

A Model to Evaluate Solubility of Sparingly Soluble Salts in Electrolyte Solutions

HAMZEH M. ABDEL-HALIM*, AYMAN A. ISSA and ADNAN S. ABU-SURRAH

Department of Chemistry, The Hashemite University, College of Science

P.O. Box 150459, Zarqa 13115, Jordan

E-mail: hamzehah@hu.edu.jo

A simple model to evaluate the solubility of sparingly soluble salts in aqueous electrolyte solutions at various ionic strengths is presented. The calculations are based on a model presented earlier, which calculates the mean activity coefficient using an extended Debye-Hückel formulation. Calculations were performed, in aqueous solutions at 25°C, for various salts with concentration range between 0.10–7.0 m. The calculated solubility and the conditional solubility product constant were compared with experimental values reported in literature. Good agreement is observed over a wide range of ionic strength.

Key Words: Solubility, Salts, Electrolyte solutions.

INTRODUCTION

Solubility is an important phenomenon that plays a significant role in determining the physical and chemical properties of solutions. For sparingly soluble electrolytes, a dynamic equilibrium exists for the solid in contact with its saturated solution. The solubility of a salt in an electrolyte solution depends on many factors; among these is the interaction between ions of the electrolyte in the solution. At high concentrations, this interaction becomes extremely important to the extent that it will determine the solubility of the salt in the solution. Unfortunately, theoretical investigations of ionic interaction effect on solubility are scarce. The present study is an attempt to contribute to our understanding in this area.

Experimental determination of solubility and solubility product has been widely investigated by several researchers for a vast number of salts using various analytical and physical methods^{1–17}. Employing a solvent extraction method using thenoyltrifluoroacetone (TTA) and ²³³U, Fujiwara *et al.*² determined the hydrolysis constants and solubility product of UO₂·xH₂O. Values for the solubility product, the enthalpies of solution and the formation constants for silver halide complexes were listed and compared. Fujiwara *et al.*⁴ measured the solubility of PuO₂·xH₂O at 25°C in an NaClO₄ solution containing Na₂S₂O₄ as a reductant. The experiment was carried out by an over-saturation method at ionic strength

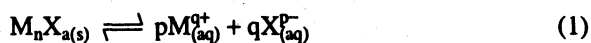
$I = 1.0$ and by an under saturation method at $I = 0.5, 1.0$ and 2.0 . From the obtained results, the solubility product constant of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, for $\text{PuO}_2 \cdot x\text{H}_2\text{O} = \text{Pu}^{4+} + 4\text{OH}^- + (x - 2)\text{H}_2\text{O}$ at $I = 0.5, 1.0$ and 2.0 was determined. The solubility and the solubility product of crystalline $\text{Ni}(\text{OH})_2$ were studied in solutions of 0.01 M NaClO_4 with pH ranging from 7 to near 14 by Mattigod *et al.*¹⁰ These data, in conjunction with Pitzer ion interaction parameters given in the literature, were used to model the reported solubilities of $\text{Ni}(\text{OH})_2$ in chloride, sodium acetate and potassium chloride solutions. They found that the model predictions for these systems were in agreement with the experimental data from the literature. The solubility product constant of mercurous acetate at various ionic strengths in aqueous medium was determined by de Moraes *et al.*¹². The conditional and thermodynamic solubility products were determined in aqueous solution at 25°C and ionic strength between 0.300 and 3.000 mol/L (NaClO_4). By emf measurements, free energy of formation and solubility product constant of mercuric sulfide were determined by Goates *et al.*¹⁷

Theoretical treatment of interaction between ions has been considered by several investigators¹⁸⁻²⁶. However, little emphasis has been given on theoretical modeling of the solubility and solubility product constant. Theoretical models for the interpretation of properties of strong electrolytes in dilute solutions have been based on the Debye-Hückel (DH) law¹⁸⁻²⁰. However, in the high concentration range of practical importance, ions cannot be treated as point charges and their size in solution has to be considered. Little theoretical progress has been made in this area. Furthermore, the available models for calculation of activity coefficients, and hence, the solubility product constant, at high concentrations have many limitations²¹⁻²⁶. Most of the above models did not pay sufficient attention to the effect of ionic charge and size on the value of the activity coefficient. In addition, these models tend to lack simplicity, use complex mathematical approaches and need elaborate calculations. Abdel-Halim²⁷ introduced a simple, easy to use and flexible model for the evaluation of activity coefficients. This model takes into consideration the size, charge and concentration of ions.

