65,

$$\bar{v}_1 = \left(\frac{\partial V}{\partial g_1}\right)_{g_o} = \phi_1 + g_1 \left(\frac{\partial \phi_1}{\partial g_1}\right) \qquad 2.3$$

The weight fractions, W, of the two components o, and 1, are given by,

$$W_o = \frac{g_o}{g_1 + g_o} \qquad 2.4$$

and $$W_1 = \frac{g_1}{g_1 + g_o} \quad , \text{ respectively.} \qquad 2.5$$

And $$W_o + W_1 = 1 \qquad 2.6$$

From equation 2.2, $$\phi_1 = \frac{V - V_o}{g_1} \quad , \qquad 2.2$$

$$\phi_1 = \frac{V/(g_1 + g_o) - V_o/(g_1 + g_o)}{g_1/(g_1 + g_o)} \qquad 2.7$$

Hence, $$\phi_1 = \frac{1/d - W_o/d_o}{W_1} \quad , \qquad 2.8$$

where d is the density of the solution, and d_o is the density of the pure solvent.

$\therefore$ $$\phi_1 = \frac{1/d - (1 - W_1)/d_o}{W_1} \qquad 2.9$$

$$= \frac{1}{d_o}\left[\frac{d_o/d - (1 - W_1)}{W_1}\right]$$

$$\phi_1 = \frac{1}{d_o}\left[1 - \left\{\frac{(d - d_o)}{dW_1}\right\}\right] \qquad 2.10$$

Hence ϕ_1 may be found from the slope of a graph of $(d - d_o)/d$, which is very sensitive to errors in the density, against the weight fraction, W_1.

The Magnetic Float Method

The density measurements were made by the Magnetic Float method originated by Lamb and Lee[1].

Apparatus

The apparatus, shown in Figure 2.1, was essentially similar to that described by MacInnes et. al.[2-4]. A glass float, G, in the shape of an inverted flask, and containing in its stem a permanent magnet, M, was so weighted with lead shot, L, that it just failed to sink in water at 25°C.. In the density determinations, small platinum weights were placed in a depression on top of the float until it sank slowly. It was then caused to rise by passing small currents through the solenoid, C. The relative speed of rise of the float was determined by observing the motion of its tip, B.

However the apparatus differed from that of MacInnes et. al., particularly in its mounting. The float was contained in a thick-walled glass vessel of 350 ml. capacity, fitted with a triple-necked top by a ground glass joint lightly smeared with Apeizon grease. The whole apparatus was mounted in a brass frame, F, by means of two perspex platforms, R, and a perspex jaw which was screwed to the upper platform, and could be tightened by two further brass screws. This frame was suspended in a glass-fronted water-bath regulated at 25.000 $\pm$ 0.002°C., so

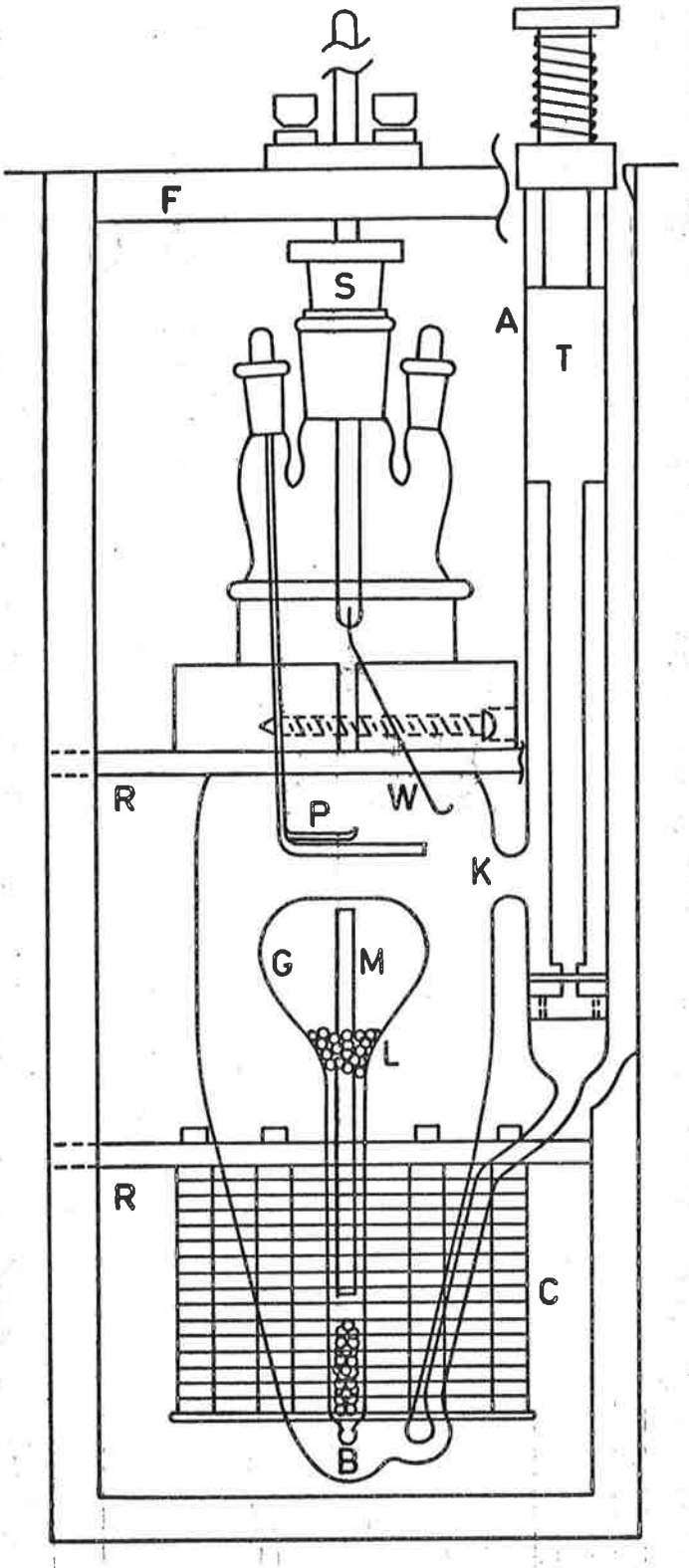

Figure 2.1. Magnetic Float Apparatus.
(Half Actual Size)

that the water level lay just above the bottom of the stopper, S.

The solenoid, C, consisted of 50 turns of 26 gauge enamelled copper wire, lathe-wound,on a former of perspex rods, to have a diameter of approximately 3".

Platinum weights were made from 0.005" diameter wire, and weighed on a Mettler microbalance. They were cleaned by washing with twice distilled water, and flaming in a microburner. Immediately before use they were reweighed, and the reading corrected to vacuum. Before passing a weight through the liquid surface,it was found necessary to flame it again, or it would be held there by surface tension. When weights were removed from the float,they were placed on the platform, P, which lay below the liquid surface. This platform rested on a glass horse-shoe which limited the rise of the float.

The weights were manipulated by means of a hooked platinum wire, W, of heavier gauge, sealed into a glass rod which passed through the polypropylene stopper, S. The flexibility of the stopper allowed adjustment of the position of the rod,so that the wire could be projected to reach the platform,or withdrawn,as desired. Prior to the addition of a new weight, this wire was also washed and flamed.

Stirring was effected by means of a spring-loaded Teflon plunger, T, incorporating at its extremity a simple valve, and carefully machined to fit the side arm, A. A gentle circulating-pump action was achieved,which was demonstrated by operating the plunger after placing a few crystals of potassium permanganate in the bottom of the float chamber filled with water, and also after lowering the water level beneath that of the connecting tube, K.

The passage of the tip of the float between two lines on the reticule* of a telescope, was timed with a Heuer stopwatch. The measured times ranged between 8 and 300 seconds. It was necessary to fit an auxiliary lens to the telescope, which was mounted reproducibly on a vertical rod fixed to the bath. On this same rod was mounted the projector lamp used to illuminate the tip.

Another apparatus was constructed,with an externally-fitting ground-glass joint, and thus a larger working volume. A decrease in the taper of the float vessel and an increase in the average radius of its cyclindrical portion,were also made. However this apparatus has yet to be calibrated.

*Ruled by S.O.L.A. (Scientific and Optical Laboratories of Australia) Ltd., Melbourne.

Electrical Circuit

The desired current through the solenoid could be set using a variable resistance housed with a milliammeter. A 2 volt lead-acid accumulator was the D.C. source. Following the measurement of a rise-time, this current could be accurately measured as the voltage drop across a series standard resistance of 10 ohm. Switching to another position caused a current of approximately 100 m.a. to pass in the opposite direction through the coil, thus returning the float to the bottom of the vessel. The current was then switched through a shunt of similar resistance, and a new value selected. Meanwhile the float adopted its equilibrium position on the bottom of the vessel. The selected current was then switched through the coil, and a further determination made.

Derived Equations

For a weighted float of volume, V, at equilibrium in a solution of density d, the weight of the liquid displaced by the float and by the platinum weights would be equal to the weight of the float and the platinum less the lifting effect of the current, i. If W and w are the weights of the float and the platinum load of density, ρ, respectively, and f is the lifting effect of unit current, then,

$$d\left(V + \frac{w}{\rho}\right) = W + w - fi \qquad 2.11$$

Hence $$d = (W + w\,(1 - d/\rho\,) - fi)/V \quad , \qquad 2.12$$

and the relative density is given by,

$$\frac{d}{d_o} = \frac{W + w\,(1 - d/\rho\,) - fi}{W + w_o(1 - d_o/\rho) - fi} \quad , \qquad 2.13$$

where the subscript, o, denotes pure solvent.

$$\therefore \quad d = d_o \left[1 + \frac{(w - w_o)(1 - d_o/\rho\,) - f\,(i - i_o)}{W + w_o + (w - w_o)d_o/\rho \; - fi_o} \right] \qquad 2.14$$

The value, 21.43 gm./cc., of the density of platinum, determined by MacInnes et. al.[2], was used.

Calibration of the Float

The effect of a current through the solenoid was to raise the float from the bottom of the vessel, where it always adopted the same rest position. Throughout its rise, the float was oriented at the centre of the uniform field of the solenoid. Since a net force acted, the rise was necessarily accelerated, and it was found that a linear extrapolation of the plots of reciprocal rise-time against current, as adopted by MacInnes et. al.[2], was unsuitable. Contrary to expectation, the motion of the float did not prove erratic for the longer rise times, and hence a reliable extrapolation could be performed, to the limiting current at which the float would neither rise nor sink in the liquid. $(1/t = 0)$. A theoretical discussion of this extrapolation may be found on pp.169-173.

In order to calculate densities from equation 2.14, it was necessary to obtain a value for f, the lifting effect of unit current through the solenoid. This required the measurement of limiting currents with different weights on the float, in the same liquid.

Since the float was compressible, it was necessary to correct all limiting currents to a common pressure, which was chosen for convenience as 760 mm. A pressure correction factor was determined by measuring limiting currents at different atmospheric pressures, with the same weight on the float, and pure water in the vessel. Determinations, prior to each of the major series of runs, yielded a value of 2.0 ma./mm., which was also obtained in a previous study[5].

The values obtained for the factor, f, after correction from weight in vacuum to weight in water, namely 6.44×10^{-2} mg./ma., prior to the mannitol run, and 6.63×10^{-2} mg./ma. prior to the D.N.A. addition run, were comparable with a former value of 6.9×10^{-2}[5].

A complete summary of the data from which the necessary factors were determined, is provided in Table 3.1.

Density Determinations

In all the density determinations, the solutions were prepared within the vessel. Before each run, approximately 275 ml. of

twice-distilled water was accurately weighed into the vessel from a long-stemmed weight-burette. After the apparatus had been clamped in a reproducible position in the water-bath, an equilibration period of half an hour was allowed, before determining the reference limiting current (i_o), with the weight, w_o, on the float. This determination was usually repeated several times. The suction applied, in filling the burette, degassed the solvent. This was essential, since any bubbles formed during equilibration, would adhere persistently to the float and produce spurious results.

D.N.A. Addition Run

From a smaller weight-burette, 5-10 ml. amounts of D.N.A. stock solution, similarly degassed, were then weighed into the vessel as required, and the solutions mixed by gentle movement of the Teflon plunger. After each density determination, a 5 ml. sample of solution was removed from the float chamber, with a siliconed A-grade pipette. The samples were refrigerated in 50 ml. Quickfit flasks sealed with Parafilm, and were later studied spectrophotometrically.

