Thermodynamics of Ion Association in the Saturated Solution of The Mixed Solvent (methanol+water) and Ion Pairing at 25.0°C

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ABSTRACT

In this study, the ion association phenomenon in the saturated solution of KCl in the mixed solvent (methanol+water) was studied. The solubility of this compound in the mixed solvent (methanol+ water by value percent of methanol = 60%), and in the presence of various molarities of $NaNO_3$ was determined by the solvent evaporation method at 25.0°C. The results enable us to estimate the value of thermodynamic solubility product, $K_{sp(th)}$, of KCl in the mixed solvent upon the extrapolation method ($K_{sp(th)}$ = 0.1356). Although the model solubility product, $K_{sp(m)}$, was calculated upon the semi theoretical semi experimental Debey-Huckle theory shows ($K_{sp(m)}$ = 0.2308). Comparing the values of $K_{sp(th)}$ and $K_{sp(m)}$ with the concentration solubility product, ($K_{sp(c)}$ = 0.5537), we can see that the differences are noticeable.
We assume that, part of the differences comes from non-ideality and the other part from ion association phenomenon.

Keywords: Solubility; Ion-Pair; Thermodynamic; Solubility product constant; Mixed solvent

INTRODUCTION

Most physicochemical properties of ionic solutions are influenced by ionic strength and the solvent′s dielectric constant. Indeed, in the context of solution chemistry, solvent polarity, the dielectric constant of the solvent, and the ionic strength of the medium are of great interest as a measure of the solvent′ s ability to stabilize charges or dipoles. As an example, the dissolution of an ionic salt in a solvent or in a mixed solvent depends on the relative permittivity and the polarity of the solvent as well as on the lattice energy of the solute and the ionic strength of the medium. Most of the theories that have been applied to predict the changes in the solubility with the variation of solvent nature depend on the changes in the electrostatic properties of the solvent and the ionic strength of the medium [1].

For an ionic compound, such as BA, we may consider the following equilibrium in it′s saturated solution at a given constant temperature.

$$BA_{(s)} \rightleftharpoons B^+_{(aq)} + A^-_{(aq)} \quad K_{sp(th)} = a_+ a_- \quad (1)$$
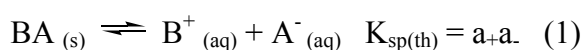
Where $K_{sp(th)}$ denotes the thermodynamic solubility product constant and a^+ and a^- refer to activity of B^+ and A^- in the solution, respectively. If the solubility of BA is very low, it may replace the activity of each ion by its concentration, so,

$$K_{sp(th)} = s_o^2 \quad (2)$$

Where s_o represents the molarity of BA in the very dilute solution. Now, in the presence of

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a little additional ionic strength, I, it could be inferred that

$$K_{sp(th)} = s^2 \gamma_\pm^2 \qquad (3)$$
$$s_\circ^2 = s^2 \gamma_\pm^2 \qquad (4)$$
$$s_\circ = s \gamma_\pm \qquad (5)$$

where s is the solubility of BA in the presence of an additional ionic strength, I, and γ± is the mean activity coefficient of the respective compound. Applying the Deby-Huckel limiting law [2] for γ±, we conclude that:

$$\text{Log } (s/s^\circ) = 0.509 \sqrt{I} \qquad \text{or}$$
$$(s/s^\circ) > 1 \qquad (6)$$

This equation is only valid for low ionic strengths in methanol and water at 25.0°C. Then it is necessary to find another relation in the moderate or high ionic strengths. On the other hand the solubility of an ionic compound may decrease when the additional ionic strength is fairly high or very high.

EXPERIMENTAL

KCl and NaNO₃ and methanol were purchased from Merck Company with high degree of purity and used without further purification. The mixed solvent,

(methanol+water by value percent of methanol = 60%), was prepared from deionized water and fairly pure methanol.

Then, the solubilities, s, of KCl in the mixed solvent at the presence of various concentrations of NaNO₃, were determined by the solvent evaporating method at 25 °C (Fig. 1 and Table 1).

In general, a plot of log s versus $\sqrt{I}$ may give a better insight into the relationship between s and $\sqrt{I}$ (Fig.2).
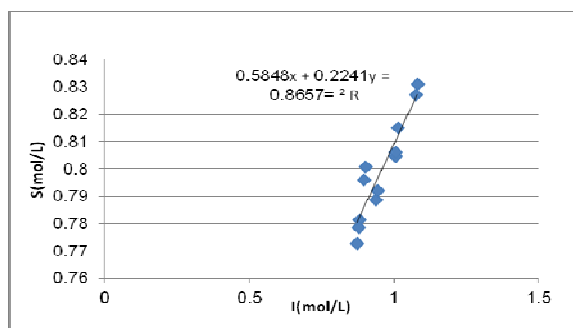

Fig. 1. Plot of s versus I for the solubilities of KCl in the mixed solvent (methanol+water with value percent of methanol = 60%), at 25.0°C and various molarities of NaNO₃.