In the present work, a simple model to calculate the solubility and the conditional solubility product constant is presented. Calculations were performed for aqueous solutions of various salts in different electrolytes, over a wide concentration range, at 25°C . The model was checked by comparing calculated values with experimental results. Good agreement is found.

The model

The solubility of sparingly soluble salt, M_nX_m , in aqueous solution, can be presented by the mass-action equilibrium equation, given by:



Here, p and q represent the valancies of the cation, M , and the anion, X , in the salt, respectively. The thermodynamic solubility product constant, K_{sp} , for this salt is given by the expression

$$K_{sp} = a_M^p a_X^q \quad (2)$$

where 'a' is the activity, defined by the concentration of the ion in solution and its activity coefficient, γ , such that

$$a^p = [M^{q+}]^p \gamma_X^p \quad (3)$$

$$a^q = [X^{p-}]^q \gamma_X^q \quad (4)$$

The solubility product constant for the salt is then given by

$$K_{sp} = [M^{q+}]^p [X^{p-}]^q \gamma_M^p \gamma_X^q \quad (5)$$

The solubility of the salt, s , is related to K_{sp} by the relation

$$K_{sp} = (p \times s)^p (q \times s)^q \gamma_M^p \gamma_X^q \quad (6)$$

For the salt $M_p X_q$ dissolved in an electrolytic solution, $A_m B_n$, electrical neutrality requires that $m|Z_+| = n|Z_-|$, where Z_+ and Z_- are the charges of cation (A^{n+}) and anion (B^{m-}), respectively. The mean activity coefficient, γ_{\pm} , is given by

$$\log \gamma_{\pm} = \frac{1}{p + q + m + n} (p \log \gamma_+ + q \log \gamma_- + m \log \gamma_+ + n \log \gamma_-) \quad (7)$$

For a sparingly soluble salt $M_p X_q$, with $K_{sp} < 10^{-10}$, its contribution to the activity coefficient is negligible. Therefore, the mean activity coefficient is given by

$$\log \gamma_{\pm} = \frac{1}{(m + n)} (m \log \gamma_+ + n \log \gamma_-) \quad (8)$$

The solubility product constant is then given by

$$K_{sp} = (p \times s)^p (q \times s)^q \gamma_{\pm} \quad (9)$$

The calculations of solubility for a salt in aqueous solution require knowledge of its activity coefficient. Basic treatment of the activity coefficient is presented by the Debye-Hückel Limiting Law (DHLL). According to DHLL, the mean activity coefficient is given by

$$\log \gamma_{\pm} = -Z_+ |Z_-| B \sqrt{I} \quad (10)$$

where I is the ionic strength and B is a constant given by

$$B = \frac{e^3}{2.303 \times 8\pi} \left(\frac{2L}{\epsilon_0^3 e^3 k^3 T^3} \right)^{1/2} \quad (11)$$

Here, L is Avogadro's constant, k is Boltzmann's constant, T is the temperature

of the solution, e is the electronic charge, ϵ is the dielectric constant for the solvent and ϵ_0 is the permittivity of vacuum.

Using Eqn. (10) in Eqn. (9) in the calculations yields lower solubility values than those found experimentally. Eqn. (10), which is known as the Debye-Hückel limiting law (DHLL), is adequate at low concentrations. However, at high concentrations, experimental observations indicate that the value of $\log \gamma_{\pm}$ is significantly less negative than predicted by Eqn. (10), and at sufficiently high concentrations, it may actually attain positive values and large deviation from experimental values is observed.

An important factor that accounts for the deviation from experimental observations is the assumption that ions are point charges. Actually, ions occupy spaces and have definite sizes. The centres of the ions can approach each other only to a distance (a), the distance of closest approach. Also, the work need to remove some solvent molecules from effective parking in the ionic solution's activity has to be considered. The work in this process must be added to the work done in building up the ionic atmosphere.

Taking this into consideration, Abdel-Halim²⁷ introduced an empirical model to calculate the activity coefficient. The model included correction factors which account for the distance of closest approach and the work needed to remove the solvent molecules from the effective parking of the ionic solution's activity. The model is proven to agree well with experimental values, given by

$$\log \gamma_{\pm} = -Z_+ |Z_-| B \sqrt{I} \frac{1}{1 + (a/r_a)} + CI - D \sqrt{I} \quad (12)$$

where C and D are empirical parameters that depend on the nature of the ion, ' a ' is the distance of closest approach, and r_a is the thickness of the ionic atmosphere around ions, given by

$$r_a = \left(\frac{\epsilon_0 \epsilon k T}{2e^2 L I} \right)^{1/2} \quad (13)$$

Equations (9) and (12) were used to calculate the solubility of sparingly soluble salts in electrolyte solutions for various salts at 25°C over a wide concentration range.