In the mannitol run, the stock solution was added similarly. Its concentration was limited by the relatively low solubility of mannitol.

D.N.A. Dilution Run

Two 50 ml. amounts of water were first removed from the float chamber. A calculated quantity of highly concentrated D.N.A. stock was added from a large weight-burette, and the solution mixed thoroughly. Its density was then determined. A 25 ml. sample of this solution was set aside, as above, for spectrophotometric measurement. 50 ml. of vacuum-degassed water was then added to the remaining solution. Successive measurement, sampling, and dilution was continued until a sufficiently low concentration was reached. Calibrated 25 ml. and 50 ml. siliconed pipettes were used.

Cleaning

After each run, the apparatus was removed from its frame and the chamber-top removed. Petroleum ether on cotton wool was used to remove the grease from the ground-glass joint. With the rod supporting the platform, P, undetached, the top was then washed with distilled water. After the Teflon plunger had been removed, the float chamber was emptied, and the washing of the float conducted therein.

Following this, and preceding each run, the float was immersed in chromic acid in the chamber for one day, and for an equal time in distilled water. The top, and attached platform, were also cleaned with chromic acid. Meanwhile, the Teflon

plunger and the polypropylene stopper, with the glass-mounted platinum wire undetached, were successively soaked in 2N sodium hydroxide, 2N hydrochloric acid, and distilled water. Finally all the components were repeatedly rinsed with distilled water.

As the float was withdrawn from its chamber, contact with extra-hard filter paper removed any droplets of water adhering to its surface. Stainless steel forceps, the tips of which were cushioned with clear rubber, were used to transfer it to a desiccator containing silica-gel. The chamber was steam cleaned, and, with the other components, dried in air for several days. At no stage was the chamber removed from its perspex collar.

Optical Density

For a parallel beam of monochromatic light passing through a homogeneous medium of thickness, L, in which an absorbing species is present in molar concentration, C, the intensity of the transmitted light (I) and that of the incident light (I_o) are in the ratio,

$$\frac{I}{I_o} = -kCL \quad , \qquad 2.15$$

where k is a constant.

This relationship, which is the basis for most quantitative studies of light absorption by solutions, is commonly known as Beer's law. Actually it is a combination of a law concerning

the thickness of the sample, propounded by Bougner (1729) and later by Lambert, and one concerning the concentration, put forward by Beer (1852)[6]. The logarithmic form,

$$D = \log_{10}(I_o/I) = \epsilon CL \qquad 2.16$$

is usually employed, where D is known as the optical density (O.D.), extinction, or absorbance, and ϵ, as the molar extinction coefficient.

There is good theoretical ground for supposing that the Beer-Lambert law should hold rigorously for monochromatic light and for sufficiently narrow slits[6]. However, in practice, a single wavelength is unattainable. If a light source has a continuous spectrum, and a monochromator is used to isolate one waveband, the wavelength range included depends on the width of the slits, which must be at least wide enough to give adequate intensity for measurement. Because absorption bands in the ultraviolet and visible, especially of species in solution, are generally broad compared with the normal slit ranges[6], however, the optical densities obtained should need no correction.

The Spectrophotometer

The optical densities were measured in a Unicam. S.P.500 spectrophotometer[7]. In this instrument, the incident and emergent beams pass through the same slit. Optical density and percentage-transmission readings may be obtained directly from the scale of a potentiometer incorporated into the detector circuit. Choice of two mounted barrier-layer photocells gives the instrument a wavelength range from 200 to 1,000 m.μ.. Both a hot-cathode hydrogen tube and a tungsten filament lamp are mounted, and can be switched on as required. Since stability of the source emission during each measurement is essential, both lamps are run from circuits giving stabilized currents.

The solutions were contained in precision silica cells, which could be reproducibly mounted in the instrument. The appropriate reference solvent was always contained in an identical cell.

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CHAPTER 3

EXPERIMENTAL

EXPERIMENTAL

I. MATERIALS

Sodium Deoxyribonucleate (D.N.A.)

The D.N.A. was isolated from calf thymus by Ellerton and Reinfelds[1], using the method of Kay, Simmons and Dounce[2] with the following modifications:

(a) Homogenisation was carried out for 1 minute.

(b) Centrifugation was carried out at 10,000 r.p.m. for 10 minutes using a M.S.E. refrigerated centrifuge, type R.H.S.

(c) The sample was redissolved in 0.01 molar sodium chloride instead of pure water, in order to reduce the possibility of denaturation.

The D.N.A. was stored over phosphorus pentoxide in an evacuated desiccator.

Mannitol

B.D.H. Microanalytical mannitol was dried in vacuum at 30°C. prior to use.

A value of 182.17 for the molecular weight[3] was used, and one of 1.489 gm./cc. for the solid density[3].

Preparation of Solutions

All solutions were prepared with twice-distilled water of average specific conductivity 1.3×10^{-6} ohms $cm.^{-1}$. Immediately prior to use, the water was vacuum-degassed.

The D.N.A. stock solutions were prepared, by weight, to have concentrations above the estimated critical value, and the D.N.A. was dissolved by gentle manual swirling. Centrifugation of the stock solutions was conducted at 4,500 r.p.m. in a Beckmann Model L. ultracentrifuge, and at 4,700 r.p.m. (identical G.) in a Servall SS-1 centrifuge, for the D.N.A. dilution run and the D.N.A. addition run respectively. Without disturbing the residues, the solution was, in each case, carefully pipetted from the cellulose nitrate tubes and transferred to a Quickfit stoppered flask, which was then sealed with Parafilm and stored in a refrigerator.

The mannitol solution was prepared by weight, and vacuum corrections applied.

Weight Analysis of D.N.A. Solutions

The stock solution for the D.N.A. addition run was analysed, in triplicate, by drying[4] weighed samples of approximately 6.5 ml. to residues of constant weight. Warming to evaporate the bulk of the water was followed by heating at 110°C. under vacuum, and cooling over phosphorus pentoxide in a desiccator. After 2 days

the residues were weighed promptly on a Mettler M5 microbalance.

Since it was shown, by a prolonged series of weighings, that the dry weights of Pyrex glass containers could not be obtained with sufficient reproducibility, they were considered unsuitable for use in such analyses. This lack of reproducibility probably derives largely from the uncertainty in the air density determined for the purpose of vacuum correction of the weights. In order to attain a precision of $\pm$ 5 μg. in the weight of a 10 gm. glass vessel, it was necessary that the density (approximately 1.2×10^{-3} gm./cc.) of the air, in the balance case, be known to $\pm$ 0.002×10^{-3} gm./cc. Hence, gold-plated stainless-steel bottles were used, which had a density sufficiently close to that of the balance masses, to make vacuum correction unnecessary. Duplicate weighings of these bottles, empty and dry, prior to the above analysis, agreed within 0.00003 percent (6 μg.).

The average weight percent, by analysis, was 0.09706; the average deviation,of the triplicates from the mean, being $\pm$ 0.00025.

Although a similar analysis was conducted on the stock solution for the D.N.A. dilution run, the results were later considered unreliable, since insufficient time may have been allowed for equilibration of the residues over the desiccant.

The weighing bottles were cleaned with strong detergent solution.

II. RESULTS

Float Calibration Data

The data obtained in the calibration of the magnetic float apparatus prior to the Mannitol run, and the D.N.A. dilution run which followed, and in that prior to the D.N.A. addition run, are presented in Table 3.1.

TABLE 3.1

Float Calibration Data

Weight (mg.) on Float	Pressure (m.m.)	Limiting Current (m.a.)	Limiting Current at 760 m.m.
28.23	766.60	28.5	15.5[a]
28.23	764.65	24.6	15.4[a]
28.23	761.95	19.2	15.4[a]
32.75	757.15	74.9	80.5[a]
28.24	760.50	16.8	15.8[b]
31.40	747.80	38.6	62.6[b]
31.40	760.50	63.6	62.6[b]

[a] Measurements made immediately prior to D.N.A. addition run.

[b] Measurements made immediately prior to Mannitol run.

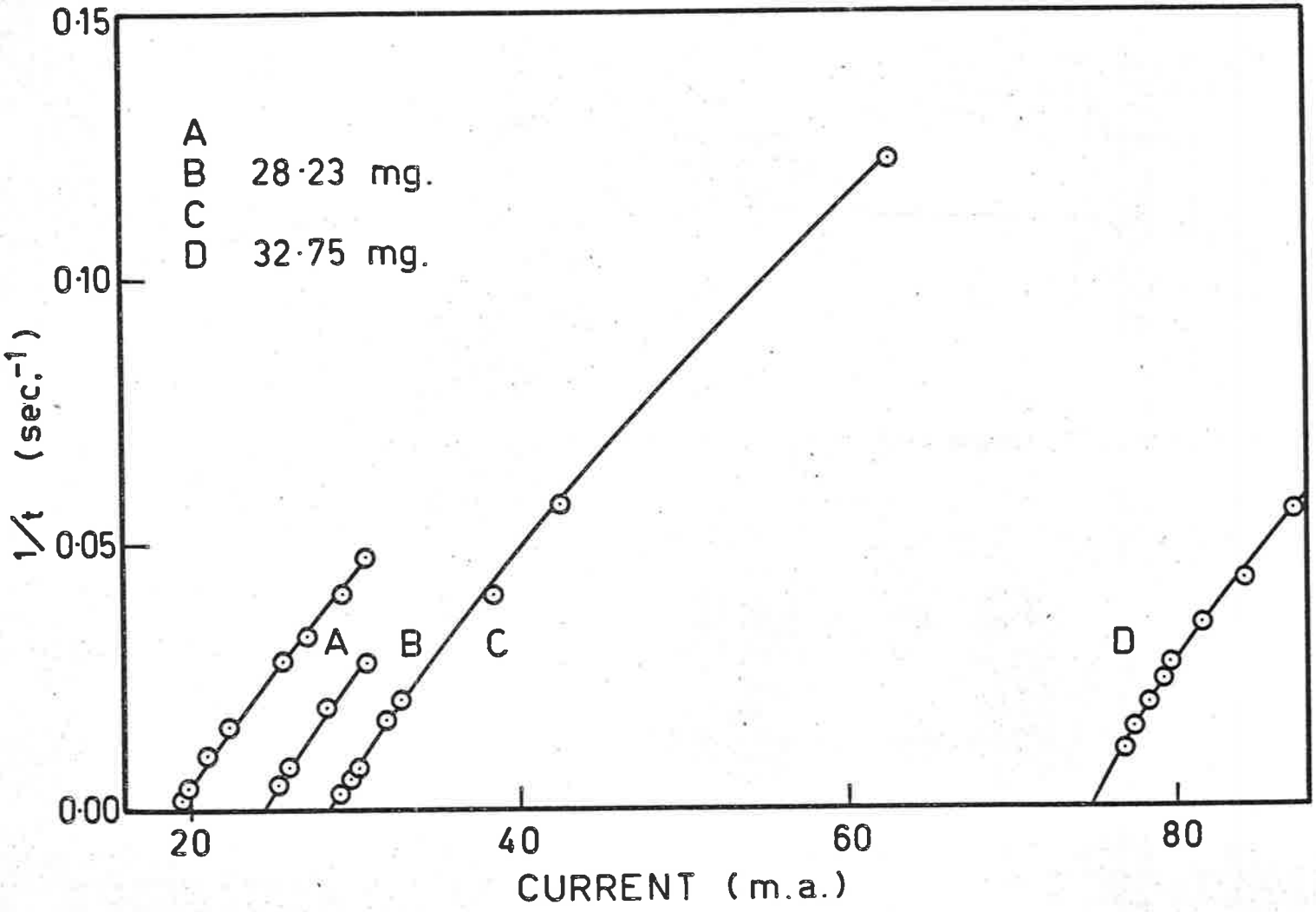

Figure 3.1. Float Calibration Curves.

