Solubility Product of K_2SO_4 in a Mixed Solvent Medium and Ion-Pair Formation at 25 °C[†]

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The solubility of K_2SO_4 in the mixed solvent, (water (1) + ethanol (2)) with mass fraction $w_1 = 0.9$, was determined by using the evaporating method in the presence of various concentrations, (0, 0.100, 0.150, 0.200, 0.300, 0.400, 0.500, 0.600, 0.700, and 0.800) $\mathrm{mol \cdot L^{-1}}$, of $NaNO_3$ at 25 °C. The values of solubility and solubility product constant were evaluated at zero ionic strength for ions in the saturated solution (at a molarity of $NaNO_3 = 0\ \mathrm{mol \cdot L^{-1}}$) by using the Van Rysselberghe and Eisenberg model, and the ion-pairing extension was calculated in the considered solution by an extrapolating method that uses the experimental results and estimates the mean activity coefficient at 25 °C.

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 changes in solubility with the variation of solvent depend on changes in the electrostatic properties of the solvent and the ionic strength of the medium.

Several relationships between the solubility of electrolytes and the relative permittivity of the solvent, *D*, could be found in the literature. One relation that has been largely used is

$$\log s = A_1 + \frac{A_2}{D} \tag{1}$$

where *s* is the solubility and A_1 and A_2 are constants.[1] Nevertheless, it is easy to find many exceptions to eq 1. For instance, the solubilities of NaF in water, methanol, and ethanol at 25 °C are (0.973, 0.16, and 0.04) $\mathrm{mol \cdot kg^{-1}}$, respectively, while their relative permittivities are 78.54, 32.6, and 24.3, respectively.[1,2] It is apparent, however, that the relative permittivity is not the main determinant of solubility, but it rather depends on the ion solvation, which depends on the solvent's base strength as well as the hydrogen-bonding capacity of the solvent and the ionic strength of the medium. Hence, any improvement of this relationship should be based on the Gibbs energy calculation.

To discuss the solubility dependence of a given ionic salt, such as BA, with ionic strength, *I*, we consider the following equilibrium

$$BA_{(s)} \Leftrightarrow B_{(aq)}{}^{+} + A_{(aq)}{}^{-} \quad K_{sp(th)} = a_{+}a_{-} \tag{2}$$

where $K_{sp(th)}$ denotes the thermodynamic solubility product constant and a_+ and a_- refer to activity of $B_{(aq)}{}^{+}$ and $A_{(aq)}{}^{-}$ in the solution, respectively. If the solubility of BA at a given temperature is very low, it may replace the activity of each ion by its concentration, s_0,

$$K_{sp(th)} = s_0{}^{2} \tag{3}$$

where s_0 represents the molarity of BA in the dilute saturated solution. Now, in the presence of a little additional ionic strength, *I*, it could be inferred that

$$s_0{}^{2} = s^2 f_{\pm}{}^{2} \Rightarrow s_0 = s f_{\pm} \tag{4}$$

where *s* is the solubility of BA in the presence of an additional ionic strength, *I*, and $f_\pm$ is the mean activity coefficient of the respective ions. Applying the Debye−Huckel limiting law[3] for $f_\pm$, we conclude that:

$$\log\left(\frac{s}{s_0}\right) = 0.509 I^{1/2} \tag{5}$$

This equation is only valid for low ionic strengths. Then it is necessary to find another relation in moderate or high ionic strength. On the other hand the solubility of an ionic compound could decrease when the additional ionic strength is fairly high or very high.

Experimental Section

K_2SO_4 and other chemicals were purchased from Merck Company with high degree of purity and used without further purification. The mixed solvent, (water (1) + ethanol (2)) with $w_1 = 0.9$, was prepared from deionized water and fairly pure ethanol.

Then, the solubilities, *s*, of K_2SO_4 in the mixed solvent at the presence of various concentrations of $NaNO_3$, (0.100, 0.150, 0.200, 0.300, 0.400, 0.500, 0.600, 0.700, and 0.08) $\mathrm{mol \cdot L^{-1}}$, were determined by the solvent evaporating method at 25 °C (Table 1 and Figure 1).

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Table 1. Solubilities of K_2SO_4 in (Water (1) + Ethanol (2)) with $w_1 = 0.9$ at Various Ionic Strengths at 25 °C

$C(NaNO_3)$ mol·L^{-1}	I mol·L^{-1}	$s(K_2SO_4)^a$ mol·L^{-1}
0	0.822	0.2741
0.100	0.977	0.2922
0.150	1.067	0.3056
0.200	1.137	0.3122
0.300	1.293	0.3312
0.400	1.465	0.3551
0.500	1.629	0.3762
0.600	1.770	0.3900
0.700	1.908	0.4028
0.800	1.983	0.3942

[a] Each value of s is an average of five independent measurements.

