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**EVALUATION OF THE SOLUBILITY OF
ELECTROLYTES FROM
CONDUCTIVITY MEASUREMENTS**

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THE EVALUATION OF THE SOLUBILITY OF ELECTROLYTES FROM CONDUCTIVITY MEASUREMENTS

The existence of reliable theoretical expressions for the concentration dependence of electrolytic conductivity facilitates the calculation of solubility from the value of molar conductivity of the saturated solution. A procedure is recommended and the expressions for the concentration dependence of the molar conductivity are given. They may be used for all strong electrolytes and for weak symmetric electrolytes. It may be advantageous for solubility determinations to measure the conductivity of the saturated solution as well as those of the solutions prepared by diluting it.

Electrochemical techniques are frequently used to determine the solubility of salts in solution. In particular, measurements of EMF and of electrolytic conductivity in the saturated solutions would yield directly the values of the ionic concentration of the saturated solutions if they were to behave ideally. When interionic interactions in the solutions of strong electrolytes are adequately described by the Debye-Hückel-Onsager approach for electrolyte solutions, there are theoretical treatments which permit the calculation of the ionic concentration whenever the saturated solution is not very concentrated (ca. 0.1 molal). Further calculation or treatment of the experimental data is necessary for the determination of solubility whenever the electrolytes are not completely dissociated.

When conductivity measurements are used, calculations from experimental data are facilitated by the existence of several well established theoretical expressions that describe accurately the variation of molar conductivity with concentration (up to 0.1 molal). With these expressions and additional information about ionic mobilities from the literature (*i.e.*, conductivities at infinite dilution), it is possible to calculate from the measured conductivity a precise value for the ionic concentration in the saturated solution.

In detail the method proceeds as follows: (a) The specific conductivity of the saturated solution is determined and the contribution of the solvent conductivity to the total conductivity is subtracted from the experimental value. This step is particularly important in the case of sparingly soluble salts because the solvent may contribute a significant fraction of the total ionic concentration observed in the saturated solution. In general, solvents of good quality may be considered to contribute to the ionic concentration less than 10^{-6} moles per dm^3 , but this contribution may easily amount to ten times more if the solvent is not carefully purified. (b) The value obtained for the conductivity of the solution and a theoretical expression giving the change of molar conductivity with ionic concentration, c_1 , is used to calculate the actual values of c_1 for the saturated solution.

The procedure suggested by Popovych (ref. 1) should be followed whenever possible (especially for solvent systems where little information about the behaviour of electrolytes is available). This procedure consists in taking measurements of the conductivity of solutions prepared by diluting the saturated solution by a known factor. In this way, provided the values of the dielectric constant and the viscosity of the solvent system are known, a self-consistent set of data may be obtained from which the solubility of the electrolyte may be calculated even when no values of the ionic conductivities at infinite dilution (λ^∞) are available in the literature. In this case, one has a normal set of Λ^0 molar conductivity values as function of concentration, which can be processed self-consistently. The only difference to more typical conductivity work (ref. 2) being the fact that there will be only a few concentration points and the highest concentration will correspond to that of the saturated solution.

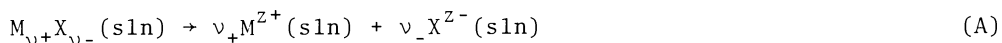
For sparingly soluble salts where the saturated solution is very dilute, it may not be necessary to make the complete correction for the concentration dependence of the molar conductivity and simpler equations can be employed. This is particularly important for unsymmetrical electrolytes where the mathematical expressions that must be employed are more involved, thus justifying a simpler procedure from the practical point of view.

In what follows, methods of dealing with conductivity data corresponding to the saturated solution for the case of dissociated binary electrolyte solutions are considered. At this point it is important to mention that for unsymmetrical electrolytes which are appreciably associated, the electrolyte solution must be considered a ternary system; in this case the equations to be employed become much more complicated and we do not consider that conductivity is a suitable technique to determine the solubility of associated unsymmetrical electrolytes.