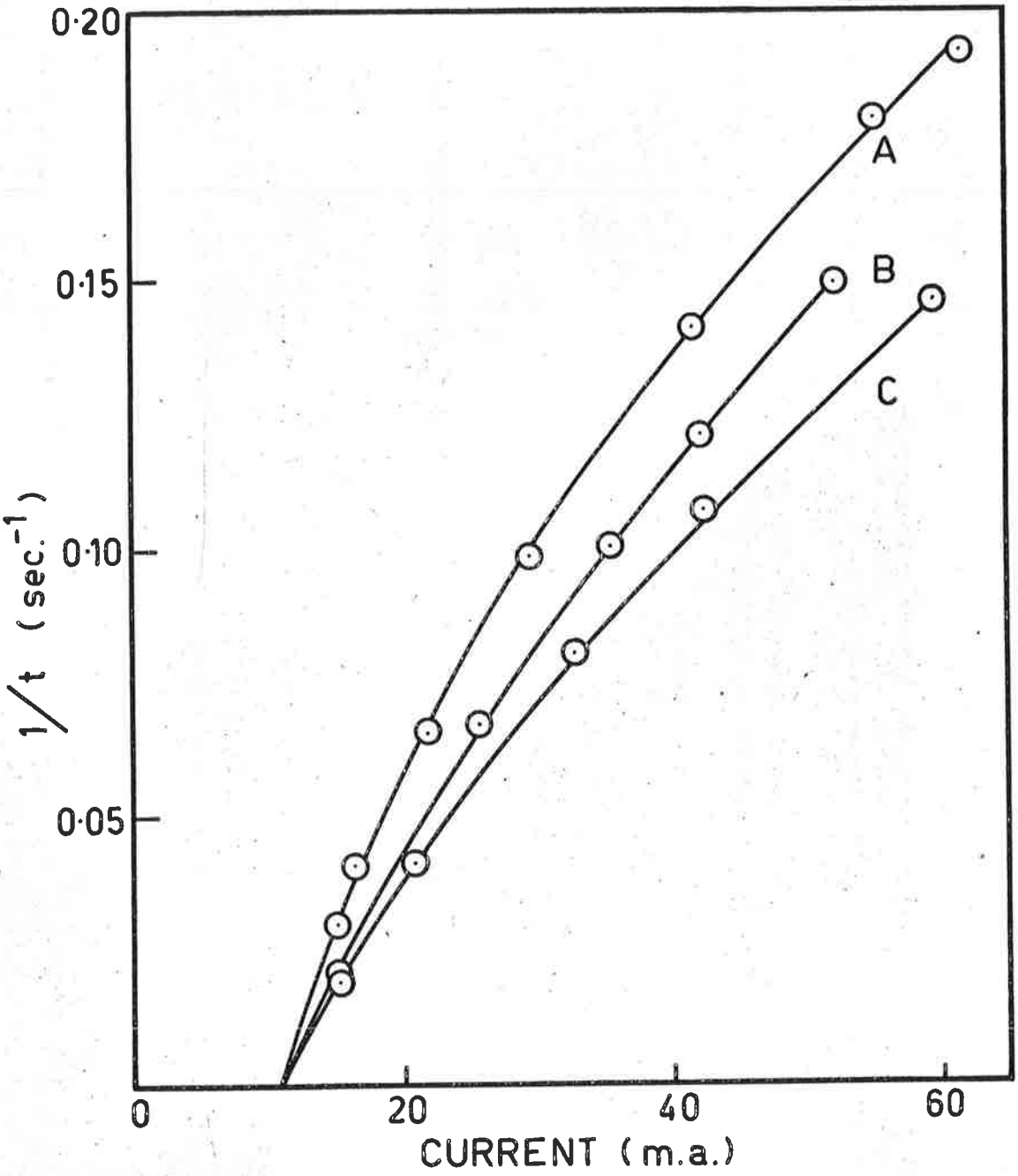

Figure 3.2. Calibration Curves obtained,

(A) with the telescope in its optimum position,

(B) with the telescope slightly lowered on its vertical mount,

(C) with the telescope further lowered; but under otherwise identical conditions.

From these data, the calibration factors quoted in the previous chapter were determined. In Figure 3.1 the extrapolations are shown, which yielded the quoted limiting currents for the latter calibration.

It was observed that calibration data obtained by this extrapolation procedure were independent, within the limits of the study, of the section of its vertical path over which the motion of the float was timed. This is verified in Figure 3.2, which also serves to illustrate the accelerated nature of this motion.

Equation of Motion for the Magnetic Float

Consider a weighted float of mass, M, in a vessel of the type shown in Figure 2.1. Let the radius of the cylindrical section of this vessel be R, and let r be the radius of a sphere equivalent to the float.

If i_s is the steady current which must be passed through the external coil in order to maintain the float stationary in a solution of viscosity, η, and if the passage of a current, i, through this coil, causes the float to attain a velocity, v, at a time t, then, neglecting wall effects,

$$\text{Upthrust} = fi_s \qquad 3.1$$

and $$fi - fi_s - 6\pi\eta rv = M\frac{dv}{dt} \; * \qquad 3.2$$

Let $$f(i - i_s) = A \;, \qquad 3.3$$

and $$6\pi\eta r = B \qquad 3.4$$

then $$\frac{dv}{dt} = \frac{A - Bv}{M} \qquad 3.5$$

i.e. $$dt = \frac{M\,dv}{A - Bv} \qquad 3.6$$

Integrating,

$$\int_0^t dt = M\int_0^v \frac{dv}{A - Bv} \qquad 3.7$$

$$\therefore \quad t = -\frac{M}{B}\ln(1 - Bv/A) \qquad 3.8$$

Re-arranging,

$$v = \frac{A}{B}(1 - e^{-Bt/M}) = \frac{dx}{dt} \qquad 3.9$$

If positive displacement on the vertical axis of the float chamber is represented by x, and x = 0 at t = 0,

$$x = \frac{A}{B}\int_0^t (1 - e^{-Bt/M})\,dt \qquad 3.10$$

i.e. $$x = \frac{A}{B}\left[t + \frac{M}{B}(e^{-Bt/M} - 1)\right] \qquad 3.11$$

* Note: that in this derivation the symbol d is used to signify the familiar differential operator, and not a density, as in the remainder of the thesis.

For simplicity, let $i_o = 0$.

Then $$A = fi. \qquad 3.12$$

Correction for Wall Effects

For a sphere moving on the axis of a cylindrical tube, a correction, K, for wall effects may be incorporated into equation 3.4.

$$B = 6\pi\eta r \cdot K \qquad 3.13$$

Happel and Brenner[5] have presented the calculated data of Haberman and Sayre[6], in the form of a graph of K, against the ratio of the radius of the sphere to that of the tube.

For a chosen (r/R) ratio of 0.76, corresponding to an r value of 2.9 cm., which is greater than the measured radius (2.2 cm.) of the spherical portion of the unsymmetrical float, this graph yields the value,

$$K = 50 \; . \qquad 3.14$$

If values are assigned as follows,

$$f = 0.069 \text{ gm./ma.}, \qquad 3.15$$

$$r = 3 \text{ cm.}, \qquad 3.16$$

$$\eta = 0.0089 \text{ poise} = \eta_{H_2O} \; , \qquad 3.17$$

to the remaining parameters of equations 3.12 and 3.13,

then, $$\underline{B = 25.16} \; , \qquad 3.18$$

and the value of A may be determined at any desired current.

Substitution of these values of A and B, and a value of 50 gm. for M, into equation 3.11, permits calculation of the dis-

placement of an arbitrary point on the float, at a series of times, t. By interpolation, values of t may then be obtained at the x values of 0.2 and 0.9 cm. respectively, and the time of transit of the arbitrary point (say the float tip) between these positions found by subtraction.

Hence a simulated series of measurements may be generated, as a function of the current i, of the time of rise of the float tip between two rulings on a telescope reticule.

Two such series are presented in Table 3.2. Series I, obtained as above, simulates measurements made on pure water, and series II, similarly obtained, simulates measurements made on a liquid of twice the viscosity. The graphs of these data, which are shown in Figure 3.3, conform closely to those obtained experimentally. From this figure it can be seen that the linear extrapolation procedure adopted, in their original study, by MacInnes et.al.[7], and in the precursor[8] of the present research, is only valid for the more viscous solution. Arrows indicate the limits, of $1/\Delta t$, within which points were obtained in these studies. Thus longer extrapolations were necessary for the more viscous solutions, and the uncertainty of the results was consequently increased. It is interesting to note that in their next study[9] McInnes et.al. also abandoned this procedure.

TABLE 3.2

Theorectical Analysis of the Motion of the Magnetic Float.

Calculated Rise Times (Δt) for Various Current Values.

I. η = 0.0089 poise = ηH_2O

i	(m.a.)	Δt (sec.)	$1/\Delta t$
	10	25.33	0.0395
	25	10.59	0.0945
	32	8.39	0.1192
	40	6.83	0.1464
	50	5.60	0.1786

II. η = 0.0089 x 2

i	(m.a.)	Δt (sec.)	$1/\Delta t$
	10	53.85	0.0186
	25	21.53	0.0465
	30	17.95	0.0557
	40	13.46	0.0743
	50	10.77	0.0929
	60	8.97	0.1110

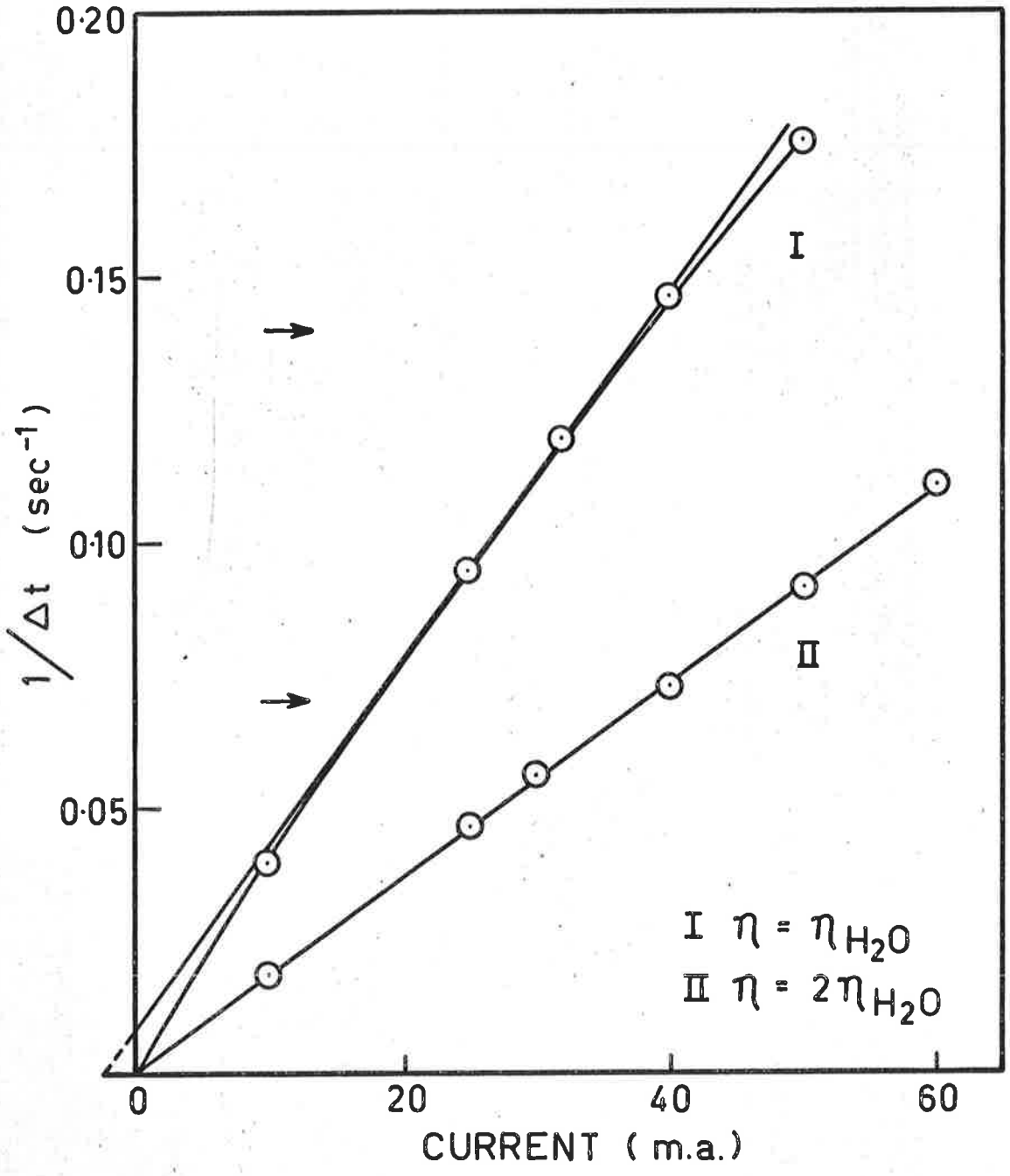

Figure 3.3. Results of the Theoretical Analysis of the Motion of the Magnetic Float. (The error, which would result from the use of a linear extrapolation procedure on points obtained between the indicated limits, is shown.)