RESULTS AND DISCUSSION

The solubility of several partially soluble salts in solutions of a large number of electrolytes in aqueous medium were calculated at 25°C. Calculations were performed in electrolyte solutions of uni-, di- and trivalent cation halides. The parameters a , C and D in Eqn. (12) have to be determined. They were determined following a previously published method²⁷.

The distance of closest approach is calculated using the formula²⁷

$$a = r_{ac} + \frac{1.10 |\Delta r| Z_c}{I_c^{0.7(2-Z_c)}} \times CF_a \quad (14)$$

where r_{ac} is the sum of Pauling ionic radii of the cation and the anion, Δr is the difference in the ionic radii of the ions, Z_c is the charge of the cation, r_c is the radius of the cation and CF_a is a correction factor that depends on the nature of the cation²⁷.

The parameters C and D for uni-, di-, and trivalent cations were calculated using the formulae²⁷:

$$(1) \text{ Salts of univalent cations: } C_{\text{salt}} = C_{\text{NaCl}} \times CF_1$$

$$D_{\text{salt}} = D_{\text{NaCl}} \times CF_1$$

where

$$CF_1 = \left(\frac{r_{\text{Na}^+}}{r^+} \right)^3 \left(\frac{r^-}{r_{\text{Cl}^-}} \right)^3 \quad (15)$$

$$(2) \text{ Salts of divalent cations: } C_{\text{salt}} = C(\text{MgCl}_2) \times CF_2$$

$$D_{\text{salt}} = D(\text{MgCl}_2) \times CF_2$$

where

$$CF_2 = \left(\frac{r_{\text{Mg}^{2+}}}{r^{2+}} \right)^{0.47} \left(\frac{r^-}{r_{\text{Cl}^-}} \right)^{2.3} \quad (16)$$

$$(3) \text{ Salts of trivalent cations: } C_{\text{salt}} = C(\text{AlCl}_3) \times CF_3$$

$$D_{\text{salt}} = D(\text{AlCl}_3) \times CF_3$$

where

$$CF_3 = \left(\frac{r_{\text{Al}^{3+}}}{r^{3+}} \right)^{XCF}$$

and

$$XCF = \frac{r^{3+} - r_{\text{Al}^{3+}}}{r^{3+} + r_{\text{Al}^{3+}}} \quad (17)$$

Here, r^+ and r^- are the radii of cation and anion, respectively. Values of C and D for NaCl, MgCl₂ and AlCl₃ are reported²⁷.

To make comparison with experimental data, the conditional solubility product constant, K'_{sp} , is calculated from the thermodynamic equilibrium constant, K_{sp} , using the relation

$$K_{sp} = [M^{q+}]^p [X^{p-}]^q \gamma_{\pm} = K'_{sp} \gamma_{\pm} \quad (18)$$

Using Eqn. (9) and Eqns. (11) through (18), a FORTRAN computer program has been prepared to evaluate the solubility and the conditional solubility product constant of the salt. Calculations were performed for a large number of salts in several electrolytes aqueous solutions, with wide range of concentrations, at 25°C. Table-1 shows the results of calculations for ten selected salts in five different electrolyte solutions.

TABLE-1

SOLUBILITY AND CONDITIONAL SOLUBILITY PRODUCT CONSTANT K'_{sp}
(IN PARENTHESES) OF SOME SPARINGLY SOLUBLE SALTS IN AQUEOUS
ELECTROLYTE SOLUTIONS OF VARIOUS CONCENTRATIONS AT 25°C