Table 2. Values of $K_{sp(c),K_2SO_4}$ in the Mixed Solvent, (Water (1) + Ethanol (2)), with $w_1 = 0.9$ at Various Ionic Strengths at 25 °C

$s(K_2SO_4)$ mol·L^{-1}	$K_{sp(c)}$ mol^3·L^{-3}	$\ln(K_{sp(c)}/\text{mol}^3\cdot\text{L}^{-3})$	I total mol·L^{-1}
0.2741	0.0823	−2.497	0.822
0.2922	0.0998	−2.305	0.977
0.3056	0.1142	−2.170	1.067
0.3122	0.1217	−2.106	1.137
0.3312	0.1453	−1.929	1.293
0.3551	0.1791	−1.720	1.465
0.3762	0.2130	−1.546	1.629
0.3900	0.2373	−1.458	1.770
0.4028	0.2614	−1.342	1.908
0.3942	0.2451	−1.406	1.983

In general, a plot of ln s versus $I^{1/2}$ gives a better insight into the relationship between ln s and $I^{1/2}$ (see Figure 2).

Discussion

As we can see from Figure 2, the solubility dependence of K_2SO_4 with $I^{1/2}$ is fairly linear on a wide range of ionic strength. The interception of the line with the y-axis for $I^{1/2} \rightarrow 0$ gives:

$$s_0 = 0.1291 \text{ mol} \cdot \text{L}^{-1} (\pm 0.0002) \qquad (6)$$

where s_0 is the solubility of K_2SO_4 in the mixed solvent (water (1) + ethanol (2)) with $w_1 = 0.9$ at 25 °C and no additional ionic strength. Obviously the behavior of ions at $I \rightarrow 0$ can be assumed to be ideal, and then $K_{sp(th)} = 4s_0^3$ for an ionic compound with the formula B_2A or BA_2. So,

$$K_{sp(th),K_2SO_4}/\text{mol}^3 \cdot \text{L}^{-3} = 4s_0^{\ 3} = 8.6067 \cdot 10^{-3} \qquad (7)$$

On the other hand, it can be considered that the concentration solubility product constant ($K_{sp(c)}$) of K_2SO_4 in any saturated solution is:

$$K_{sp(c)} = 4s^3 \qquad (8)$$

Thus, the values of $K_{sp(c)}$ for K_2SO_4 were obtained from the solubility values of Table 1. They are presented in Table 2 and were plotted in Figure 3 (ln $K_{sp(c)}$ versus $I^{1/2}$). As it is clear, the plot is linear on a wide range of ionic strength root, $I^{1/2}$. As before, when $I^{1/2} \rightarrow 0$, the solution would act as an ideal solution, and then it could be concluded that:

$$K_{sp(c)} = K_{sp(th)} \qquad I \rightarrow 0 \qquad (9)$$

The resultant value of $K_{sp(th)}$ at this circumstances agrees with the previous resulted value

$$K_{sp(c)} = K_{sp(th)} = 8.752 \cdot 10^{-3} \qquad I \rightarrow 0$$

Estimated Solubility Product Constant, $K_{sp(es)}$. The estimation of the activity coefficient of ions by using a suitable model and the calculation of the solubility product constant, $K_{sp(es)}$, is a very straightforward process

$$K_{sp(es)} = 4s^3 f_{\pm}^{\ 3} \qquad (10)$$

So we used the Van Rysselberghe and Eisenberg[4] model to estimate the mean activity coefficient:

$$\log f_{\pm} = -\frac{A\sqrt{c}}{1 + a\sqrt{\dfrac{c}{3.042}}} + 2.206 \cdot 10^{-3} c a^3 + 26.27 \cdot 10^{-7} c^2 a^6 \qquad (11)$$

where $A = 0.5059$ at 25.0 °C for water as the solvent, c is the concentration in mol·L^{-1}, and a is a measure of the hydrated ion size.

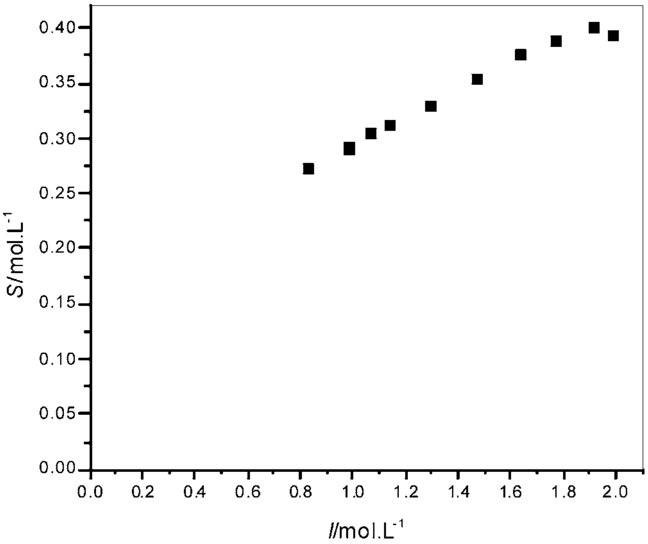

Figure 1. Plot of s versus I for the solubilities of K_2SO_4 in (water (1) + ethanol (2)) with $w_1 = 0.9$ in the presence of various molarities of $NaNO_3$ at 25 °C.