Densities of Mannitol Solutions

The densities of four mannitol solutions at 25°C., are presented in Table 3.3. These densities, which were shown graphically to be in excellent agreement with values determined by pycnometry[10], were measured prior to the first of the D.N.A. density runs, and based on the same calibrations.

Densities of D.N.A. Solutions

No discontinuity was observed in the weight concentration dependence of the density of D.N.A. solutions at 25°C., whether the solutions were prepared by dilution of a concentrated stock solution, or by a sequence of additions of such a stock to pure water. This dependence is represented in Figure 3.4, and the data appear in Table 3.4. The linear graphs obtained from the D.N.A. dilution and addition runs were identical when the uncorrected concentrations were used. A linear graph of $(d - d_o)/d$ against the weight fraction, based on the weight analysis of the stock solution, was also obtained in the latter case. From the slope of this graph, a single partial specific volume, at 25°C., of 0.501 ± 0.01 ml./g. was calculated.

It may therefore be concluded that no change in the partial specific volume occurs on dilution denaturation of D.N.A. at 25°C., and that the variation in density of aqueous D.N.A. solutions at this temperature is perfectly reversible over the concentration range studied. However, it has not been established,

TABLE 3.3

Densities of Mannitol Solutions at 25°C.

Molarity	Density, d (gm./c.c.)	$\frac{\Delta d}{C}$	$\frac{\Delta d}{C}$ * (Pycnometry)
0.029103	0.998882	0.06305	0.06308
0.064402	1.001106	0.06304	0.06306
0.089816	1.002711	0.06306	0.06304
0.116160	1.004366	0.06302	0.06302

d_o = 0.997047 gm./c.c.

* Obtained by interpolation and extrapolation of a linear plot against C.

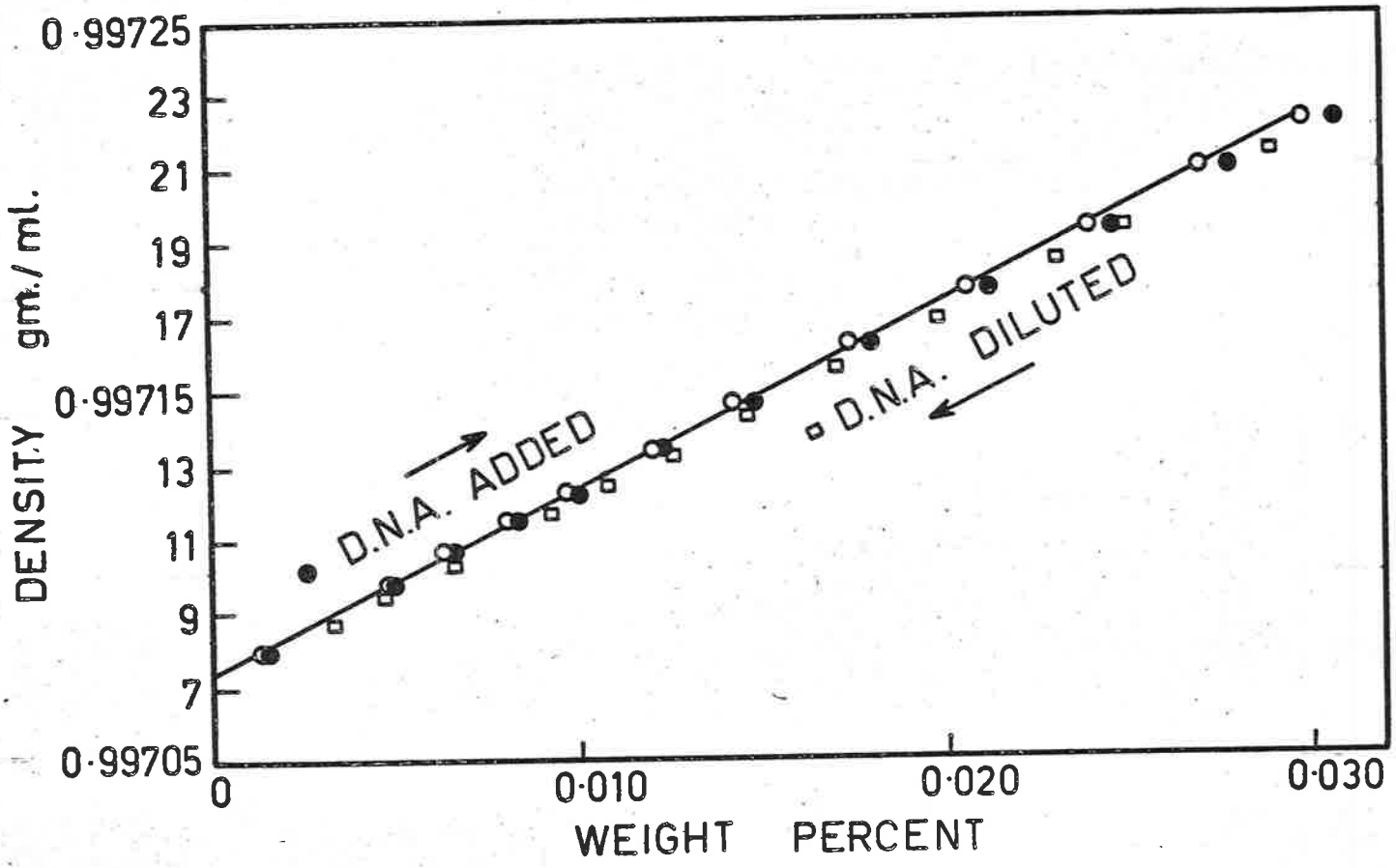

Figure 3.4. Concentration Dependence of the Density of D.N.A. Solutions at 25°C. The open circles, through which the straight line has been drawn, represent the data from the D.N.A. addition run after correction by weight analysis.

TABLE 3.4

Densities of Aqueous D.N.A. Solutions at 25°C.

I Dilution Run.		II Addition Run.				
Weight* Percent	Density, d (gm./ml.)	Weight** Percent	Weight Fraction x 10^4	Density, d (gm./ml.)	$(d - d_o)$ x 10^6	$(d - d_o)/d$ x 10^4
0.00343	0.997088[a]	0.001497	0.1497	0.997080	6	0.060
0.00478	0.997095	0.00487	0.487	0.997098	24	0.241
0.00667	0.997104	0.00640	0.640	0.997107	33	0.331
0.00930	0.997117[b]	0.00810	0.810	0.997115	41	0.411
0.01083	0.997124	0.00970	0.970	0.997122	48	0.481
0.01262	0.997133	0.01205	1.205	0.997134[e]	60	0.602
0.01469	0.997144	0.01434	1.434	0.997146	72	0.722
0.01711	0.997156	0.01751	1.751	0.997162[f]	88	0.883
0.01994	0.997169	0.02073	2.073	0.997177	103	1.033
0.02321	0.997184	0.02402	2.402	0.997193	119	1.193
0.02499	0.997193[c]	0.02708	2.708	0.997209	135	1.354
0.02910	0.997213	0.02991	2.991	0.997222[g]	148	1.484

Footnotes - see overleaf

Footnotes to TABLE 3.4

* Uncorrected by Weight Analysis.

** Corrected by Weight Analysis.

a Two weeks after the original measurement an identical result was obtained.

b Duplicates identical.

c Duplicates 0.997192 and 0.997193. The former result was obtained 1 hour after dilution, the latter after an overnight interval.

e Duplicates identical.

f Duplicates 0.997161_5, and 0.997161, were obtained with 32.75 mg. and 34.75 mg. weights on the float respectively.

g Duplicates identical, and, after three days, identical duplicates were obtained of 0.997223.

d_o = 0.997074 gm./ml.

in the foregoing, that a change in the nature of the D.N.A. did, in fact, occur. Corroborative evidence to this effect is therefore required.

Corroborative Evidence for the Denaturation of the D.N.A.

Such evidence is provided in the results of the spectrophotometric studies made on the solution samples removed from the float chamber during each of the D.N.A. density runs. Optical density measurements made directly, on the solutions removed during the D.N.A. dilution run, and the D.N.A. addition run, respectively, provide the basis for the curves D, and A_1, in Figure 3.5. Curve A_2 is based upon measurements made on the latter solutions, after dilution with sodium chloride solutions to a concentration corresponding to the optimum optical density reading (0.434^{11}), with a supporting salt concentration of 0.2M. The data are presented in Tables 3.5 and 3.6.

The curves A_1, and D, have an almost constant vertical separation, and each indicates that the quantity, O.D./Weight percent, changed significantly over the range of concentrations studied. The separation may be interpreted as the increment, in the ordinate, due to the presence, in the solutions sampled during the Addition run, of an excess of denatured D.N.A.; part of that formed following the initial additions.

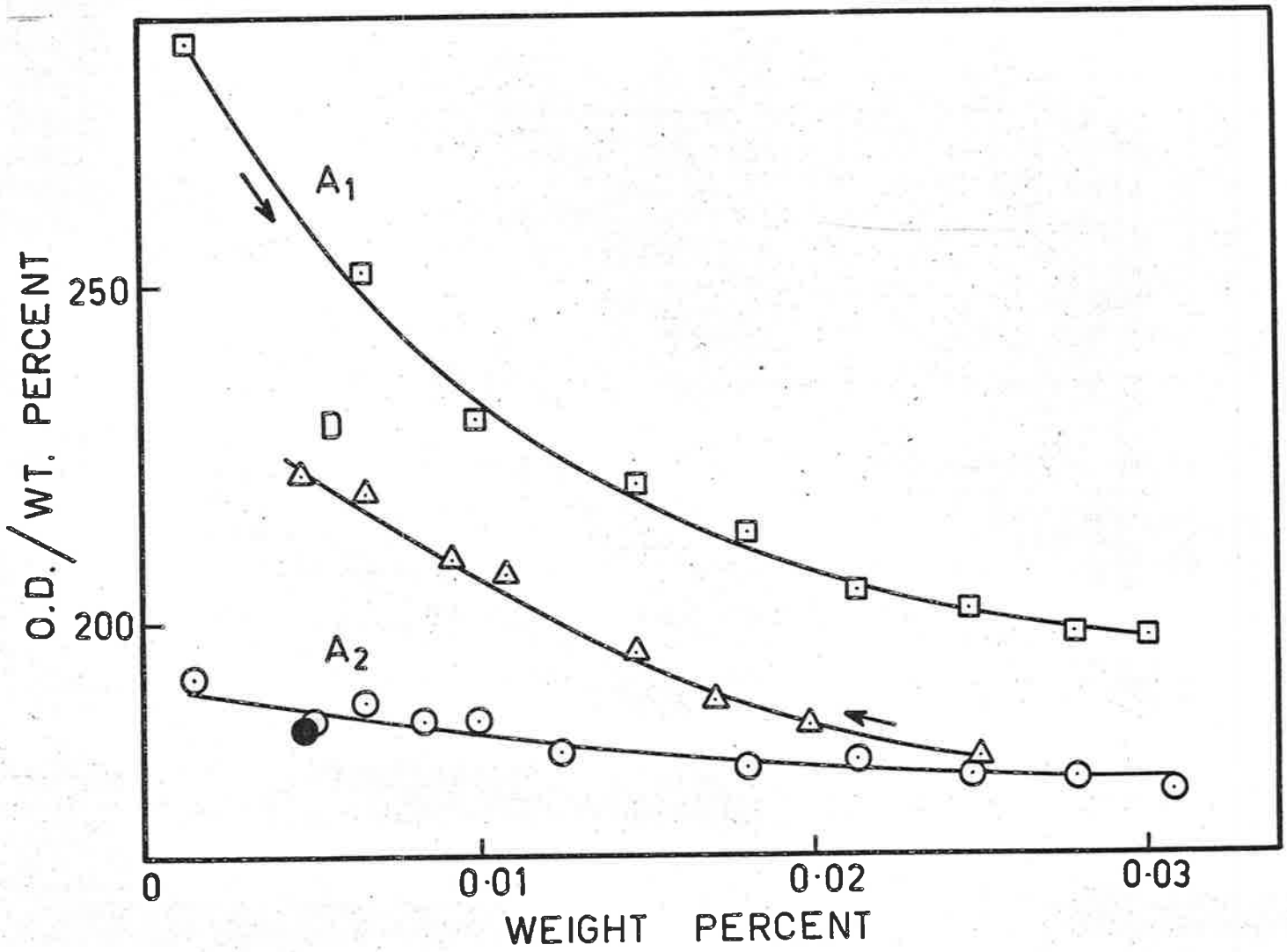

Figure 3.5. Results of the U.V. Spectrophotometric Studies made in conjunction with the D.N.A. Addition (A) and Dilution (D) Runs.

