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The Solubility of Potassium Sulfate in Thermodynamic view

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ABSTRACT

The solubility of K2SO4 in water at 25°C was determined. Comparing the value of thermodynamic solubility product constant, Ksp(th), (Ksp(th) = exp $(-\Delta G^{o}_{diss}$ / RT) of the mentioned salt to the value of concentration solubility product, Ksp(c) which is obtained from the observed solubility, s/moL^{-1}, Ksp(c) = 4s3, revealed a great difference. The difference can be satisfactorily explained using Debye- Hückel law and ion assocaition phenomenon.

Keywords: Solubility product; Activity coefficient; Non ideality

INTRODUCTION

Comparative studies of aqueous electrolyte solutions generally always require consideration of non- ideality and ion-association. It is vital,, therefore, that one regards these phenomena in order to interpret the related experimental data. A strong electrolyte solution deviate, partly by non-ideality arising from activity coefficients (physical factor) and partly by ion- association (chemical factor) from ideality. The non-ideality contribution respect to the physical factor could be evaluated by activity coefficients which can be estimated upon some theoretical models [1-5]. The ion- association contribution, in turn, can be studied both theoretically and experimentally by using several approaches [6-14].

When the concentration of an electrolyte solution tends toward zero, the ions are sufficiently far apart that coulombic interactions between them are negligible. Under these circumstance the ions behavior is independent from each other and the electrolyte behaves almost as an ideal solution. As the concentration increases, the average distance between the ions decreases, so interactions between them become considerable and the solution becomes progressively less ideal. In addition, the ion- solvent interactions that are present even in the ideal solution also become increasingly modified as the concentration increases, again making a progressively increasing contribution to non- ideality. The effects of non- ideality and ion- association can be observed from the way in which certain properties of the solution, such as its molar conductivity, vapour pressure, ... vary with concentration.

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BACKGROUND

Consider an ionic compound such as B_2A which is composed of $2B^+$ and A^{2-} ions and assume that its solubility in water at room temperature is fairly small. Therefore, in saturated solution of this ionic compound, B_2A, one can consider the following equilibrium

$$B_2A_{(s)} \Leftrightarrow 2B^+_{(aq)} + A^{2-}_{(aq)} : K_{sp(th)} \qquad (1)$$

$$K_{sp(th)} = a^2_{B^+}\, a_{A^{2-}} ; (a_i = activity\ of\ ion\ i)$$

$$K_{sp(th)} = \exp(-\Delta G^\circ_{diss} / RT) \qquad (2)$$

$$\Delta G^\circ_{diss} = \Delta H^\circ_{diss} - T\,\Delta S^\circ_{diss} \qquad (3)$$

Where ΔG°_{diss}, ΔH°_{diss} and ΔS°_{diss} represent standard Gibbs free energy, standard enthalpy and standard entropy change related to the equilibrium (1).

On the other hand, one can consider the estimated solubility product, $K_{sp(est)}$, of equilibrium (1) as follow

$$K_{sp(est)} = [B^+]^2 [A^{2-}] f_+^2 f_- \qquad (4)$$

where [i] represents the molarity of species i in the solution and fi denotes the activity coefficient of that species in the same solution. It is worthwhile to denote that the ion- association phenomenon has been neglected in introducing equation (4) with the assumption that f_+ and f_- can be estimated upon a suitable model, such as Debey- Hückle theory.

For many ionic compounds, it has been seen that there is a considerable difference among the concentration solubility product, Ksp(c) = $4s^3$, estimated solubility product, Ksp(est) and thermodynamic solubility product, Ksp(th), and almost always Ksp(c) is greater than Ksp(th) and Ksp(est) [15,16].

One way of explaining the difference, is to consider the non ideality and ion- association phenomena in electrolyte solutions. For many decades ion- association in electrolyte solutions has been an area of active research interest [6-20]. Bjerum theoretical approach provides following results for association constant, KA, of ion- pair formation in dilute solutions of electrolytes with B A formula [6]

$$B^+_{(aq)} + A^-_{\ )} \Leftrightarrow B^+A^-_{(ion-pair)} ; K_A \qquad (5)$$

$$K_A = \frac{4\pi N a^3 b^3}{1000} Q_{(b)} \qquad (6)$$

$$Q_{(b)} = \int_2^b e^x x^{-4} dx \qquad (7)$$

$$b = \frac{|z_+ z_-| e^2}{a\varepsilon kT} ; x = \frac{|z_+ z_-|}{r\varepsilon kT} \qquad (8)$$

where, N is Avogadro constant, a is the closest of approach of ions, ε represents the dielectric constant, k is Boltzmann constant, T denotes temperature in Kelvin and B^+A^- refers to the respective ion- pair. On the other hand, Fuoss theoretical approach leads to the contact ion- pair and the following expression for KA [6, 11]

$$K_A = ca^3 e^{c'/a\varepsilon T} \qquad (9)$$

where a is the parameter of the closest approach of ions in cm, c = 2.522×10^{21} and c' = 1.66×10^{-3}

EXPERIMENTAL

K2SO4 and other chemicals were purchased from Merck Company and used without further purification. The saturated solution of K2SO4 in deionized water was prepared at 25.0°C, and then the solubility of it in water was determined using Solvent Evaporating method. Our experimental results are given in table 1.