Completely dissociated electrolytes

There are a number of theoretical treatments which describe accurately the change of molar conductivity with electrolyte concentration. These have been fully tested for symmetrical electrolytes (ref. 2). Recently, two theoretical expressions for unsymmetrical salts and for electrolyte mixtures have become available (refs. 3,4), however they have not been so fully tested so far. For this reason and for the purpose of solubility determinations we shall give an expression which is very well established for symmetrical electrolytes and a different one for the case of an unsymmetrical pure binary electrolyte. The latter is very close to the former expression when $|z_+| = |z_-|$, but not exactly the same.

Let us consider the salt $M_{\nu_+}X_{\nu_-}$, which upon dissolution dissociates into ions according to:



Due to electroneutrality $\nu_+|z_+| = \nu_-|z_-|$. If c is the molar concentration of the electrolyte, then $C = \nu_+|z_+| = \nu_-|z_-|$ gives the number of moles per dm^3 of the substance

$$\left\{ \frac{1}{\nu_+|z_+|} M_{\nu_+}X_{\nu_-} \right\}$$

i.e., its equivalent concentration. In this work we shall give expressions for the molar conductivity of that substance, which strictly should be denoted by (ref. 5)

$$\Lambda \left(\frac{1}{\nu_+|z_+|} M_{\nu_+}X_{\nu_-} \right)$$

This quantity coincides with what was called equivalent conductivity in the older literature. For the sake of simplicity, however, we shall denote this quantity in what follows directly by Λ .

The (concentration) ionic strength is given by

$$I = \frac{1}{2}(\nu_+z_+^2 + \nu_-z_-^2)c = \frac{1}{2}(|z_+| + |z_-|)C \quad (1)$$

For symmetrical electrolytes (*i.e.*, having $z = |z_+| = |z_-|$ and $\nu_+ = \nu_- = 1$, eq. (1) becomes:

$$I = z^2c = zC \quad (2)$$

All the theoretical treatments of electrolytic conductivity derive expressions for the concentration dependence of the molar conductivity which upon expansion give an equation of the form (ref. 2)

$$\Lambda = \Lambda^\infty - S\sqrt{I} + E\ln(I) + J_1I - J_2I^{3/2} \quad (3)$$

For the purpose of having a means to determine the solubility of electrolytes from conductivity data for the saturated solution, the use of an expanded equation of the form of eq. (3) does not require further justification. All the theoretical treatments agree that the coefficients S and E of eq. (3) depend only on the charge type of the electrolyte being considered, on the

mobility of the ions and on the dielectric constant and viscosity of the solvent and the temperature of the solution. On the other hand, the expressions for the J_i coefficients depend on the particular theoretical treatment employed to derive eq. (3), but in all cases the J_i coefficients depend also on an electrolyte-specific parameter d , which corresponds to the minimum distance at which two oppositely charged *free* ions can approach each other.

The equations recommended in the present work are that of Fuoss-Hsia (ref. 2) for symmetrical electrolytes and that of Quint and Viallard (ref. 4) for unsymmetrical electrolytes. It must be noted that the latter treatment was derived for mixtures of ions and should thus apply also to electrolyte mixtures. However, it does not seem justifiable for solubility determinations to go beyond the case of pure binary unsymmetrical electrolytes. Furthermore, due to its algebraic complications the eq.(3) from Quint and Viallard has been restricted to the term linear in concentration (*i.e.*, the J_1 term). The coefficient in eq.(3) for the two theoretical treatments are given in Table 1. The following quantities are necessary to use Table 1:

$$\begin{aligned} \frac{\kappa}{\sqrt{I}} &= \left(\frac{8\pi e}{\epsilon kT}\right)^{1/2} = \frac{50.2901}{(\epsilon T)^{1/2}} \text{Å}^{-1} \\ (bd) &= \frac{|z_+ z_-| e^2}{\epsilon kT} = \frac{16.7102 \cdot 10^4 |z_+ z_-|}{\epsilon T} \text{Å} \\ q &= \frac{|z_+ z_-| \Lambda^\infty}{(|z_+| + |z_-|)(|z_-| \lambda_+^\infty + |z_+| \lambda_-^\infty)} \quad (= \frac{1}{2} \text{ for } |z_+| = |z_-|). \\ B &= \frac{(1-q)^3 \ln(1+q^{1/2}) + q(q^2 - q + 2) \ln(2+q^{1/2}) + 2q(1-2q) \ln(1+2q^{1/2})}{2q(1-q)} + \\ &+ 0.5772 - \frac{6+15q^{1/2}+30q+23q^{3/2}-6q^2}{12q^{1/2}(1+q^{1/2})^2} \quad (4) \\ A &= 1 + \frac{(z_+ + z_-)(|z_+|z_+ + |z_-|z_-)}{q|z_+ z_-|(|z_+| + |z_-|)} \quad (= 1 \text{ for } |z_+| = |z_-|). \\ D &= \frac{(q^3 - q^2 + 5q - 1) \ln(1+q^{1/2}) + q(1-q)(q-4) \ln(2+q^{1/2}) - 4q \ln 2}{2q(1-q)} + 0.3456 + \\ &+ \frac{6+19q^{1/2}-5q-6q^{3/2}}{12q^{1/2}(1+q^{1/2})} - \frac{(|z_+|z_+ + |z_-|z_-)(z_+ + z_-)}{q|z_+ z_-|(|z_+| + |z_-|)} (2.5407) \end{aligned}$$

The numerical constants appearing in these expressions were calculated employing the tabulation of fundamental constants compiled by McGlashan, Paul and Whiffen (ref. 5). For the viscosity the SI units are employed, *i.e.* Pa.s = 10 poise = 1 dapoise.

Depending on the ionic strength of the saturated solution it may be necessary to take into account the contribution of the higher order terms in eq.(3). To simplify the calculations it is convenient to suggest two levels of precision:

- i) Very dilute saturated solutions. The J_i terms may be omitted in the calculations so that no size parameter for the electrolyte needs to be used in this case.
- ii) Whenever the ionic concentration of the saturated solution is above ca. 0.001 mol/dm³, all terms in eq.(3) should be used for the calculation.

In the calculation of the solubility it will be necessary to have the value of Λ^∞ for the electrolyte being considered. These values can be obtained from the available literature either directly or calculated by application of the principle of independent migration to values of Λ^∞ reported for electrolytes in the same solvent system which are related to the one being studied, so that,

$$\Lambda_{MX}^\infty = \Lambda_{NX}^\infty + \Lambda_{MY}^\infty - \Lambda_{NY}^\infty \quad (5)$$

With regard to the size parameter d , the best choice is to take it equal to

TABLE 1. Expressions for the Coefficients of the conductivity eq. (3).
(Units S.cm²mol⁻¹)