AgCl					
Electrolyte	Molality, m				
	0.1	1.0	3.0	5.0	7.0
LiCl	1.32×10^{-05} (1.73×10^{-10})	1.11×10^{-05} (1.22×10^{-10})	7.49×10^{-06} (5.61×10^{-11})	5.07×10^{-06} (2.57×10^{-11})	3.42×10^{-06} (1.17×10^{-11})
NaCl	1.34×10^{-05} (1.78×10^{-10})	1.28×10^{-05} (1.63×10^{-10})	1.16×10^{-05} (1.34×10^{-10})	1.05×10^{-05} (1.10×10^{-10})	9.51×10^{-06} (9.05×10^{-11})
KCl	1.34×10^{-05} (1.79×10^{-10})	1.32×10^{-05} (1.74×10^{-10})	1.27×10^{-05} (1.62×10^{-10})	1.23×10^{-05} (1.51×10^{-10})	1.18×10^{-05} (1.40×10^{-10})
MgCl ₂	1.36×10^{-05} (1.86×10^{-10})	1.04×10^{-05} (1.08×10^{-10})	4.89×10^{-06} (2.40×10^{-11})	2.20×10^{-06} (4.84×10^{-12})	9.71×10^{-07} (9.43×10^{-13})
AlCl ₃	1.34×10^{-05} (1.78×10^{-10})	8.16×10^{-06} (6.66×10^{-11})	2.32×10^{-06} (5.39×10^{-12})	3.26×10^{-07} (1.06×10^{-13})	1.68×10^{-07} (2.81×10^{-14})
Hg ₂ Cl ₂					
LiCl	1.16×10^{-09} (1.35×10^{-18})	9.76×10^{-10} (9.52×10^{-19})	6.60×10^{-10} (4.36×10^{-19})	4.47×10^{-10} (2.00×10^{-19})	3.02×10^{-10} (9.12×10^{-20})
NaCl	1.18×10^{-09} (1.39×10^{-18})	1.13×10^{-09} (1.27×10^{-18})	1.02×10^{-09} (1.04×10^{-18})	9.26×10^{-10} (8.57×10^{-19})	8.39×10^{-10} (7.04×10^{-19})
KCl	1.18×10^{-09} (1.40×10^{-18})	1.16×10^{-09} (1.35×10^{-18})	1.12×10^{-09} (1.26×10^{-18})	1.08×10^{-09} (1.17×10^{-18})	1.04×10^{-09} (1.09×10^{-18})
MgCl ₂	1.20×10^{-09} (1.45×10^{-18})	1.09×10^{-09} (1.18×10^{-18})	4.32×10^{-10} (1.86×10^{-19})	1.94×10^{-10} (3.77×10^{-20})	8.56×10^{-11} (7.33×10^{-21})
AlCl ₃	1.18×10^{-09} (1.39×10^{-18})	7.20×10^{-10} (5.18×10^{-19})	2.05×10^{-10} (4.19×10^{-20})	5.56×10^{-11} (3.09×10^{-21})	1.48×10^{-11} (2.19×10^{-22})
MgCO ₃					
LiCl	2.56×10^{-03} (6.55×10^{-06})	2.15×10^{-03} (4.62×10^{-06})	1.46×10^{-03} (2.12×10^{-06})	9.84×10^{-04} (9.69×10^{-07})	6.66×10^{-04} (4.43×10^{-07})
NaCl	2.60×10^{-03} (6.74×10^{-06})	2.48×10^{-03} (6.17×10^{-06})	2.25×10^{-03} (5.07×10^{-06})	2.04×10^{-03} (4.16×10^{-06})	1.85×10^{-03} (3.42×10^{-06})
KCl	2.60×10^{-03} (6.78×10^{-06})	2.56×10^{-03} (6.56×10^{-06})	2.47×10^{-03} (6.11×10^{-06})	2.38×10^{-03} (5.69×10^{-06})	2.30×10^{-03} (5.29×10^{-06})
MgCl ₂	2.65×10^{-03} (7.03×10^{-06})	2.02×10^{-03} (4.10×10^{-06})	9.51×10^{-04} (9.05×10^{-07})	4.28×10^{-04} (1.83×10^{-07})	1.89×10^{-04} (3.56×10^{-08})
AlCl ₃	2.60×10^{-03} (6.74×10^{-06})	1.59×10^{-03} (2.52×10^{-06})	4.51×10^{-04} (2.04×10^{-07})	1.22×10^{-04} (1.50×10^{-08})	3.26×10^{-05} (1.06×10^{-09})

TABLE-1 (Contd.)