Table 1. Solubility, s, (mol L^{-1}) of K2SO4, in water at 25.0°C (using solvent evaporating method)

Iteration	Solubility, s,/mol L^{-1}
1	0.7035
2	0.6955
3	0.6944
4	0.7001
5	0.7024
6	0.7001
	Average 0.6993 ± 0.0033 mol L^{-1}

DISCUSSION

In the saturated solution of K2SO4 at constant temperature, we can assume the following equilibrium

$$K_2SO_{4(s)} \Leftrightarrow K^+_{(aq)} + SO^{2-}_{4(aq)} \qquad (10)$$

Denoting the solubility of K2SO4 in equilibrium (10) by s mol L^{-1}, then the concentration solubility product of it is

$$K_{sp(c)} = [K^+]^2 [SO_4^{2}] = [2s]^2 [s] = 4s^3 \qquad (11)$$

Inserting the value of experimental solubility of K2SO4, 0.6993 mol L^{-1}, (table 1) in the equation (11), we get

Ksp(c) = 1.368 $mol^3\ L^{-3}$ (at 25.0°C)

Now, we evaluate the thermodynamic solubility product, Ksp(th), based on the data of table (2) and equations (2) and (3).

Table2. Thermodynamic functions of $K^+_{(aq)}, SO^{2-}_{4(aq)}$ and $K_2SO_{4(s)}$ at 298 K

Species	$\Delta H_f^0\ /kJ\ mol^{-1}$	S° / JK⁻¹ mol⁻¹	$\Delta G_f^0\ /kJ\ mol^{-1}$	Ref.
$K^+_{(aq)}$	-252.38	102.5	-283.27	[21,23]
$SO^{2-}_{4(aq)}$	-909.27	20.1	-744.53	[21,23]
$K_2SO_{4(s)}$	-1434.00	176.0	-1316.00	[23]

$$\Delta H^{\circ}_{diss} = [2\Delta H^{\circ}_{f(K^+)} + \Delta H^{\circ}_{f(SO_4^{2-})}] - \Delta H^{\circ}_{f(K_2SO_4)}$$
$$= [2\times(-252.38 + 1\times(-909.27)] - [1\times(-1434.00)]$$
$$= 19970 J\ mol^{-1}$$

$$\Delta S^{\circ}_{diss} = (2\times 102.5 + 20.1) - (176.0)$$
$$= 49.1 JK^{-1}\ mol^{-1}$$

$$\Delta G^{\circ}_{diss} = \Delta H^{\circ}_{diss} - T\,\Delta S^{\circ}_{diss}$$
$$= 19970 J\ mol^{-1} - 298.15K \times 49.1 JK^{-1}\ mol^{-1}$$
$$= 5331 Jmol^{-1}$$

$$K_{sp(th)} = \exp(-\Delta G^{\circ}_{diss}/RT)$$
$$= 0.1164$$

As we can see, the value of Ksp(th) = 0.1164 is quite different from Ksp(c) =1.368. The difference is due to the non ideality and ion-association phenomena.

The non ideality of ions in the solution can be taken into account by estimating activity coefficients , fis. Several equations are introducing for estimating activity coefficient of ions in aqueous electrolyte solution. Here, we look to the semi empirical extended Debey-Hückle equation in the following form:

$$\log f_{\pm} = \frac{0.509 z_+ z_- \sqrt{I}}{1 + 0.324 a_{\pm} \sqrt{I}} + 0.2\sqrt{I} \quad (at\ 25.0\ ^{0}C) \quad (12)$$

where $a_{\pm} = (a_+ + a_-)/2$ and a_+ or a_- is the size parameter of considered ion in angstrom, °A,.For K2SO4 (aq), we take $a_{\pm} = (3+4)/2 = 3.5\ ^{\circ}A$ [12].

So

$$\log f_{\pm}\ (K2SO4, aq) = -\frac{1.018\sqrt{I}}{1 + 1.134\sqrt{I}} + 0.2\sqrt{I} \qquad (13)$$

I is ionic strength and I = 3s for the saturated solution of K2SO4, while s represents the solubility of K2SO4 in mol L^{-1}. After table(1), s = 0.6993 mol L^{-1}, so, $\sqrt{I}$ = 1.4484 and

$$\log f_{\pm}(K_2SO_{4,aq}) = -\frac{1.4745}{2.6425} + 0.2897 = -0.2683$$

$$\Rightarrow f_{\pm} = 0.5391$$

$$K_{sp(est)} = 4s^3 f_{\pm}^3 = 0.2143$$

As we can see, the calculated Ksp(est) is nearly two times Ksp(th) = 0.1164. This difference can be attributed to the ion association phenomenon in the saturated solution of K2SO4 at 25.0°C, if the equation (12) could be reasonable in this condition.

CONCLUSION

Saturated aqueous solution of K2SO4 is far from ideality. The non- ideality of the solution may be interpreted as due partly to physical (activity coefficients) and partly to chemical (ion-association) factors and these contributions do predict a concordant fit of experimental data. The solubility of K2SO4 could be divided in three contributions; one, $\sqrt[3]{K_{sp(th)}/4} = 0.3076 mol\ L^{-1}$, the other, $[K^+SO_4^{2-}]_{i-p} = 0.2000 mol\ L^{-1}$ and the physical factor contribution= 0.1917 mol L^{-1}. The percentage of each contribution is 44%, 28.5% and 27.5% respectively.

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