Term	Coef.	Asymmetric electrolyte (ref. 4)	Symmetric electrolyte (ref. 2)
$\gamma\sqrt{I} = \frac{(\kappa b d)}{3} \frac{q}{1+\sqrt{q}}$	γ	$S = \gamma\Lambda^\infty + \beta$ $2.8012 \cdot 10^6 \frac{ z_+z_- }{(\epsilon T)^{3/2}} \frac{q}{(1+\sqrt{q})}$	$S = \gamma\Lambda^\infty + \beta$ $82.045 \cdot 10^4 \frac{z^2}{(\epsilon T)^{3/2}}$
$\beta\sqrt{I} = \frac{(z_+ + z_-)}{6\pi\eta} eF\kappa$	β	$4.1243 \frac{(z_+ + z_-)}{\eta(\epsilon T)^{1/2}}$	$8.2487 \frac{z}{\eta(\epsilon T)^{1/2}}$
$E_1 I = \frac{(\kappa b d)^2}{12} q$	E_1	$E = E_1\Lambda^\infty - 2E_2$ $5.8850 \cdot 10^{12} q \frac{(z_+z_-)^2}{(\epsilon T)^3}$	$E = E_1\Lambda^\infty - E_2$ $2.9425 \cdot 10^{12} \frac{z^4}{(\epsilon T)^3}$
$2E_2 I = \frac{\kappa b d}{8} \beta (2qA) = 2E_2'(2qA)$	E_2	$2.1662 \cdot 10^6 (2qA) \cdot \frac{ z_+z_- (z_+ + z_-)}{\eta(\epsilon T)^2}$	$4.3324 \cdot 10^6 \frac{z^3}{\eta(\epsilon T)^2}$
$\sigma_1 I = 2E_1 \{ \Delta_1 + \ln(\kappa d/\sqrt{I}) \}$	Δ_1	$J_1 = \sigma_1\Lambda^\infty + \sigma_2$ $\frac{2b^2+2b-1}{b^3} + B$	$J_1 = \sigma_1\Lambda^\infty + \sigma_2$ $\frac{2b^2+2b-1}{b^3} - 0.90735$ (for $b=2$, $\Delta_1=2.2824$)
$\sigma_2 I = 4E_2' q \{ \Delta_2 - 2A \ln(\kappa d/\sqrt{I}) \}$	Δ_2	$D + \frac{6q+(24-13q)b}{6qb^2}$	$\frac{22}{3b} + 0.01420$ (for $b=2$, $\Delta_2=3.6808$)
$\sigma_3 I^{3/2} = 4\kappa b d E_1 \Delta_3$	Δ_3		$J_2 = \sigma_3\Lambda^\infty + \sigma_4$ $\frac{0.9571}{b^3} + \frac{1.1187}{b^2} + \frac{0.1523}{b}$ (for $b=2$, $\Delta_3=0.47546$)
$\sigma_4 I^{3/2} = 2\kappa b d E_2' \Delta_4 - \Delta_5 E_2' \beta / \Lambda^\infty$	Δ_4		$\frac{1}{b^3} (0.5738b^2 + 7.0572b - \frac{2}{3}) - 0.6461$ (for $b=2$, $\Delta_4=1.3218$).
	Δ_5		$\frac{4}{3b} - 2.2194$ (for $b=2$, $\Delta_5=1.5527$)

the Bjerrum distance, *i.e.*, $d = |z_+ z_-| e^2 / 2\epsilon kT$. However if the ion sizes are known to exceed this value, the sum of crystallographic radii should be used or some educated guess of the closest distance of approach of oppositely charged ions in that solvent medium. The use of the Bjerrum characteristic distance implies that $b=2$; Table 1 records the expressions for J_1 and J_2 when $b=2$.

For electrolytes having a closest distance of approach of ions smaller than the value of the Bjerrum distance, association will usually be observed. However, it should be noted that even when $d < |z_+ z_-| e^2 / 2\epsilon kT$, electrolytes may be treated as completely dissociated if the difference between both distance parameters is relatively small (*e.g.*, KCl in water at 298 K).

The conductivity studies of Justice and coworkers (ref. 6) for solvent media having a dielectric constant smaller than 20, as well as the case of (2-2) sulfates in water (ref. 7), show that the Bjerrum distance is a good choice for the minimum distance of closest approach of *free* ions, even when the interionic electrostatic interactions may be rather large.

Incompletely dissociated electrolytes

For partially dissociated symmetric electrolytes, the equilibrium



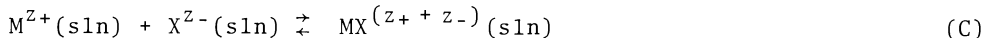
has to be considered. This process reduces the ionic concentration of the solution by ion-pairing. The ionic strength is now given by

$$I = z^2 \alpha c \quad (6)$$

where α is the degree of dissociation of the electrolyte. The molar conductivity of the species $\{ \frac{1}{2} MX \}$ is given by

$$\Lambda = \alpha(\Lambda^\infty - S\sqrt{I} + EI \ln(I) + J_1 I - J_2 I^{3/2}) \quad (7)$$

For unsymmetrical electrolytes, on the other hand, the association process leads to the formation of ion pairs which will have a net charge and, consequently will contribute to the total conductivity of the solution. That is, if ion pairing is described by