Electrolyte	Molality, m				
	0.1	1.0	3.0	5.0	7.0
CaF ₂					
LiCl	3.31×10^{-04} (1.45×10^{-10})	2.94×10^{-04} (1.02×10^{-10})	2.27×10^{-04} (4.67×10^{-11})	1.75×10^{-04} (2.14×10^{-11})	1.35×10^{-04} (9.77×10^{-12})
NaCl	3.34×10^{-04} (1.49×10^{-10})	3.24×10^{-04} (1.36×10^{-10})	3.03×10^{-04} (1.12×10^{-10})	2.84×10^{-04} (9.18×10^{-11})	2.66×10^{-04} (7.54×10^{-11})
KCl	3.34×10^{-04} (1.49×10^{-10})	3.31×10^{-04} (1.45×10^{-10})	3.23×10^{-04} (1.35×10^{-10})	3.15×10^{-04} (1.25×10^{-10})	3.08×10^{-04} (1.17×10^{-10})
MgCl ₂	3.39×10^{-04} (1.55×10^{-10})	2.04×10^{-04} (9.03×10^{-11})	1.71×10^{-04} (2.00×10^{-11})	1.00×10^{-04} (4.03×10^{-12})	5.81×10^{-05} (7.86×10^{-13})
AlCl ₃	3.34×10^{-04} (1.49×10^{-10})	2.40×10^{-04} (5.55×10^{-11})	1.04×10^{-04} (4.49×10^{-12})	4.36×10^{-05} (3.31×10^{-13})	1.80×10^{-05} (2.34×10^{-14})
PbI ₂					
LiCl	3.22×10^{-04} (1.34×10^{-10})	2.87×10^{-04} (9.45×10^{-11})	2.21×10^{-04} (4.33×10^{-11})	1.70×10^{-04} (1.98×10^{-11})	1.31×10^{-04} (9.05×10^{-12})
NaCl	3.25×10^{-04} (1.38×10^{-10})	3.16×10^{-04} (1.26×10^{-10})	2.96×10^{-04} (1.04×10^{-10})	2.77×10^{-04} (8.51×10^{-11})	2.59×10^{-04} (6.99×10^{-11})
KCl	3.26×10^{-04} (1.39×10^{-10})	3.22×10^{-04} (1.34×10^{-10})	3.15×10^{-04} (1.25×10^{-10})	3.07×10^{-04} (1.16×10^{-10})	3.00×10^{-04} (1.08×10^{-10})
MgCl ₂	3.30×10^{-04} (1.44×10^{-10})	2.76×10^{-04} (8.37×10^{-11})	1.67×10^{-04} (1.85×10^{-11})	9.78×10^{-05} (3.74×10^{-12})	5.67×10^{-05} (7.28×10^{-13})
AlCl ₃	3.25×10^{-04} (1.38×10^{-10})	2.34×10^{-04} (5.15×10^{-11})	1.01×10^{-04} (4.17×10^{-12})	4.25×10^{-05} (3.07×10^{-13})	1.76×10^{-05} (2.17×10^{-14})
Mg(OH) ₂					
LiCl	1.11×10^{-04} (5.40×10^{-12})	9.84×10^{-05} (3.81×10^{-12})	7.58×10^{-05} (1.75×10^{-12})	5.84×10^{-05} (7.98×10^{-13})	4.50×10^{-05} (3.65×10^{-13})
NaCl	1.12×10^{-04} (5.55×10^{-12})	1.08×10^{-04} (5.08×10^{-12})	1.01×10^{-04} (4.17×10^{-12})	9.50×10^{-05} (3.43×10^{-12})	8.89×10^{-05} (2.81×10^{-12})
KCl	1.12×10^{-04} (5.58×10^{-12})	1.11×10^{-04} (5.41×10^{-12})	1.08×10^{-04} (5.03×10^{-12})	1.05×10^{-04} (4.68×10^{-12})	1.03×10^{-04} (4.36×10^{-12})
MgCl ₂	1.13×10^{-04} (5.79×10^{-12})	9.45×10^{-05} (3.37×10^{-12})	5.71×10^{-05} (7.45×10^{-13})	3.35×10^{-05} (1.51×10^{-13})	1.94×10^{-05} (2.93×10^{-14})
AlCl ₃	1.12×10^{-04} (5.55×10^{-12})	8.03×10^{-05} (2.07×10^{-12})	3.47×10^{-05} (1.68×10^{-13})	1.46×10^{-05} (1.24×10^{-14})	6.02×10^{-06} (8.74×10^{-16})

TABLE-1 (Contd.)

