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Second-class postage paid at Easton, Pennsylvania.

PRINTED IN THE U. S. A.

The Proceedings of the National Academy of Sciences is published monthly by The National Academy of Sciences
MECHANISMS UNDERLYING THE EQUILIBRIUM REACTIONS BETWEEN IONS AND ION-PAIRS IN SOLUTIONS OF ELECTROLYTES, II. THE EFFECT OF TEMPERATURE*

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Communicated December 12, 1962

The properties of electrolyte solutions are determined by the size, structure, and constitution of the ions of the electrolyte on the one hand and on the size, structure, and constitution of the solvent molecules on the other. The observed properties also depend on the independent variables: concentration, temperature, and pressure. Unless the dependence of the properties on the independent variables is known, it is not possible to determine how these properties may depend on the various constitutional factors of the electrolyte and solvent. Since most measurements are carried out at or near atmospheric pressure and the observed properties are not highly sensitive to this variable, pressure has little effect on most properties as ordinarily observed. However, the properties are quite sensitive to temperature and concentration, particularly the latter.

In the first paper of this series,1 data were presented on the conductance, viscosity, and density of solutions of 

\((n\text{-amyl})_4\text{NCNS}\) in \(p\)-xylene at 52° from a concentration of about \(1 \times 10^{-4} \text{N}\) to the molten electrolyte. Data were also presented for solutions of 

\((n\text{-butyl})_4\text{NCNS}\) in benzene at 25° from a concentration of approximately \(1 \times 10^{-4} \text{N}\) up to the limit of solubility (2.05 N).2 On the basis of these data and other data in the literature3 relating to solutions of the thiocyanate and other electrolytes in benzene at 25°, mechanisms underlying the equilibrium reactions between ions and ion-pairs have been proposed which account qualitatively for observations in \(p\)-xylene at 52° and in benzene at 25° at concentrations above as well as below the conductance minimum.

At concentrations below the conductance minimum, ion-pairs are formed by the interaction of oppositely charged ions due to Coulomb forces. These ion-pairs are dissociated by the impact of solvent molecules whose thermal energy is sufficiently great to do this. These mechanisms are in accord with the law of mass action as commonly accepted and account for the equilibrium between ions and ion-pairs in solvents of various dielectric constant.

At concentrations near and immediately above that of the conductance minimum, a new mechanism comes into play, as a result of which the ion-fraction, \(F_i\), of electrolyte increases with increasing concentration of electrolyte, as shown by an increase in the equivalent conductance. Such an increase in the ion-fraction
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