A PHYSICO-CHEMICAL STUDY OF DILUTE POLYELECTROLYTE SOLUTIONS

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REFERENCES
Summary.

A Physico-Chemical Study of Dilute Polyelectrolyte Solutions.

The discontinuous concentration dependence of various physico-chemical properties of polyvinylpyridinium chloride in dilute aqueous solutions was studied by means of viscosity, conductance, ultraviolet absorption, and pH measurements. Light-scattering measurements failed to confirm the previous interpretation of the above phenomena in terms of aggregation of the polyions. An alternative interpretation in terms of variations in the degree of hydrolysis of the polyions is proposed.

The viscosity behaviour of a number of other strong polyelectrolytes at very high dilutions was investigated. Provided that suitable precautions were taken to ensure the purity of the water used to prepare solutions, the reduced viscosities were found to increase monotonically with dilution, and an approximate value of the intrinsic viscosity could be obtained by the use of the empirical Fuoss equation. These extrapolated values were found to be higher than those calculated on the basis of a fully stretched configuration of the polyions. This discrepancy
is attributed to the polydispersity of the polyelectrolyte samples used.

Some electrochemical properties of aqueous solutions of polyvinylbenzyltrimethylammonium chloride (PBTA-Cl) and polyvinylbuty1pyridinium bromide (PVP-Br) were investigated in the concentration range $5 \times 10^{-5} - 3 \times 10^{-3}$ gram molar. Electrophoretic mobilities of the polyions, determined by the Hittorf method, were found to increase on dilution. The degree of counterion binding, obtained by combining conductance and mobility data, was found to be essentially constant over most of the concentration range studied. Similar behaviour was observed for the counterion activity coefficients. Several possible sources of error in the determination of the degree of binding were investigated. The product of solvent viscosity and polyion mobility, as well as the degree of counterion binding, was found to be almost independent of temperature in the range 5 - 55°. The degree of counterion binding in ethanol solutions of PVP-Br was found to be markedly greater than in aqueous solutions. The results of measurements of counterion binding were in qualitative accord with the predictions of several current theories based on a rod-like polyion model.