Electrolyte	Molality, m				
	0.1	1.0	3.0	5.0	7.0
Ag₃PO₄					
LiCl	4.22×10^{-05} (8.58×10^{-17})	3.87×10^{-05} (6.05×10^{-17})	3.18×10^{-05} (2.77×10^{-17})	2.62×10^{-05} (1.27×10^{-17})	2.15×10^{-05} (5.80×10^{-18})
NaCl	4.25×10^{-05} (8.82×10^{-17})	4.16×10^{-05} (8.08×10^{-17})	3.96×10^{-05} (6.63×10^{-17})	3.77×10^{-05} (5.45×10^{-17})	3.59×10^{-05} (4.47×10^{-17})
KCl	4.26×10^{-05} (8.87×10^{-17})	4.22×10^{-05} (8.59×10^{-17})	4.15×10^{-05} (8.00×10^{-17})	4.07×10^{-05} (7.44×10^{-17})	4.00×10^{-05} (6.93×10^{-17})
MgCl ₂	4.30×10^{-05} (9.21×10^{-17})	3.75×10^{-05} (5.36×10^{-17})	2.57×10^{-05} (1.18×10^{-17})	1.73×10^{-05} (2.39×10^{-18})	1.15×10^{-05} (4.66×10^{-19})
AlCl ₃	4.25×10^{-05} (8.82×10^{-17})	3.32×10^{-05} (3.30×10^{-17})	1.77×10^{-05} (2.67×10^{-18})	9.23×10^{-06} (1.96×10^{-19})	4.76×10^{-06} (1.39×10^{-20})
BaSO₄					
LiCl	1.03×10^{-05} (1.06×10^{-10})	8.65×10^{-06} (7.48×10^{-11})	5.85×10^{-06} (3.43×10^{-11})	3.96×10^{-06} (1.57×10^{-11})	2.68×10^{-06} (7.17×10^{-12})
NaCl	1.04×10^{-05} (1.09×10^{-10})	9.99×10^{-06} (9.98×10^{-11})	9.06×10^{-06} (8.20×10^{-11})	8.21×10^{-06} (6.73×10^{-11})	7.449×10^{-06} (5.53×10^{-11})
KCl	1.05×10^{-05} (1.10×10^{-10})	1.03×10^{-05} (1.06×10^{-10})	9.94×10^{-06} (9.88×10^{-11})	9.59×10^{-06} (9.20×10^{-11})	9.25×10^{-06} (8.56×10^{-11})
MgCl ₂	1.07×10^{-05} (1.14×10^{-10})	8.14×10^{-06} (6.63×10^{-11})	3.83×10^{-06} (1.46×10^{-11})	1.72×10^{-06} (2.96×10^{-12})	7.59×10^{-07} (5.76×10^{-13})
AlCl ₃	1.04×10^{-05} (1.09×10^{-10})	6.38×10^{-06} (4.07×10^{-11})	1.82×10^{-06} (3.30×10^{-12})	4.93×10^{-07} (2.43×10^{-13})	1.31×10^{-07} (1.72×10^{-14})
Hg₂(C₂H₃O₂)₂					
LiCl	1.96×10^{-05} (3.85×10^{-10})	1.65×10^{-05} (2.72×10^{-10})	1.12×10^{-05} (1.25×10^{-10})	7.55×10^{-06} (5.70×10^{-11})	5.10×10^{-06} (2.61×10^{-11})
NaCl	1.99×10^{-05} (3.96×10^{-10})	1.91×10^{-05} (3.63×10^{-10})	1.73×10^{-05} (2.98×10^{-10})	1.56×10^{-05} (2.45×10^{-10})	1.42×10^{-05} (2.01×10^{-10})
KCl	2.00×10^{-05} (3.99×10^{-10})	1.96×10^{-05} (3.86×10^{-10})	1.90×10^{-05} (3.59×10^{-10})	1.83×10^{-05} (3.34×10^{-10})	1.76×10^{-05} (3.11×10^{-10})
MgCl ₂	2.03×10^{-05} (4.14×10^{-10})	1.55×10^{-05} (2.41×10^{-10})	7.30×10^{-06} (5.32×10^{-11})	3.28×10^{-06} (1.08×10^{-11})	1.45×10^{-06} (2.10×10^{-12})
AlCl ₃	1.99×10^{-05} (3.96×10^{-10})	1.22×10^{-05} (1.48×10^{-10})	3.46×10^{-06} (1.20×10^{-11})	9.39×10^{-07} (8.82×10^{-13})	2.50×10^{-07} (6.25×10^{-14})

TABLE-1 (Contd.)