Table 1. Solubilities of KCl and values of $K_{sp,KCl}$ in the mixed solvent (methanol+water with value percent of methanol = 60%), at 25.0°C and various molarities of NaNO₃

[NaNO₃] (mol/L)	s(mol/L)	I(mol/L)	√I(mol/L)^½	log s	$K_{sp(c)}$	logK_sp
0	0.7598	0.7598	0.8716	-0.1193	0.5773	-0.2385
0	0.7652	0.7652	0.8747	-0.1162	0.5855	-0.2325
0	0.7283	0.7283	0.8534	-0.1377	0.5304	-0.2754
0	0.7230	0.7230	0.855	-0.1408	0.5227	-0.2817
0.1	0.8007	0.9007	0.9490	-0.0965	0.6411	-0.193
0.1	0.7726	0.8726	0.9341	-0.112	0.5997	-0.222
0.1	0.7814	0.8814	0.9388	-0.1071	0.6106	-0.2142
0.1	0.7787	0.8787	0.9374	-0.1086	0.6064	-0.2172
0.1	0.7961	0.8961	0.9466	-0.099	0.6338	-0.198
0.15	0.7887	0.9387	0.9688	-0.1031	0.622	-0.2062
0.15	0.7921	0.9421	0.9706	-0.1012	0.6274	-0.2024
0.2	0.8048	1.0048	1.0024	-0.0943	0.6477	-0.1886
0.2	0.8149	1.0149	1.0074	-0.0889	0.6641	-0.1777
0.2	0.8062	1.0062	1.0031	-0.0935	0.6499	-0.1871
0.25	0.827	1.077	1.0378	-0.0825	0.6839	-0.165
0.25	0.831	1.081	1.0397	-0.0804	0.6906	-0.1607

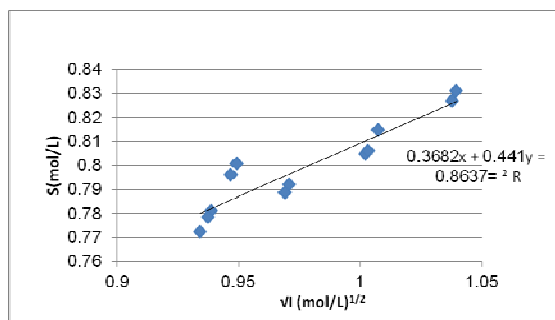**Fig. 2.** Plot of s versus √I for the solubilities of KCl in the mixed solvent (methanol+water with value percent of methanol = 60%), at 25.0˚C and various molarities of NaNO$_3$.

RESULTS AND DISCUSSION

As we can see from Fig.2 the solubility dependence of KCl with √I is fairly linear on a wide range of ionic strength. The interception of the line with the y-axis for √I →0 gives:

$$s_{\circ} = 0.3682 \ \text{mol/L} \qquad (7)$$

Where $s_{\circ}$ is the solubility of KCl in the mixed solvent (methanol+water with value percent of methanol = 60%), at 25.0˚C at the condition √I →0 . Obviously the behavior of ions at I→0 can be assumed to be ideal, and then, $K_{sp(th)}=s_{\circ}^2$ for an ionic compound with the BA formula. So,

$$K_{sp(th),KCl} = s_{\circ}^2 = 0.1356 \ \text{mol}^2/\text{L}^2 \qquad (8)$$

On the other hand, the concentration solubility product constant($K_{sp(c)}$) of KCl in the saturated solution is:

$$K_{sp(c)} = s^2 \qquad (9)$$

In the condition of [NaNO$_3$] = 0, we obtained s = 0.7441 mol/L for KCl in the mixed solvent at 25.0 ˚C (methanol+water with value percent of methanol = 60%). Then,

$$K_{sp(c)} = (o.7441)^2 = 0.5537 \ \text{mol}^2/\text{L}^2 \qquad (10)$$

Now, we focus on the solubility product constant, $K_{sp(m)}$, by using a suitable model for estimating the mean activity coefficient, $\gamma_\pm$,of ions.

$$K_{sp(m)} = s^2 \gamma_\pm^2 \qquad (11)$$

We assume that a Deby-Huckel model in following from is adequate for estimating the mean activity coefficient, $\gamma_\pm$:

$$\log \gamma_\pm = \frac{-A\left|Z_+ Z_-\right|\sqrt{I}}{1+Ba\sqrt{I}} + 0.161 \qquad (12)$$

To apply the above equation for evaluating the mean activity coefficient, $\gamma_\pm$, of the ions in the mixed solvent, we must evaluate the value of A and relative to the mixed solvent as follows [3,4].

$$A' = \frac{0.5059\left(d_{Mix}/d_{H20}\right)^{\frac{1}{2}}}{\left(D_{Mix}/D_{H20}\right)^{\frac{3}{2}}} \qquad (13)$$

$$B' = \frac{0.328}{\left(D_{Mix}/D_{H20}\right)^{\frac{1}{2}}} \qquad (14)$$

Where d and D represent the density and dielectric constant, respectively. So

$$A' = \frac{0.5059\left(0.9167/1\right)^{\frac{1}{2}}}{\left(60.1194/78.54\right)^{\frac{3}{2}}} = 0.7232 \ \text{at } 25°C \ (15)$$

and

$$B' = \frac{0.328}{\left(60.1194/78.54\right)^{\frac{1}{2}}} = 0.3749 \ \text{at } 25°C \ (16)$$