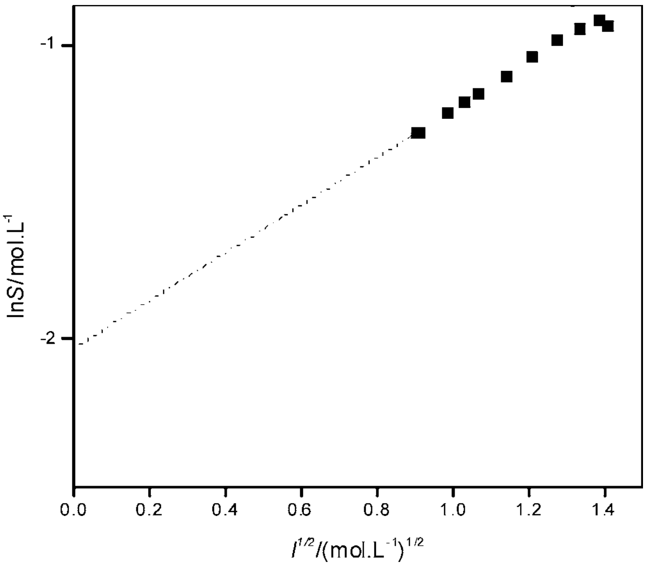

Figure 2. Plot of ln s versus $I^{1/2}$ for the solubilities of K_2SO_4 in (water (1) + ethanol (2)) with $w_1 = 0.9$ in the presence of various molarities of $NaNO_3$ at 25 °C; slope = 0.8306 ± 0.0134, intercept = −2.0470 ± 0.0156.

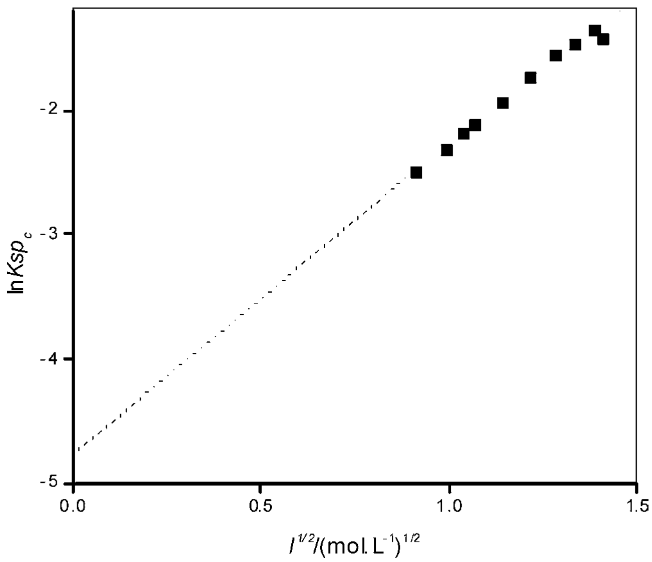

Figure 3. Plot of ln $K_{sp(c)}$ in term of $I^{1/2}$ in the mixed solvent, (water (1) + ethanol (2)) with $w_1 = 0.9$ at various ionic strengths at 25 °C; slope = 2.4757 ± 0.0423, intercept = −4.7385 ± 0.0490.

To apply the above equation for evaluating the mean activity coefficient, $f_\pm$, of the ions in the mixed solvent, we estimate the value of A relative to the mixed solvent as follows:[5,6]

$$A' = \frac{A(d_{\text{mixed}}/d_{\text{water}})^{1/2}}{(D_{\text{mixed}}/D_{\text{water}})^{3/2}} \tag{12}$$

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

$$A' = \frac{0.5059(1.0152/1.00)^{1/2}}{(75.9744/78.54)^{3/2}} = 0.5358 \quad \text{at } 25\ °\text{C}$$

We replaced c by $c_\pm$ in eq 11

$$c_\pm = (c_+^2 + c_-^1)^{1/2} = (4s^3)^{1/3} = 0.4351\ \text{mol}\cdot\text{L}^{-1} \tag{13}$$

The ion size (7) in eq 11 can be evaluated as follows:

$$a_\pm = \frac{1}{2}(a_+ + a_-) = \frac{1}{2}(3.13A° + 3.79A°) = 3.55A° \tag{14}$$