Electrolyte	Molality, m				
	0.1	1.0	3.0	5.0	7.0
Ag_2CrO_4					
LiCl	7.84×10^{-05} (1.93×10^{-12})	6.98×10^{-05} (1.36×10^{-12})	5.38×10^{-05} (6.23×10^{-13})	4.15×10^{-05} (2.85×10^{-13})	3.19×10^{-05} (1.30×10^{-13})
NaCl	7.91×10^{-05} (1.98×10^{-12})	7.68×10^{-05} (1.81×10^{-12})	7.20×10^{-05} (1.49×10^{-12})	6.74×10^{-05} (1.22×10^{-12})	6.31×10^{-05} (1.01×10^{-12})
KCl	7.93×10^{-05} (1.99×10^{-12})	7.84×10^{-05} (1.93×10^{-12})	7.66×10^{-05} (1.80×10^{-12})	7.48×10^{-05} (1.67×10^{-12})	7.30×10^{-05} (1.56×10^{-12})
MgCl ₂	8.03×10^{-05} (2.07×10^{-12})	6.70×10^{-05} (1.20×10^{-12})	4.05×10^{-05} (2.66×10^{-13})	2.38×10^{-05} (5.38×10^{-14})	1.38×10^{-05} (1.05×10^{-14})
AlCl ₃	7.91×10^{-05} (1.98×10^{-12})	5.70×10^{-05} (7.40×10^{-13})	2.47×10^{-05} (5.99×10^{-14})	1.03×10^{-05} (4.41×10^{-15})	4.27×10^{-06} (3.12×10^{-16})

To check for the validity of the model in predict solubility at a given ionic strength, a comparison is made between calculated and experimental solubility values. Table-2 shows experimental solubilities, for some salts reported in literature, along with the calculated values. The agreement is extremely good for a wide range of ionic strength. For further check of the validity of the model, the experimental values of the conditional solubility product constant for mercurous acetate, a common salt extensively studied and reported in literature, are compared with the calculated values. Table-3 shows a comparison between experimental and calculated values at various ionic strengths. Take into consideration that the solubility product constants are extremely difficult to obtain experimentally, because of the necessity to identify all chemical species and processes present in the chemical system used to obtain their values. The literature K_{sp} values, and hence solubility, may disagree widely, even by several orders of magnitudes. Even though, the agreement is good and acceptable as shown in Table-3.

TABLE-2
CALCULATED AND EXPERIMENTAL (IN PARENTHESES) VALUES OF SOLUBILITIES FOR SALTS IN ELECTROLYTE SOLUTIONS OF VARIOUS IONIC STRENGTH

Salt	Ionic strength		
	0.1	0.5	2.0
Zn(OH) ₂ (ref. 28)			1.27×10^{-06} (1.36×10^{-06})
Th(OH) ₄ (ref. 29)		4.15×10^{-10} (4.19×10^{-10})	
LaF ₃ (ref. 30)	3.29×10^{-08} (3.29×10^{-08})		
Hf(OH) ₄ (ref. 31)	1.44×10^{-11} (1.44×10^{-11})		
Co(OH) ₂ (ref. 32)		7.80×10^{-06} (7.93×10^{-06})	
ThO ₂ (ref. 33)		4.73×10^{-04} (4.74×10^{-04})	

Experimental data reference is shown in parentheses under the salt.

TABLE-3
CALCULATED AND EXPERIMENTAL¹² (IN PARENTHESIS) CONDITIONAL
SOLUBILITY PRODUCT CONSTANT, K'_{sp} , FOR MERCUROUS ACETATE AT
VARIOUS IONIC STRENGTHS

Salt Ionic strength	Hg ₂ Ac ₂
0.300	3.14 × 10 ⁻¹⁰ (3.09 × 10 ⁻¹⁰)
0.500	3.08 × 10 ⁻¹⁰ (2.95 × 10 ⁻¹⁰)
0.700	3.02 × 10 ⁻¹⁰ (2.88 × 10 ⁻¹⁰)
0.900	2.97 × 10 ⁻¹⁰ (2.82 × 10 ⁻¹⁰)
1.200	2.88 × 10 ⁻¹⁰ (2.69 × 10 ⁻¹⁰)
1.500	2.80 × 10 ⁻¹⁰ (2.57 × 10 ⁻¹⁰)
1.800	2.71 × 10 ⁻¹⁰ (2.46 × 10 ⁻¹⁰)
2.100	2.64 × 10 ⁻¹⁰ (2.34 × 10 ⁻¹⁰)
2.400	(2.56 × 10 ⁻¹⁰) (2.24 × 10 ⁻¹⁰)
2.700	(2.48 × 10 ⁻¹⁰) (2.41 × 10 ⁻¹⁰)
3.000	(2.41 × 10 ⁻¹⁰) (2.00 × 10 ⁻¹⁰)

In summary, this new and simple model has been shown to be fairly effective in calculating solubility and conditional solubility product constant for salt in electrolyte solutions. A desktop calculator, or a simple computer program, can be used to perform the operations. Though simple, the model has been demonstrated to be very accurate in predicting the solubility and the solubility product for various salts over a wide concentration range of electrolyte solutions.