TABLE 3.5

Optical Density of D.N.A. Solutions. I.

Dilution of Concentrated D.N.A. Stock

Concentration* (Weight percent)	O.D.	$\frac{O.D.}{Conc.}$
0.00343		
0.00478	1.06[a]	222
0.00667	1.46[b]	219
0.00930	1.94[b]	209
0.01083	2.24[b]	207
0.01262		
0.01469	2.86[b]	195
0.01711	3.22[b]	188
0.01994	3.67[b]	184
0.02321		
0.02499	4.46[b]	179
0.02910		
0.00478 + Excess NaCl.	0.882[a]	184

* Uncorrected by weight analysis.

a O.D. at 259 m.μ., in 1 cm. silica cells, of samples removed from magnetic float vessel.

b O.D. at 259 m.μ., in 1 mm. silica cells.

Experimental Readings x 10.

TABLE 3.6

Optical Density of D.N.A. Solutions. II.

Addition of Concentrated D.N.A. Stock

Concentration[a] (Weight percent)	O.D.$_1$ *	$\frac{\text{O.D.}_1}{\text{Conc.}}$	O.D.$_2$	$\frac{\text{O.D.}_2}{\text{Conc.}}$
0.001541	0.44	286	0.296	192
0.00504			0.930	185
0.00662	1.67	252	1.244	188
0.00836			1.544	185
0.01001	2.30	230	1.856	185
0.01243			2.241	180
0.01478	3.25	220		
0.01804	3.85	213	3.213	178
0.02136	4.36	204	3.824	179
0.02474	4.98	201	4.380	177
0.02790	5.51	198	4.912	176
0.03081	6.06	197	5.352	174

a Uncorrected by Weight Analysis.

* O.D.$_1$ - O.D. at 259 m.μ., in 1 mm. Silica cells, of samples removed from magnetic float vessel.

Experimental readings x 10.

* O.D.$_2$ - O.D. at 259 m.μ., in 1 cm. Silica cells, of these samples, after dilution with NaCl solutions to a concentration corresponding to the optimum O.D. reading, and a NaCl concentration of 0.2M.

Experimental readings scaled accordingly.

A comparison of the curves A_1 and A_2, provides further evidence for the occurrence of denaturation. The large decrease in the ordinate, produced by the addition of sodium chloride, suggests that a considerable degree of "re-naturation" was thus effected, in the solutions concerned. It should be noted that a decrease to a value, indicated by the solid circle, close to the latter curve, was produced by the addition of excess solid sodium chloride to a solution sampled during the Dilution run.

If curve D, is extrapolated, its union with curve A_2, at a concentration of approximately 0.028 weight percent, where the latter becomes horizontal, may be attributed to the absence of denatured material from the corresponding solutions.

Evidence that the original stock solution, for the D.N.A. Dilution run, contained little, if any, denatured material, is provided from a further source. Stewart[12] obtained a curve, characteristic of heat denaturation, from a study of the variation of the relative viscosity of a sample of this solution with temperature, over the range 20° - 95°C.

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CHAPTER 4

DISCUSSION.

DISCUSSION

A value of 0.501 ± 0.01, for the partial specific volume ($\bar{v}$) of D.N.A. in aqueous solution at 25°C., was obtained.

The density data from which this quantity was determined, were reproducible to within one part in a million, and their greatest deviation from a linear fit was twice this amount.

Reproducible, and sufficiently precise values, of the weight concentration of the D.N.A. stock solutions, were obtained using the technique described. Apparently, a prolonged equilibration above a strong desiccant was necessary, in order that all the absorbed water be removed from the residues.

Since, within the concentration range studied, denaturation of the D.N.A. apparantly occurred, it seems reasonable to conclude that the absence of any inflection in the linear concentration dependence of the solution densities, and that of the function $(d - d_o)/d$, indicates that no detectable change in the partial specific volume of D.N.A. occurs on denaturation. It has previously been suggested (see Chapter 1) that denaturation is not usually accompanied by a change in molecular weight, that is, by a complete separation of the two strands which form the double helix of native D.N.A.

On the basis of the theore tical analysis presented, of the motion of the magnetic float, and in view of the discrepancy between the concentration dependence of the solution density obtained in a preliminary study, and that obtained in this research, several sets of current-time data from the D.N.A. addition run were extrapolated using the former technique, and the corresponding densities recalculated. It was not possible, by this means, to reproduce the concentration dependence previously obtained, which must therefore remain in doubt.

This study of the partial specific volume of D.N.A. was undertaken from a physico-chemical viewpoint, the chief aim being the determination of a meaningful value of this important quantity. Hence it is not proposed to attempt an explanation of its observed constancy over a concentration range within which denaturation may be presumed to have occurred. However, the role of the solvent in the process of denaturation of the D.N.A. macro-ion may be an important consideration in this regard. Helical macromolecular structures[1] are thought to be maintained, in solution, by a balance of hydrophobic[2] and hydrogen bonding and also, in the case of polyelectrolytes, by the stabilisation of the surface charge.

Comparison of the results of this study with those of previous work, is rendered difficult by the lack of detail in some of the papers consulted. Certain references made in the literature, to the partial specific volume of D.N.A., refer in fact to the specific volume of the dried material. The available values of the partial specific volume of D.N.A. in aqueous solution are: 0.528 at an unspecified concentration at 20°C.[3], 0.62 ± 0.05 between 0.125 and 2.0 percent D.N.A. at 30°C.[4], 0.54 at an unstated temperature and concentration[5], and 0.46, 0.57 and 0.55 for differing samples[6]. For D.N.A. dissolved in 1 percent aqueous sodium chloride solutions at 25°C., Tennent and Vilbrant[7] obtained values of 0.55 ± 0.01, for concentrations of D.N.A. between 0.07 and 0.49 percent.

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APPENDIX A

VISOSITY DATA

Reference numbers apply to Chapter 3 of Part I of the main text.

TABLE A.1

Relative Viscosities, Flow Times and Densities of Sodium Chloride Solutions in Water at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{c}$
0.000991	0.031483	795.45[a]	0.997089	1.0002	1.0003	0.5	0.007 ± .007
0.001975	0.044444	795.49[a]	0.997128	1.0003	1.0004	1.2	0.007
0.004949	0.070351	795.72[a]	0.997254	1.0007	1.0008	1.0	0.010
0.009940	0.099698	795.94[a]	0.997461	1.0012	1.0014	2.0	0.012
0.019841	0.140857	796.56[a]	0.997873	1.0024	1.0025	0.6	0.017
0.024915	0.157844	796.90[b]	0.998083	1.0031	1.0030	- 1.5	0.020
0.047287	0.217456	797.77[a]	0.999008	1.0051	1.0051	0.8	0.023
0.049810	0.223181	798.05[b]	0.999112	1.0056	1.0054	- 2.1	0.025
0.074684	0.273283	798.89[b]	1.000137	1.0077	1.0077	0.2	0.028
0.099132	0.314853	799.90[b]	1.001140	1.0100	1.0100	- 0.3	0.032
0.124358	0.352644	800.91[b]	1.002173	1.0123	1.0122	- 0.6	0.035
0.149168	0.386222	801.82[b]	1.003186	1.0145	1.0145	- 0.2	0.037
0.173950	0.417073	802.68[b]	1.004196	1.0166	1.0167	0.7	0.040
0.198722	0.445783	803.64[b]	1.005204	1.0188	1.0188	0.2	0.042

Footnotes to TABLE A.1

d_o = 0.997047 gm./cc. a. t_o = 795.31 sec. b. t_o = 795.25 sec.

*Calculated from the Root equation presented by Jones and Christian[24].

TABLE A.2

Relative Viscosities, Flow Times and Densities of Potassium Chloride Solutions in Water at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{C}$
0.001954	0.044203	795.28	0.997128	1.0001	1.0002	1.4	0.001 ± 0.002
0.004887	0.069904	795.28	0.997273	1.0002	1.0003	0.8	0.003
0.009754	0.098761	795.27	0.997498	1.0004	1.0004	- 0.5	0.004
0.025038	0.158234	794.77	0.998223	1.0005	1.0005	- 0.5	0.003
0.049030	0.221428	793.88	0.999363	1.0005	1.0005	- 0.8	0.002
0.074994	0.273851	792.74	1.000573	1.0003	1.0004	0.7	0.0011
0.097851	0.312812	791.89	1.001633	1.0003	1.0003	- 0.2	0.0009
0.120943	0.347769	790.89	1.002718	1.0001	1.0001	0.3	0.0003 ± 0.0003
0.147700	0.384317	789.79	1.003973	1.0000	1.0000	0.0	- 0.0001
0.171721	0.414392	788.81	1.005083	0.9998	0.9998	- 0.3	- 0.0004
0.197426	0.444326	787.68	1.006298	0.9996	0.9996	0.1	- 0.0009

Footnotes to TABLE A.2

*Calculated by graphical interpolation of the data of Jones and Talley[25], using successive approximations to the molarity of the solutions.

d_o = 0.997047 gm./cc. t_o = 795.30 sec.

TABLE A.3

Relative Viscosities, Flow Times and Densities of Cesium Chloride Solutions in Water at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{c}$
0.004792	0.069227	794.71[a]	0.99765	1.0000	1.0001	0.8	0.0001 ± 0.0005
0.012457	0.111611	794.10[b]	0.99867	1.0001	1.0000	- 1.0	0.0000 ± 0.0004
0.024904	0.157811	792.55[b]	1.00027	0.9997	0.9996	- 1.3	- 0.0002
0.048639	0.220543	789.05[a]	1.00331	0.9985	0.9987	1.6	- 0.0007
0.072175	0.268655	786.02[a]	1.00638	0.9978	0.9978	0.2	- 0.0008
0.074560	0.273057	786.01[b]	1.00666	0.9978	0.9977	- 1.0	- 0.0008
0.098295	0.313520	782.48[a]	1.00969	0.9965	0.9967	1.7	- 0.0011
0.123886	0.351975	779.51[b]	1.01297	0.9957	0.9956	- 1.1	- 0.0012
0.148668	0.385575	776.16[b]	1.01612	0.9945	0.9946	0.2	- 0.0014
0.173241	0.416222	772.95[b]	1.019286[c]	0.9935	0.9935	- 0.2	- 0.0016
0.197446	0.444349	769.48[a]	1.022391[c]	0.9922	0.9924	2.4	- 0.0018
0.197801	0.444748	769.89[b]	1.02240	0.9926	0.9924	- 2.3	- 0.0017

Footnotes to TABLE A.3

* The densities indexed c were determined experimentally, and the remainder obtained by graphical interpolation from the total of five measured values, (see Table B.1).

d_o = 0.997047 gm./cc. a. t_o = 795.16 sec. b. t_o = 795.35 sec.

TABLE A.4

Relative Viscosities, Flow Times and Densities of Sodium Iodide Solutions in Water at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.009840	0.099198	795.06[a]	0.99800[c]	1.0007	1.0006	- 0.3
0.024754	0.157333	793.97[a]	0.999886	1.0012	1.0011	- 0.9
0.049423	0.222313	792.29[b]	1.002713	1.0017	1.0017	- 0.5
0.074399	0.272762	790.35[b]	1.005565	1.0021	1.0022	0.8
0.097721	0.312604	788.66[b]	1.008216	1.0026	1.0026	0.3
0.122280	0.349685	786.78[b]	1.011038	1.0030	1.0031	0.6
0.146557	0.382828	785.01[b]	1.013809	1.0035	1.0035	- 0.1
0.172133	0.414889	783.01[b]	1.016728	1.0038	1.0039	0.9
0.198000	0.444972	781.10[a]	1.019688	1.0044	1.0043	- 1.2

* The value indexed c was determined by graphical interpolation from the measured density values, (see Table B.1).

d_o = 0.997047 gm./cc. a. t_o = 795.30 sec. b. t_o = 795.43 sec.