$MX^{(z_+ + z_-)}$ ions are produced and these will contribute a fraction to the total charge being transported through the solution. Just to illustrate one instance in which the ion pair $A \equiv MX^{(z_+ + z_-)}$ has a positive charge, we have

$$\Lambda = \alpha \Lambda \left\{ \frac{1}{v_+ z_+} M_{v_+} X_{v_-} \right\} + (1-\alpha) \frac{|z_+ + z_-|}{z_+} \Lambda \left\{ \frac{1}{|z_+ + z_-|} AX_{v_-} \right\} \quad (8)$$

with α equal to the fraction of dissociated cations (M^{z+}). Eq.8 shows that it is effectively a solution with two electrolytes $M_{v_+} X_{v_-}$ and AX_{v_-} and it is therefore necessary to know the conductivity at infinite dilution of the salt AX_{v_-} . Thus, the system is constituted by three different ionic species (M^{z+} , X^{z-} and $A^{(z_+ + z_-)}$) and the complete equation for the conductivity of electrolyte mixtures should be used. This case will not be considered here because the need of values for the conductivity at infinite dilution of the ion pairs ($\lambda^\infty(A^{(z_+ + z_-)})$) and the cumbersome nature of the numerical calculation involved implies that conductivity is not the best tool to determine the solubility of these type of electrolytes.

Returning now to the case of associated symmetrical electrolytes, the equilibrium constant (K_A) describing the association process (B), is

$$K_A = \frac{1-\alpha}{\alpha^2 c_s \gamma_{\pm}^2} \quad (9)$$

where the solubility c_s is related to the ionic concentration by $c_i = \alpha c_s$, *i.e.* the ionic concentration of the saturated solution; γ_{\pm}^2 is the mean activity coefficient of the free ions in the molarity scale of concentration and is given by the Debye-Hückel expression:

$$\ln y_{\pm} = - \frac{bdk}{2(1+\kappa d)} \quad (10)$$

Using eq. (9), eq. (7) may be written in the form

$$\Lambda = \Lambda^{\infty} - S\sqrt{I_s} + EI_s \ln(I_s) + J_1 I_s - J_2 I_s^{3/2} - K_A I_s y_{\pm}^2 \Lambda / z^2 \quad (11)$$

where I_s denotes the ionic strength of the saturated solution. It is clear that the concentration variable in eq. (11) is the ionic concentration of the saturated solution.

In order to deal with associated symmetric electrolytes having as the only experimental data the conductivity of the saturated solution, it is necessary to know the value of K_A unless the conditions are such that the difference between c_i and c_s does not justify the correction for incomplete dissociation, e.g. very dilute saturated solution or very small K_A .

Up to this point if the value of K_A were known from other experimental measurements, the nature of the association process (B) is completely irrelevant in order to calculate the solubility from eq. (11) except for the fact that only a simple pair of ions with no net charge should result from the association process.

For the case of typical electrostatic ionic association as described by Bjerrum (ref. 8), it is possible to calculate K_A . On the other hand, when the association process of the ions is governed by other types of interactions (non-electrostatic), there is no general expression for the calculation of K_A . In this case it is necessary to obtain the value of the association constant from other experimental studies or from a self-consistent set of conductivity measurements, as suggested by Popovych (ref. 1), from which not only the solubility of the electrolyte, but also K_A can be calculated. Whenever there are more than one conductivity value for the particular electrolyte-solvent system being studied, a set of equations of the type:

$$\Lambda_i = \Lambda^{\infty} - g(\alpha c_s f_i; K_A, \Lambda) \quad (12)$$

may be written, where f_i is the dilution factor and $g(x,y,\dots)$ gives the concentration dependence of the molar conductivity. Depending on the number of conductivity data available, the eqs. (12) will allow the calculation of the values of some of the parameters, e.g. K_A or Λ^{∞} , by fitting the data to that system of equations. Using an iterative method, the solubility K_A and Λ^{∞} can in principle be determined.

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