REFERENCES

1. F. Hernandez-Luis, M.V. Vazquez and M.A. Esteso, *J. Mol. Liq.*, **108**, 283 (2003).
2. K. Fujiwara, H. Yamana, T. Fujii and H. Moriyama, *Radiochim. Acta*, **91**, 345 (2003).
3. W.E. Waghorne, *Monatshfte Chem.*, **134**, 655 (2003).
4. K. Fujiwara, H. Yamana, T. Fujii and H. Moriyama, *Radiochim. Acta*, **90**, 857 (2002).
5. R. Knopp, V. Neck and J.I. Kim, *Radiochim. Acta*, **86**, 101 (1999).
6. X. Liu and F.J. Millero, *Geochim. Cosmochim. Acta*, **63**, 3487 (1999).
7. A. Chhetry, Z. Wang, J.L. Fox, A.A. Baig, H. Zhuang and W.I. Higuchi, *J. Coll. Inter. Sci.*, **218**, 47 (1999).
8. S.J. Friedfeld, S. He and M.B. Tomson, *Langmuir*, **14**, 3698 (1998).

9. D. Chung, E. Kim, E. Lee and J. Yoo, *J. Ind. Eng. Chem.*, **4**, 277 (1998).
10. S.V. Mattigod, D. Rai, A.R. Felmy and L. Rao, *J. Sol. Chem.*, **26**, 391 (1997).
11. H. Fan, H. Jia, Y. Jiang and J. Pan, *Chuan. Jishu Xuebao*, **9**, 33 (1996).
12. M. de Moraes, L. Pezza, C.B. Melios, M. Molina, R. Pezza, A.M. Peres, A.C. Villafranca and J. Carloni, *Ecletica Quimica*, **21**, 133 (1996).
13. S. Zhang, Z. He and K. Yang, *Ziran Kexueban*, **15**, 82 (1992).
14. T.P. Dirkse, *J. Electrochem. Soc.*, **133**, 1656 (1986).
15. M.P. Menon, *J. Chem. Eng. Data*, **27**, 81 (1982).
16. J.B. Macaskill and R.G. Bates, *J. Phys. Chem.*, **81**, 496 (1977).
17. J.R. Goates, A.G. Cole and E.L. Gray, *J. Am. Chem. Soc.*, **73**, 3596 (1951).
18. P. Debye and E.Hückel, *Phys. Z.*, **24**, 185 (1923).
19. H.S. Harned and B.B. Owen, *Physical Chemistry of Electrolyte Solutions*, Reinhold, New York (1958).
20. R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, Butterworth, London (1965).
21. F. Vaslow, *Water and Aqueous Solutions*, Wiley, New York (1972).
22. H.P. Bennetto, *Ann. Rev. Chem. Soc.*, **70**, 223 (1973).
23. H.L. Friedman, C.V. Krishnan and C. Jolicoeur, *Ann. N.Y. Acad. Sci.*, **204**, 79 (1973).
24. R.H. Fowler, *Proc. Camb. Phil. Soc.*, **22**, 861 (1925).
25. J.G. Kirkwood and J. C. Poirier, *J. Phys. Chem.*, **58**, 591 (1954).
26. H.P. Bennetto and J. Spitzer, *J. Am. Chem. Soc.*, **9**, 2108 (1976).
27. H.M. Abdel-Halim, *Asian J. Chem.*, **6**, 370 (1994).
28. S. Xu and L. Xu, *Ziran Kexueban*, **4**, 7 (2002).
29. V. Neck, R. Muller, M. Bouby, M. Altmaier, J. Rothe, M.A. Denecke and J.I. Kim, *Radiochim. Acta*, **90**, 485 (2002).
30. S. Shi, S. Yin and Y. Guo, *Fenxi Ceshi Xuebao*, **21**, 44 (2002).
31. G. Gerefice, M. Draye, K. Noyes and K. Czerwinski, *Materials Research Society Symposium Proceedings*, 556: Scientific Basis for Nuclear Waste Management-XXII, p. 1025 (1999).
32. V.E. Mironov, G.L. Pashkov, T.V. StuPko and Z.A. Pavlovskaya, *Zhurnal Neorganicheskoi Khimii*, **40**, 116 (1995).
33. E. Oesthols, J. Bruno and I. Grenthe, *Geochimica et Cosmochimica Acta*, **58**, 613 (1994).

(Received: 15 May 2004; Accepted: 10 September 2004)

AJC-3564