TABLE A.5

Relative Viscosities, Flow Times and Densities of Potassium Iodide Solutions in Water at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.009905	0.099523	794.04	0.998236	0.9997	0.9997	- 0.1
0.024367	0.156101	791.97	0.999988	0.9988	0.9988	- 0.8
0.048594	0.220441	788.21	1.002906	0.9970	0.9971	0.6
0.073362	0.270854	784.46	1.005879	0.9952	0.9952	0.4
0.096931	0.311337	780.90	1.008718	0.9935	0.9935	- 0.1
0.122133	0.349476	777.07	1.011741	0.9916	0.9915	- 0.3
0.147173	0.383632	773.29	1.014745	0.9897	0.9896	- 0.6
0.171596	0.414241	769.42	1.017677	0.9876	0.9877	1.5
0.197602	0.444524	765.66	1.020811	0.9858	0.9857	- 0.8

* See Table B.2.

d_o = 0.997047 gm./cc. t_o = 795.23 sec.

TABLE A.6

Relative Viscosities, Flow Times and Densities of Cesium Iodide Solutions in Water at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.001945	0.044098	794.91	0.997436	1.0000	0.9999	- 0.3
0.004886	0.069899	794.40	0.998028	0.9999	0.9997	- 2.3
0.024489	0.156491	790.21	1.001977	0.9980	0.9978	- 2.5
0.049117	0.221623	783.50	1.006965	0.9950	0.9951	1.0
0.073959	0.271954	777.51	1.011984	0.9924	0.9924	1.0
0.096730	0.311014	772.01	1.016567	0.9898	0.9900	1.6
0.120467	0.347084	766.46	1.021355	0.9873	0.9873	0.3
0.146975	0.383373	760.19	1.026687	0.9843	0.9844	0.5
0.171234	0.413804	754.57	1.031578	0.9817	0.9817	- 0.3
0.197121	0.443983	748.62	1.036820	0.9789	0.9788	- 1.3

* See Table B.1.

d_o = 0.997047 gm./cc. t_o = 795.24 sec.

TABLE A.7

Relative Viscosities, Flow Times and Densities of Potassium Bromide Solutions in Water at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.001968	0.044364	795.30	0.997216	1.0001	1.0001	0.0
0.004910	0.070070	795.11	0.997468	1.0002	1.0002	- 0.1
0.024673	0.157075	793.35	0.999145	0.9996	0.9997	0.8
0.049719	0.222978	791.03	1.001270	0.9988	0.9989	0.8
0.073741	0.271553	788.91	1.003295	0.9982	0.9980	- 1.2
0.098188	0.313349	786.60	1.005368	0.9973	0.9971	- 1.6
0.123768	0.351807	783.91	1.007525	0.9960	0.9962	1.4
0.148023	0.384738	781.60	1.009565	0.9951	0.9952	1.1
0.172543	0.415383	779.48	1.011629	0.9944	0.9942	- 1.9
0.198011	0.444984	776.81	1.013780	0.9931	0.9932	0.9

* See Table B.1.

d_o = 0.997047 gm./cc. t_o = 795.32 sec.

TABLE A.8

Relative Viscosities, Flow Times and Densities of Tetra n-Propyl Ammonium Iodide Solutions in Water at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{C}$
0.000076	0.008689	445.05	0.997047	1.0000	1.0004	4.2	
0.000992	0.031499	446.04	0.997109	1.0023	1.0020	- 3.3	0.073
0.002005	0.044774	446.54	0.997178	1.0035	1.0031	- 3.5	0.078
0.004990	0.070639	447.57	0.997360	1.0060	1.0060	0.5	0.085
0.049122	0.221634	461.53	1.000137	1.0402	1.0404	1.6	0.182
0.073900	0.271846	469.24	1.001705	1.0593	1.0595	2.4	0.218
0.094347	0.307159	475.89	1.003004	1.0757	1.0757	0.6	0.246
0.111281	0.333588	481.63	1.004080	1.0898	1.0895	- 2.8	0.269
0.142276	0.377195	492.22	1.006051	1.1160	1.1157	- 2.4	0.307
0.165012	0.406216	500.18	1.007499	1.1357	1.1358	1.2	0.334
0.189923	0.435802	509.41	1.009107	1.1585	1.1585	0.8	0.364

* These density data are presented separately in Table B.1 .

d_o = 0.997047 gm./cc. t_o = 445.05 sec.

TABLE A.9

Relative Viscosities, Flow Times and Densities of Tetra n-Propyl Ammonium Bromide Solutions in Water at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	x 10^4	$(\eta_r - 1)/\sqrt{c}$
0.000000_7	0.000837	444.73[a]	0.997047	1.0000	1.0000	0.27	
0.000019	0.004393	444.74[a]	0.997048	1.0000	1.0002	1.5	
0.000125	0.011167	445.21[a]	0.99705	1.0011	1.0004	- 6.4	0.1 ± 0.04
0.000997	0.031574	445.73[b]	0.99708	1.0022	1.0017	- 5.2	0.070
0.001871	0.043257	446.22[b]	0.99710	1.0027	1.0033	- 6.7	0.077
0.004905	0.070036	447.32[b]	0.99716	1.0056	1.0059	- 2.5	0.084
0.014404	0.120015	450.75[a]	0.99742	1.0139	1.0139	- 0.5	0.116
0.024625	0.156923	454.17[b]	0.99770	1.0218	1.0223	4.9	0.139
0.049398	0.222256	462.84[b]	0.99840	1.0421	1.0426	5.4	0.189
0.073467	0.271047	471.57[b]	0.99906	1.0624	1.0626	1.7	0.230
0.094720	0.307765	479.45[c]	0.99964	1.0810	1.0807	- 3.2	0.263
0.118788	0.344656	488.41[c]	1.00035	1.1020	1.1017	- 2.9	0.296
0.142941	0.378075	497.69[c]	1.00107	1.1237	1.1234	- 2.9	0.327

TABLE A.9 (Continued)

Relative Viscosities, Flow Times and Densities of Tetra n-Propyl Ammonium Bromide Solutions in Water at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{C}$
0.144399	0.379998	498.11[a]	1.00111	1.1246	1.1247	1.1	0.328
0.166291	0.407788	506.76[c]	1.00250	1.1450	1.1450	0.1	0.356
0.190361	0.436304	516.45[c]	1.00177	1.1677	1.1679	2.1	0.384

* Calculated by graphical interpolation of the data of C. Pepela[32].

d_o = 0.997047 gm./cc.

a. t_o = 444.73 sec. b. t_o = 444.76 sec. c. t_o = 444.69 sec.

TABLE A.10

Relative Viscosities, Flow Times and Densities of Sodium Chloride Solutions in Aqueous 20 Percent Sucrose at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{c}$
0.001098	0.033130	1407.19[a]	1.07940[c]	1.0003	1.0004	0.8	0.009 ± 0.006
0.002183	0.046722	1407.36[a]	1.07945[c]	1.0005	1.0006	1.3	0.010
0.005381	0.073354	1408.16[a]	1.07957[c]	1.0011	1.0011	- 0.4	0.016
0.011090	0.105307	1409.14[a]	1.07979[c]	1.0020	1.0019	- 1.4	0.019
0.020722	0.143953	1409.96[a]	1.08015[c]	1.0030	1.0031	1.5	0.021
0.028244	0.168061	1409.86[b]	1.080440	1.0042	1.0040	- 1.7	0.025
0.056022	0.236690	1412.59[b]	1.081552	1.0072	1.0072	0.0	0.030
0.056653	0.238020	1414.00[a]	1.08153[c]	1.0071	1.0072	1.2	0.030
0.080237	0.283262	1415.26[b]	1.082466	1.0099	1.0098	- 1.1	0.035
0.109123	0.330337	1417.99[b]	1.083573	1.0129	1.0129	- 0.1	0.039
0.142622	0.377654	1421.17[b]	1.084830	1.0164	1.0164	0.6	0.043
0.168645	0.410664	1423.59[b]	1.085816	1.0190	1.0191	1.0	0.046
0.190787	0.436792	1425.65[b]	1.08669[c]	1.0213	1.0214	0.8	0.049
0.202452	0.449947	1427.08[b]	1.08714[c]	1.0228	1.0226	- 1.7	0.051

Footnotes to TABLE A.10

* The values indexed c were determined, by graphical interpolation and extrapolation, from the measured density values (see Table B.3).

d_o = 1.07937 gm./cc.[21]

a. t_o = 1406.82 sec. b. t_o = 1405.38 sec.

TABLE A.11

Relative Viscosities, Flow Times and Densities of Potassium Chloride Solutions in Aqueous 20 Percent Sucrose at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$	$(\eta_r - 1)/\sqrt{c}$
0.010269	0.101334	1405.43[a]	1.07982[c]	1.0002	1.0005	2.9	0.002 ± 0.002
0.026963	0.164205	1404.60[a]	1.08058[c]	1.0003	1.0005	2.1	0.002
0.054727	0.233938	1402.57[b]	1.081803	1.0004	1.0003	- 0.5	0.001
0.083648	0.289219	1400.71[b]	1.083648	1.0000	0.9999	- 1.0	0.0002 ± 0.0002
0.107788	0.328310	1398.86[b]	1.08412[c]	0.9998	0.9996	- 2.4	- 0.0005 ± 0.0006
0.143116	0.378307	1396.00[b]	1.085608	0.9992	0.9990	- 1.3	- 0.002
0.166360	0.407872	1393.98[b]	1.086592	0.9986	0.9986	0.2	- 0.003
0.189794	0.435654	1392.02[b]	1.087598	0.9981	0.9982	0.8	- 0.0043
0.213978	0.462578	1390.11[b]	1.08855[c]	0.9976	0.9978	1.4	- 0.0051

* The values indexed c were determined, by graphical interpolation and extrapolation, from the measured density values (see Table B.3).

d_o = 1.07937 gm./cc.[21]

a. t_o = 1405.74 sec. b. t_o = 1405.24

TABLE A.12

Relative Viscosities, Flow Times and Densities of Cesium Chloride Solutions in Aqueous 20 Percent Sucrose at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.005254	0.072487	1405.86	1.08001[c]	1.0001	1.0000	- 0.5
0.013093	0.114426	1404.19	1.08101[c]	0.9998	0.9998	- 0.8
0.026506	0.162807	1400.81	1.082711	0.9990	0.9991	1.2
0.052805	0.229793	1395.05	1.085986	0.9979	0.9977	- 1.9
0.081225	0.285000	1387.99	1.089507	0.9961	0.9961	0.2
0.106814	0.326824	1381.90	1.092675	0.9946	0.9946	0.1
0.135579	0.368210	1374.88	1.096184	0.9927	0.9929	1.7
0.161167	0.401457	1368.94	1.099348	0.9913	0.9913	0.6
0.188191	0.433810	1362.65	1.102677	0.9897	0.9897	- 0.2
0.213814	0.462401	1365.70	1.105856	0.9882	0.9881	- 1.1

* The values indexed c were determined, by graphical extrapolation, from the measured density values (see Table B.3).

d_o = 1.07937 gm./cc.[21] t_o = 1406.56 sec.

TABLE A.13

Relative Viscosities, Flow Times and Densities of Sodium Iodide Solutions in Aqueous 20 Percent Sucrose at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.010594	0.102925	1406.95[a]	1.080591	1.0010	1.0008	- 2.6
0.026769	0.163613	1404.54[b]	1.082391	1.0014	1.0014	0.3
0.053917	0.232201	1401.76[b]	1.085379	1.0021	1.0022	1.0
0.079457	0.281880	1399.40[b]	1.088197	1.0030	1.0029	- 1.0
0.106864	0.326900	1396.46[b]	1.091237	1.0037	1.0037	- 0.8
0.134563	0.366828	1393.18[b]	1.094252	1.0041	1.0044	2.1
0.161416	0.401766	1390.42[b]	1.097209	1.0049	1.0050	1.4
0.183685	0.428584	1388.13[b]	1.099648	1.0054	1.0055	0.9
0.213845	0.462433	1385.26[b]	1.103053	1.0065	1.0062	- 2.4

* See Table B.3.

d_o = 1.07937 gm./cc.[21]

a. t_o = 1407.10 sec. b. t_o = 1406.56 sec.

