

JOURNEY FROM ION

TRIPLE ION CLUSTERS

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3.8.5. Activity Coefficients, Bjerrum's Ion Pairs, and Debye's Free Ions

What direct role do the ion pairs have in the Debye–Hückel electrostatic theory of activity coefficients? The answer is simply: None. Since ion pairs carry no net charge,²³ they are ineligible for membership in the ion cloud, where the essential qualification is *charge*. Hence, ion pairs are dismissed from a direct consideration in the Debye–Hückel theory.

This does not mean that the Debye–Hückel theory gives the right answer when there is ion-pair formation. The extent of ion-pair formation decides the value of the concentration to be used in the ionic-cloud model. By removing a fraction θ of the total number of ions, only a fraction $1 - \theta$ of the ions remain for the Debye–Hückel treatment, which interests itself only in the free charges. Thus, the Debye–Hückel expression for the activity coefficient [Eq. (3.120)] is valid for the free ions, with two important modifications: (1) Instead of there being a concentration c of ions, there is only $(1 - \theta)c$; the remainder θc is not reckoned with owing to association. (2) The distance of closest approach of free ions is q and not a . These modifications yield

$$\log f_{\pm} = - \frac{A(z_+z_-)\sqrt{(1 - \theta)c}}{1 + Bq\sqrt{(1 - \theta)c}} \quad (3.159)$$

This calculated mean activity coefficient is related to the measured mean activity coefficient of the electrolyte $(f_{\pm})_{\text{obs}}$ by the relation (for the derivation, see Appendix 3.6)

$$(f_{\pm})_{\text{obs}} = (1 - \theta)f_{\pm} \quad (3.160)$$

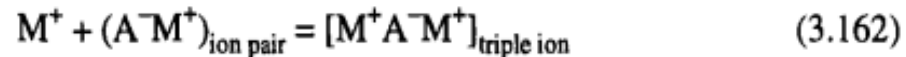
or

$$\log (f_{\pm})_{\text{obs}} = \log f_{\pm} + \log(1 - \theta)$$

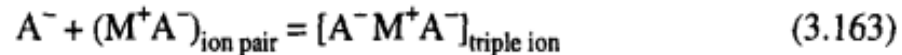
3.8.6. From Ion Pairs to Triple Ions to Clusters of Ions

The Coulombic attractive forces given by $z_+z_-e_0^2/\epsilon r^2$ are large when the dielectric constant is small. When nonaqueous solvents of low dielectric constant are used, the values of dielectric constant are small. In such solutions of electrolytes therefore it has already been stated that ion-pair formation is favored.

Suppose that the electrostatic forces are sufficiently strong then it may well happen that the ion-pair “dipoles” may attract ions and *triple ions* be formed; thus



or



Charged triple ions have been formed from uncharged ion pairs. These charged triple ions play a role in determining activity coefficients. Triple-ion formation has been suggested in solvents for which $\epsilon < 15$. The question of triple-ion formation can be treated on the same lines as those for ion-pair formation.

A further decrease of dielectric constant below a value of about 10 may make possible the formation of still larger clusters of four, five, or more ions. In fact, there is some evidence for the clustering of ions into groups containing four ions in solvents of low dielectric constant.

4.8.11. Triple Ions and Higher Aggregates Formed in Nonaqueous Solutions

When the dielectric constant of the nonaqueous solvent goes below about 15, ions can associate not only in ion pairs but also in ion triplets. This comes about by one of the ions (e.g., M^+) of an ion pair $M^+ \cdots A^-$ Coulombically attracting a free ion A^- strongly enough to overcome the thermal forces of dissociation



From the conductance point of view, ion pairs and triple ions behave quite differently. The former, being uncharged, do not respond to an external field; the latter are charged and respond to the external field by drifting and contributing to the conductance.

The extent of ion-pair formation is governed by the equilibrium between free ions and ion pairs. In like fashion, the extent of triple-ion formation depends on the equilibrium between ion pairs and triple ions.

Conduction minima

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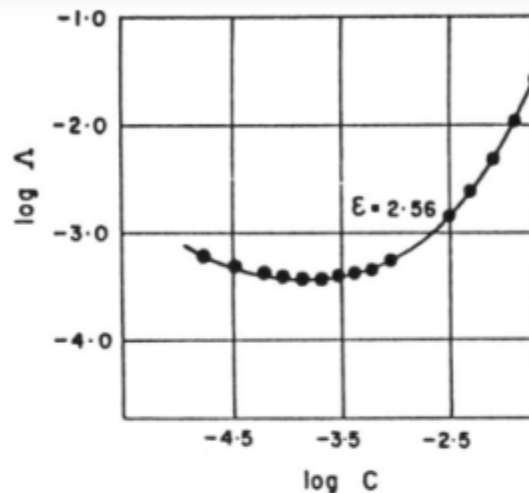
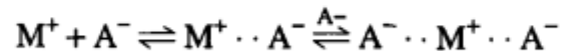


Fig. 4.109. Minimum in the curve for equivalent conductivity vs. concentration in the case of tetraisoamylammonium nitrate in a water–dioxane mixture of dielectric constant $\epsilon = 2.56$.



Thus, the greater the stoichiometric concentration, the greater is the ion-pair formation and triple-ion formation.

With increasing concentration, therefore, ion-pair formation dominates the equivalent conductivity, which decreases with increasing concentration faster than if there had been no formation. At still higher concentrations, when triple-ion formation starts becoming significant, the equivalent conductivity starts increasing after passing through a minimum. This behavior has been experimentally demonstrated (Fig. 4.109).

4.8.12. Some Conclusions about the Conductance of Nonaqueous Solutions of True Electrolytes

The change from aqueous to nonaqueous solutions of *true* electrolytes results in characteristic effects on the conductance. The order of magnitude of the equivalent conductivity at infinite dilution is approximately the same in both types of solutions and is largely dependent on the viscosity of the solvent. However, the slope

of the equivalent-conductivity versus concentration curve is considerably more negative in nonaqueous solutions than in the corresponding aqueous solutions. This means that the actual specific conductivity σ , which is the significant quantity as far as the conducting power of an actual solution is concerned, is much lower for nonaqueous solutions. Ion-pair formation worsens the conductance situation; triple-ion formation may be a slight help.

Thus, nonaqueous solutions of true electrolytes are not to be regarded with unrestrained optimism for applications in which there is a premium on high specific conductivity and minimum power losses through resistance heating. One may have to think of solutions of *potential* electrolytes where there is an ion-forming reaction between the electrolyte and the solvent (Section 2.4).

Reference Book
Bockris and Reddy "Modern Electrochemistry 1"
Second edition Ionics

Thank you