The ion size, a, in eq (12) can be evaluated as follow

$a_\pm = ½ (a_+ + a_-) = ½(3.31+3.95) = 3.63 \ °A$

so,

$$\gamma_\pm(\text{in mixed solvent}) = 0.6793 \qquad (17)$$

and then

$$K_{sp(m)}=K_{sp(c)} \ \gamma_\pm^2 = s^2 \gamma_\pm^2 = 0.2554 \ \text{mol/L} \ (18)$$

When we compare the values of $K_{sp(th)}$, $K_{sp(m)}$ and $K_{sp(c)}$ (0.1356, 0.2554, 0.5537, respectively), we conclude that:

$K_{sp(th)} < K_{sp(m)} < K_{sp(c)}$

As, we can see, these constants are different from each other. Indeed in a very dilute electrolyte solution, the ion association phenomenon may be negligible, and so, some theories such as the limiting or extended Debye-Huckle model should be adequate for estimating the activity coefficients of ions in the considered solution [5-10]. In these circumstances, the thermodynamic and modeling constants may be comparable. But, in a fairly concentrated electrolyte solution, the ion association is an important factor of non-ideality, and additionally, the models which we use for estimating the activity coefficients of ions may not be adequate [11-14].

Finally, $K_{sp(c)}$ differs from $K_{sp(th)}$ and $K_{sp(m)}$ partly due to non-ideal behavior of ions in the solution and partly due to the ion association phenomenon.

For simplicity, we consider only the ion-pair formation [10-19] and neglect the other kinds of ion association. So, if we denote the concentration of K^+Cl^- ion-pair in the saturated solution of KCl in the mixed solvent, (methanol+water with value percent of methanol = 60%), at 25.0°C by x (mol/L), then the following equation would be available

$$K_{sp(th)} = (s-x)^2 \gamma_\pm^2 \qquad (19)$$

According to eq.(8), $K_{sp(th)} = 0.1356$ mol^2/L^2. In addition from table 1: s =0.7441 mol/L.

Now, estimating the value of $\gamma_\pm$ by using eq.(12) and solving eq.(19), (Table 2). For x by iteration method, we obtained the value of x = 0.1883 mol/L.

The formation of ion-pair, K^+Cl^-, may be represented as follow:

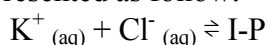$$K^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons I\text{-}P$$

Table 2. The result of iteration calculation for obtaining a reasonable value of x (x=[Ion-Pair]) in the saturated solution of KCl in mixed solvent, (methanol+ water with value percent of methanol = 60%), at 25.0°C

iteration	I (mol/L)	$\gamma_\pm$	x (mol/L)
1	0.7441	0.6793	0.2020
2	0.5421	0.6618	0.1876
3	0.5565	0.6627	0.1884
4	0.5557	0.6626	0.1883
5	0.5558	0.6626	0.1883

$$: K_{ip} = \frac{a_{ion\text{-}pair}}{a_+ a_-} \qquad (20)$$

$$K_{ip} = \frac{[I\text{-}P]}{[K^+][Cl^-]\gamma_\pm^2} \qquad (21)$$

or,

$$K_{ip} = \frac{X}{(S-X)^2 \gamma_\pm^2} \qquad (22)$$

By estimating $\gamma_\pm$ upon the Deby-Huckel model eq. (12), we get:

K_{ip} = 1.32 mol/L   (23)

A theoretical approach after Fuoss [15] is available for estimating the ion-pair constant, K_A:

$$K_{Ip} = 2.522 \times 10^{21} \times a^3 \times \exp\left(\frac{1.67 \times 10^{-3} Z^2}{aDT}\right) \qquad (24)$$

where a is the size parameter (a_{KCl} =3.63A°), D is the dielectric constant of mixed solvent, z is the ion-pair charge, T is temperature in Kelvin. So,

K_{ip} =1.58 mol/L   (25)

This value of K_{ip} is comparable to the value given in eq.(23).

CONCLUSIONS

The solubility of KCl in the mixed solvent, (methanol+water with value percent of methanol = 60%), at 25.0°C, increases linearly with the increasing ionic strength in a wide range of $NaNO_3$ concentrations from 0.1 to 1.5 mol/L as a background salt. The value of the thermodynamic solubility

product constant of KCl in the mixed solvent could be estimated upon the value of the solubility of the considered ionic compound at zero ionic strength by the extrapolating method. The saturated solution of KCl in the mixed solvent in the presence of $NaNO_3$ is perflectly non-ideal.

The non-ideality is partly due to the mean activity coefficient of ions in the solution and partly due to the ion association phenomenon. By choosing a suitable model for estimating the mean activity coefficient and using the iteration calculations, we obtained the value of ion-pair concentration and the activity coefficient contribution and ion association contribution to the solubility of the considered ionic compound in the considered mixed solvent at desired temperature [1].

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