TABLE A.14

Relative Viscosities, Flow Times and Densities of Potassium Iodide Solutions in Aqueous 20 Percent Sucrose at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.) *	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.005288	0.072717	1403.60	1.079879	0.9998	0.9997	- 0.3
0.026686	0.163359	1398.03	1.082460	0.9982	0.9979	- 2.4
0.053250	0.230760	1390.51	1.085408	0.9955	0.9955	0.3
0.080586	0.283877	1382.91	1.088565	0.9930	0.9930	0.8
0.106546	0.326413	1375.84	1.091557	0.9906	0.9906	0.2
0.132621	0.364172	1368.59	1.094564	0.9881	0.9882	0.8
0.159232	0.399039	1361.36	1.097611	0.9856	0.9857	0.5
0.186423	0.431767	1353.80	1.100745	0.9829	0.9831	1.6
0.213635	0.462207	1346.87	1.103940	0.9807	0.9805	- 2.4

* See Table B2.

d_o = 1.07937 gm./cc.[21] t_o = 1404.59 sec.

TABLE A.15

Relative Viscosities, Flow Times and Densities of Cesium Iodide Solutions in Aqueous 20 Percent Sucrose at 25°C.

C	$\sqrt{C}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.002075	0.045550	1405.06	1.079745	0.9999	0.9999	- 0.4
0.005375	0.073314	1403.83	1.080400	0.9996	0.9995	- 1.5
0.026588	0.163059	1394.30	1.084531	0.9966	0.9967	1.0
0.054010	0.232400	1382.43	1.089909	0.9930	0.9930	- 0.1
0.082249	0.286791	1370.44	1.095209[a]	0.9892	0.9892	- 0.5
0.105272	0.324456	1360.05	1.099949	0.9860	0.9860	0.3
0.131690	0.362891	1348.75	1.105125	0.9824	0.9823	- 0.4
0.157792	0.397230	1336.94	1.110496[a]	0.9785	0.9787	2.1
0.184922	0.430025	1326.26	1.115524[a]	0.9751	0.9749	- 1.5

* The values indexed a may be in error by $\pm$ 0.0002 gm./cc., and are therefore omitted from Table B.3.

d_o = 1.07937 gm./cc.[21] t_o = 1405.70 sec.

TABLE A.16

Relative Viscosities, Flow Times and Densities of Potassium Bromide Solutions in Aqueous 20 Percent Sucrose at 25°C.

c	$\sqrt{c}$	t(sec.)	d(gm./cc.)*	η_r(Expt.)	η_r(Calc.)	$\Delta \times 10^4$
0.002120	0.046039	1406.98	1.079625	1.0004	1.0002	- 1.7
0.005503	0.074182	1406.53	1.079900	1.0003	1.0002	- 1.1
0.026659	0.163277	1403.47	1.081599	0.9997	0.9995	- 2.2
0.051672	0.227316	1399.08	1.083607	0.9984	0.9983	- 1.1
0.080904	0.284435	1393.40	1.085950	0.9965	0.9968	2.9
0.106649	0.326571	1389.44	1.088084	0.9956	0.9954	- 2.1
0.129178	0.359413	1384.80	1.089819	0.9939	0.9942	2.9
0.160959	0.401197	1379.15	1.092368	0.9922	0.9924	2.5
0.191439	0.437537	1373.93	1.094806	0.9906	0.9907	0.6
0.214234	0.462854	1370.34	1.096682	0.9897	0.9894	- 3.6

* See Table B.3.

d_o = 1.07937 gm./cc.[21] t_o = 1406.78 sec.

APPENDIX B

DENSITY DATA

Reference numbers apply to Chapter 3 of Part I of the main text.

TABLE B.1

Densities of Aqueous Solutions of Electrolytes at 25°C.[a,b]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^6$
		Cesium Chloride		
0.009379	0.096847	0.998234	0.998252	18.0
0.049753	0.223053	1.003444	1.003436	- 7.5
0.099308	0.315132	1.009796	1.009798	2.0
0.173241	0.416222	1.019286	1.019286	- 0.3
0.197446	0.444349	1.022391	1.022391	0.3
		Sodium Iodide		
0.024754	0.157333	0.999886	0.999882	- 3.9
0.049423	0.222313	1.002713	1.002705	- 7.7
0.074399	0.272762	1.005565	1.005562	- 2.9
0.097721	0.312604	1.008216	1.008229	13.0
0.122280	0.349685	1.011038	1.011035	- 2.5
0.146557	0.382828	1.013809	1.013809	0.3
0.172133	0.414889	1.016728	1.016731	2.6
0.198000	0.444972	1.019688	1.019684	- 3.7

TABLE B.1 Continued

Densities of Aqueous Solutions of Electrolytes at 25°C.[a,b.]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^6$
		Cesium Iodide		
0.001945	0.044098	0.997436	0.997440	3.6
0.004886	0.069899	0.998028	0.998033	5.5
0.024489	0.156491	1.001977	1.001990	13.0
0.049117	0.221623	1.006965	1.006960	- 5.0
0.073959	0.271954	1.011984	1.011972	- 12.0
0.096730	0.311014	1.016567	1.016565	- 1.9
0.120467	0.347084	1.021355	1.021353	- 2.5
0.146975	0.383373	1.026687	1.026698	11.0
0.171234	0.413804	1.031578	1.031589	11.0
0.197121	0.443983	1.036820	1.036808	- 12.0

TABLE B.1 Continued

Densities of Aqueous Solutions of Electrolytes at 25°C.[a,b.]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^6$
		Potassium Bromide		
0.001968	0.044364	0.997216	0.997215	- 1.3
0.004910	0.070070	0.997468	0.997465	- 3.0
0.024673	0.157075	0.999145	0.999144	- 1.1
0.049719	0.222978	1.001270	1.001267	- 3.2
0.073741	0.271553	1.003295	1.003299	4.3
0.098188	0.313349	1.005368	1.005365	- 3.1
0.123768	0.351807	1.007525	1.007524	- 1.4
0.148023	0.384738	1.009565	1.009568	3.2
0.172543	0.415383	1.011629	1.011633	4.1
0.198011	0.444984	1.013780	1.013776	- 4.2

TABLE B.1 Continued

Densities of Aqueous Solutions of Electrolytes at 25°C.[a,b]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^6$
		Tetra n-Propyl Ammonium Iodide		
0.000076	0.008689	0.997047	0.997052	4.7
0.000992	0.031499	0.997109	0.997109	- 0.1
0.002005	0.044774	0.997178	0.997172	- 5.9
0.004990	0.070639	0.997360	0.997359	- 1.2
0.024492	0.156501	0.998585	0.998583	- 1.9
0.049122	0.221634	1.000137	1.000136	- 0.6
0.073900	0.271846	1.001705	1.001705	- 0.3
0.094347	0.307159	1.003004	1.003002	- 1.8
0.111281	0.333588	1.004080	1.004079	- 1.0
0.142276	0.377195	1.006051	1.006054	3.2
0.165012	0.406216	1.007499	1.007506	7.3
0.189923	0.435802	1.009107	1.009100	- 6.7

a. The Potassium Iodide data are presented in Table B.2.

b. d_o = 0.997047 gm./cc.

TABLE B.2

Densities and Apparent Molar Volumes (ϕ_v) of Potassium Iodide Solutions in Water and in Aqueous 20 Percent Sucrose at 25°C.

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^6$	ϕ_v (cc./mole)
		Aqueous Solutions[a]			
0.009905	0.099523	0.998236	0.998241	5.4	46.1
0.024367	0.156101	0.999988	0.999984	-4.0	45.4
0.048594	0.220441	1.002906	1.002901	- 5.2	45.57
0.073362	0.270854	1.005879	1.005880	1.4	45.75
0.096931	0.311337	1.008718	1.008714	- 3.8	45.74
0.122133	0.349476	1.011741	1.011743	1.8	45.83
0.147173	0.383632	1.014745	1.014750	5.5	45.89
0.171596	0.414241	1.017677	1.017683	5.7	45.92
0.197602	0.444524	1.020811	1.020804	- 7.2	45.88

TABLE B.2 Continued

Densities and Apparent Molar Volumes (ϕ_v) of Potassium Iodide Solutions in Water and in Aqueous 20 Percent Sucrose at 25°C.

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^6$	ϕ_v (cc./mole)
		20 Percent Sucrose Solutions[b]			
0.053250	0.230760	1.085408	1.085428	20	48.7
0.080586	0.283877	1.088565	1.088560	- 5	48.1
0.106546	0.326413	1.091557	1.091543	- 14	47.8
0.132621	0.364172	1.094564	1.094548	- 16	47.7
0.159232	0.399039	1.097611	1.097621	10	47.67
0.186423	0.431767	1.100745	1.100769	24	47.57
0.213635	0.462207	1.103940	1.103925	- 15	47.33

a. d_o = 0.997047 gm./cc.

b. d_o = 1.07937 gm./cc.[21]

TABLE B.3

Densities of Solutions of Electrolytes in Aqueous 20 Percent Sucrose at 25°C.[a,b.]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^5$
		Sodium Chloride		
0.028244	0.168061	1.080440	1.080468	2.8
0.056022	0.236690	1.081552	1.081538	- 1.4
0.080237	0.283262	1.082466	1.082465	- 0.1
0.109123	0.330337	1.083573	1.083565	- 0.8
0.142622	0.337654	1.084830	1.084835	0.5
0.168645	0.410664	1.085816	1.085817	0.1
		Potassium Chloride		
0.054727	0.233938	1.081803	1.081801	- 0.2
0.083648	0.289219	1.083066	1.083061	- 0.5
0.143116	0.378307	1.085608	1.085614	0.6
0.166360	0.407872	1.086592	1.086600	0.8
0.189794	0.435654	1.087598	1.087589	- 0.9

TABLE B.3 Continued

Densities of Solutions of Electrolytes in Aqueous 20 Percent Sucrose at 25°C.[a,b.]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^5$
		Cesium Chloride		
0.026506	0.162807	1.082711	1.082692	- 1.9
0.052805	0.229793	1.085986	1.085970	- 1.6
0.081225	0.285000	1.089507	1.089498	- 0.9
0.106814	0.326824	1.092675	1.092665	- 1.0
0.135579	0.368210	1.096184	1.096215	3.1
0.161167	0.401457	1.099348	1.099366	1.8
0.188191	0.433810	1.102677	1.102687	1.0
0.213814	0.462401	1.105856	1.105829	- 2.7
		Sodium Iodide		
0.010594	0.102925	1.080591	1.080552	- 3.9
0.026769	0.163613	1.082391	1.082353	- 3.8
0.053917	0.232201	1.085379	1.085366	- 1.3
0.079457	0.281880	1.088197	1.088194	- 0.3
0.106864	0.326900	1.091237	1.091223	- 1.4
0.134563	0.366828	1.094252	1.094279	2.7
0.161416	0.401766	1.097209	1.097237	2.8
0.183685	0.428584	1.099648	1.099686	3.8
0.213845	0.462433	1.103053	1.103000	- 5.3

TABLE B.3 Continued

Densities of Solutions of Electrolytes in Aqueous 20 Percent Sucrose at 25°C.[a,b.]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^5$
		Cesium Iodide		
0.002075	0.045550	1.079745	1.079770	2.5
0.005375	0.073314	1.080400	1.080409	0.9
0.026588	0.163059	1.084531	1.084529	- 0.2
0.054010	0.232400	1.089909	1.089883	- 2.6
0.105272	0.324456	1.099949	1.099945	- 0.4
0.131690	0.362891	1.105125	1.105152	2.7
0.213157	0.461690	1.121293	1.121285	- 0.9

TABLE B.3 Continued

Densities of Solutions of Electrolytes in Aqueous 20 Percent Sucrose at 25°C.[a,b.]

C	$\sqrt{C}$	$d_{Expt.}$ (gm./cc.)	$d_{Calc.}$	$\Delta \times 10^5$
		Potassium Bromide		
0.005503	0.074182	1.079883	1.079825	- 5.8
0.026659	0.163277	1.081599	1.081561	- 3.8
0.051672	0.227316	1.083607	1.083599	- 0.8
0.080904	0.284435	1.085950	1.085967	1.7
0.106649	0.326571	1.088084	1.088043	- 4.1
0.129178	0.359413	1.089819	1.089854	3.5
0.160959	0.401197	1.092368	1.092398	3.0
0.191439	0.437537	1.094806	1.094828	2.2
0.214234	0.462854	1.096682	1.096641	- 4.1

a. The Potassium Iodide data are presented in Table B.2.

b. d_o = 1.07937 gm./cc.[21]

APPENDIX C

COMPUTER PROGRAMS

1. Least Squares Program for fitting Viscosity Data to the Jones - Dole Equation: Program JONDOL.
2. Least Squares Program for fitting Viscosity Data to the Extended Jones - Dole Equation: Program JDANDS.
3. Least Squares Program for fitting Density Data to the Root Equation: Program ROOTEQ.
4. Explanatory Notes.

1. Least Squares Program for fitting Viscosity Data to the Jones - Dole Equation. (Equation 6.1).

Program JONDOL.

```
      PROGRAM JONDOL(INPUT,OUTPUT,PUNCH)
      DIMENSION U(30),Y(30),X(30),Z(30),YC(30),DEL(30)
   10 READ 20,N,M,D
   20 FORMAT(2I2,F9.6)
      IF(N)11,11,12
   12 PRINT 21
   21 FORMAT(1H1)
      E=F=G=S=T=V=0
   24 READ 22,(U(I),Y(I),I=1,N)
   22 FORMAT((F9.7,F9.6,F10.7,F9.6,F10.7,F9.6,F10.7,F9.6))
      DO4I=1,N
      X(I)=SQRT(U(I))
      Z(I)=Y(I)-D
      E=E+X(I)**2
      F=F+X(I)**3
      G=G+X(I)**4
      S=S+Z(I)*X(I)
      T=T+Z(I)*X(I)**2
      V=V+Z(I)**2
    4 CONTINUE
      B=(S*F-T*E)/(F**2-E*G)
      A=(S-B*F)/E
```

```
      XXN=N
      SA=(V-A*S-B*T)*G/((XXN-2.)*(E*G-F**2))
      SEA=SQRT(SA)
      SB=(V-A*S-B*T)*E/((XXN-2.)*(E*G-F**2))
      SEB=SQRT(SB)
      PRINT 13
      PUNCH 13
   13 FORMAT(30H      A                  B      )
      PRINT 1,A,B
      PUNCH 1,A,B
    1 FORMAT(2E15.6)
      PRINT 18
      PUNCH 18
   18 FORMAT(//30H    SEA              SEB      )
      PRINT 17,SEA,SEB
      PUNCH 17,SEA,SEB
   17 FORMAT(2E15.4)
      PRINT 15
      PUNCH 15
   15 FORMAT(//54H    C        RC        YCAL        YEXP        DIFF
     1)
      N=XXN
      D05I=1,N
      YC(I)=D+A*X(I)+B*U(I)
```

```
      DEL(I)=YC(I)-Y(I)
      PRINT 3,U(I),X(I),YC(I),Y(I),DEL(I)
      PUNCH 3,U(I),X(I),YC(I),Y(I),DEL(I)
    3 FORMAT(2F11.7,2F10.6,E10.1)
    5 CONTINUE
      IF(M)10,10,6
    6 READ 23,HI,ST,HA
   23 FORMAT(F9.7,F10.7,F10.7)
      PRINT 16
      PUNCH 16
   16 FORMAT(//29H      C          RC       YCAL       )
    8 HO=SQRT(HI)
      YO=D+A*HO+B*HO**2
      PRINT 7,HI,HO,YO
      PUNCH 7,HI,HO,YO
    7 FORMAT(2F11.7,F10.6)
      HI=HI+ST
      IF(HA-HI)10,8,8
      GOTO10
   11 STOP
      END
```

2. Least Squares Program for fitting Viscosity Data to the Extended Jones - Dole Equation. (Equation 6.4).

Program JDANDS.

```
      PROGRAM JDANDS(INPUT,OUTPUT,PUNCH)
      DIMENSION U(30),Y(30),X(30),W(30),YC(30),DEL(30)
10    READ 20,N,M,D
20    FORMAT(2I2,F9.6)
      IF(N)11,11,12
12    PRINT 21
21    FORMAT(1H1)
      E=F=G=0=Q=R=S=T=P=RS=0
24    READ 22,(U(I),Y(I),I=1,N)
22    FORMAT((F9.7,F9.6,F10.7,F9.6,F10.7,F9.6,F10.7,F9.6))
      D04I=1,N
      X(I)=SQRT(U(I))
      W(I)=U(I)**2
      Z(I)=Y(I)-D
      E=E+X(I)**2
      F=F+X(I)**3
      G=G+X(I)**4
      0=0+X(I)**5
      Q=Q+X(I)**6
      R=R+X(I)**8
      S=S+Z(I)*X(I)
```

```
      T=T+Z(I)*X(I)**2
      P=P+Z(I)*X(I)**4
      RS=RS+Z(I)**2
    4 CONTINUE
      V=E*G*R-E*Q**2+F*Q*O-R*F**2+O*F*Q-G*O**2
      A=(S*G*R-S*Q**2+T*Q*O-T*F*R+P*F*Q-P*G*O)/V
      B=(T*E*R-P*E*Q+P*F*O-S*F*R+S*O*Q-T*O**2)/V
      C=(P*E*G-T*E*Q+S*F*Q-P*F**2+T*O*F-S*O*G)/V
      TP=(RS-A*S-B*T-C*P)
      XXN=N
      SA=(TP*(G*R-Q**2))/((XXN-3.)*V)
      SEA=SQRT(SA)
      SB=(TP*(E*R-O**2))/((XXN-3.)*V)
      SEB=SQRT(SB)
      SC=(TP*(E*G-F**2))/((XXN-3.)*V)
      SEC=SQRT(SC)
      PUNCH 13
      PRINT 13
   13 FORMAT(46H        A              B              C       )
      PRINT 1,A,B,C
      PUNCH 1,A,B,C
    1 FORMAT(3E15.6)
      PRINT 18
      PUNCH 18
```

```
18 FORMAT(//47H      SEA            SEB            SEC      )
   PRINT 17,SEA,SEB,SEC
   PUNCH 17,SEA,SEB,SEC
17 FORMAT(3E15.4)
   PRINT 15
   PUNCH 15
15 FORMAT(//64H      C          RC        CSQ      YCAL      YEXP
  1  DIFF      )
   N=XXN
   DO5I=1,N
   YC(I)=D+A*X(I)+B*U(I)+C*W(I)
   DEL(I)=YC(I)-Y(I)
   PRINT 3,U(I),X(I),W(I),YC(I),Y(I),DEL(I)
   PUNCH 3,U(I),X(I),W(I),YC(I),Y(I),DEL(I)
 3 FORMAT(3F11.7,2F10.6,E10.1)
 5 CONTINUE
   IF(M)10,10,6
 6 READ 23,HI,ST,HA
23 FORMAT(F9.7,F10.7,F10.7)
   PRINT 16
   PUNCH 16
16 FORMAT(//39H      C          RC        CSQ      YCAL      )
 8 HO=SQRT(HI)
   HS=HI**2
```

```
      YO=D+A*HO+B*HO**2+C*HO**4
      PRINT 7,HI,HO,HS,YO
      PUNCH 7,HI,HO,HS,YO
    7 FORMAT(3F11.7,F10.6)
      HI=HI+ST
      IF(HA-HI)10,8,8
      GOTO10
   11 STOP
      END
```

3. Least Squares Program for fitting Density Data to the Root Equation. (Equation 3.17).

Program ROOTEQ.

```
      PROGRAM ROOTEQ(INPUT,OUTPUT,PUNCH)
      DIMENSION U(30),Y(30),X(30),YC(30),DEL(30)
   10 READ 20,N,M,A
   20 FORMAT(2I2,F9.6)
      IF(N)11,11,12
   12 PRINT 21
   21 FORMAT(1H1)
      E=F=G=S=T=V=0
   24 READ 22,(U(I),Y(I),I=1,N)
   22 FORMAT((F9.7,F9.6,F10.7,F9.6,F10.7,F9.6,F10.7,F9.6)
      DO4I=1,N
      X(I)=SQRT(U(I))
      Z(I)=Y(I)-A
      E=E+X(I)**4
      F=F+X(I)**5
      G=G+X(I)**6
      S=S+Z(I)*X(I)**2
      T=T+Z(I)*X(I)**3
      V=V+Z(I)**2
    4 CONTINUE
      D=(S*F-T*E)/(F**2-E*G)
```

```
      B=(S-D*F)/E
      XXN=N
      SD=(V-B*S-D*T)*E/((XXN-2.)*(E*G-F**2))
      SED=SQRT(SD)
      SB=(V-B*S-D*T)*G/((XXN-2.)*(E*G-F**2))
      SEB=SQRT(SB)
      PRINT 13
      PUNCH 13
   13 FORMAT(30H          C01          C02      )
      PRINT 1,B,D
      PUNCH 1,B,D
    1 FORMAT(2E15.6)
      PRINT 18
      PUNCH 18
   18 FORMAT(//30H          SE1          SE2      )
      PRINT 17,SEB,SED
      PUNCH 17,SEB,SED
   17 FORMAT(2E15.4)
      PRINT 15
      PUNCH 15
   15 FORMAT(//54H      C       RC       DCAL       DEXP       DIFF
     1)
      N=XXN
      DO5I=1,N
```

```
      YC(I)=A+B*U(I)+D*(X(I)**3)
      DEL(I)=YC(I)-Y(I)
      PRINT 3,U(I),X(I),YC(I),Y(I),DEL(I)
      PUNCH 3,U(I),X(I),YC(I),Y(I),DEL(I)
    3 FORMAT(2F11.7,2F10.6,E10.1)
    5 CONTINUE
      IF(M)10,10,6
    6 READ 23,HI,ST,HA
   23 FORMAT(F9.7,F10.7,F10.7)
      PRINT 16
      PUNCH 16
   16 FORMAT(//29H          C          RC          DCAL      )
    8 H0=SQRT(HI)
      Y0=A+B*H0**2+D*H0**3
      PRINT 7,HI,H0,Y0
      PUNCH 7,HI,H0,Y0
    7 FORMAT(2F11.7,F10.6)
      HI=HI+ST
      IF(HA-HI)9,8,8
    9 GOTO10
   11 STOP
      END
```

4. Explanatory Notes

These programs were written in Chippewa Fortran code, for use on the University of Adelaide C.D.C., 6400 Computer. Each program includes a calculation of the Standard Error in the coefficients of the appropriate equation.

Programs analogous to 1, and 3, were written in AFIT code, for use on an I.B.M. 1620 computer.

Input

The standardised input for all the programs was composed of,

N , the number of data points;

M , an integer, always chosen as unity;

D , the origin-value of the dependent variable;

U(I) and Y(I), a series of values of the concentration,and corresponding values of the variable being fitted;

and HI, ST, and HA, the origin, interval, and final value respectively,of a series of rounded concentrations for which values of the dependent variable, Y, were desired.

Output

The output contained the following information,

a. Values of the coefficients of the appropriate equation, and their respective standard errors.

b. A comparison, at each of the input concentrations, of the value of Y calculated from the equation, using the quoted values of the coefficients, with the input value of Y. The differences between these two quantities, and values of those simple functions of C upon which Y was directly dependent, were also tabulated.

c. Values of Y, calculated from the equation, at rounded concentrations, with the corresponding values of $\sqrt{C}$.

APPENDIX D

PUBLICATIONS

1. H.D. Ellerton, G. Reinfelds, D.E. Mulcahy and P.J. Dunlop,
   Activity, Density and Relative Viscosity Data for Several Amino Acids, Lactamide and Raffinose in Aqueous Solution at 25°C.
   J. Phys. Chem., 68, 398 (1964).
2. H.D. Ellerton, G. Reinfelds, D.E. Mulcahy and P.J. Dunlop,
   The Mutual Frictional Coefficients of Several Amino Acids in Aqueous Solution at 25°C.
   J. Phys. Chem., 68, 403 (1964).

No material submitted in the present thesis is contained in these publications. They contain material formerly submitted in partial fulfilment of the requirements of the Honours Degree of Bachelor of Science at the University of Adelaide.