By substituting the above values in eq 11 the following is obtained

$$f_\pm\ (\text{in mixed solvent}) = 0.7818 \tag{15}$$

and then

$$K_{\text{sp(es)}} = K_{\text{sp(c)}} f_\pm^3 = 0.0823(0.7818)^3 = 0.0393 \tag{16}$$

To summarize, the values of $K_{\text{sp(th)}}$, $K_{\text{sp(es)}}$, and $K_{\text{sp(c)}}$ are $8.752\cdot10^{-3}$, $3.930\cdot10^{-2}$, and $8.230\cdot10^{-2}$, respectively. Why these constants are so 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−Huckel model should be adequate for estimating the activity coefficients of ions in the considered solution.[7−12] In these circumstances, the thermodynamic and estimated constants may be comparable. But, in a fairly concentrated electrolyte solution, the ion association is an important factor of nonideality, and additionally, the models which we use for estimating the activity coefficients of ions may not be adequate.[13−16] Therefore, there is an appreciable difference between thermodynamic and estimated constants. Finally, $K_{\text{sp(c)}}$ differs from $K_{\text{sp(th)}}$ and $K_{\text{sp(es)}}$ partly due to nonideal behavior of ions in the solution and partly due to the ion association phenomenon.

Table 3. Results of Iteration Calculation for Obtaining a Reasonable Value of x, x = [ion-pair], in the Mixed Solvent (Water (1) + Ethanol (2)) with $w_1 = 0.9$ at Various Ionic Strengths at 25 °C

iteration	$c_\pm$ mol·L^{-1}	$f_\pm$	x mol·L^{-1}
1	0.4351	0.7818	0.1554
2	0.2636	0.7796	0.1548
3	0.2643	0.7795	0.1547
4	0.2644	0.7795	0.1547
5	0.2644	0.7795	0.1547

Estimating the Extension of Ion-Pairing. Now, we assume that the Van Rysselberghe and Eisenberg model is adequate for estimating the mean activity coefficients,$f_\pm$, and that the difference between $K_{\text{sp(th)}}$ and $K_{\text{sp(es)}}$ comes from ion association phenomenon in the studied solution. For simplicity, we consider only the ion-pair formation[11−24] and neglect the other kinds of ion association. So, if we denote the concentration of $K^+SO_4^{2-}$ ion-pair in the saturated solution of K_2SO_4 in the mixed solvent, (water (1) + ethanol (2)) with $w_1 = 0.9$, at 25 °C by x (in mol·L^{-1}), then the following equation would be available[9]

$$K_{\text{sp(th)}} = (2s - x)^2(s - x)f_\pm{}^3 \Rightarrow x^3f_\pm{}^3 - 5sx^2f_\pm{}^3 + 8s^2xf_\pm{}^3 - 4s^3f_\pm{}^3 + K_{\text{sp(th)}} = 0 \tag{17}$$

Solving eq 17 by using the relationship (9), a reasonable value is obtained,

$$x = 0.1548\ \text{mol}\cdot\text{L}^{-1} \tag{18}$$

(see Table 3).

Reason for Ion-Pair Formation. It is worthwhile to consider the fact that the nonideality of electrolyte solutions is due partly to the activity coefficient of ions in the solutions and partly to the ion-association phenomenon.[13−16] Indeed, when two ions of opposite charges approach close enough to one another, an ion-pair species may be formed.[17−23] For instance, a K^+ SO_4^{2-} ion-pair may be formed in the saturated solution of K_2SO_4 in the mixed solvent, water + ethanol, as follows:

$$K^+_{(aq)} + SO^{2-}_{(aq)} \leftrightarrow K^+SO_4{}^{2-}{}_{\text{ion-pair(aq)}} \quad K_A \tag{19}$$

$$K_A = \frac{a_{\text{ion-pair}}}{a_+a_-} = \frac{[\text{ion-pair}]f_{\text{ion-pair}}}{c_+f_+c_-f_-} \tag{20}$$

where c represents concentration in molarity. Now, if [ion-pair] = x mol·L^{-1}, then $c_+ = (2s - x)$ and $c_- = (s - x)$, while s is the solubility of K_2SO_4 in the mentioned mixed solvent at 25 °C. Now, estimating $f_\pm$ upon the Van Rysselberghe and Eisenberg model and inserting it along with the other values in eq 20, we get $K_A = 4.263$ L·mol^{-1}.

A theoretical approach after Fuoss[18] is available for estimating the ion-pair constant, K_A:

$$K_A = \frac{4\pi Na^3}{3000}e^{z^2e^2/DakT} \tag{21}$$

where N is Avogadro's constant, D is the dielectric constant of the solvent, a is the size parameter, e is the electron charge, k is the Boltzmann constant, and T is temperature in Kelvin. Equation 21 can be simplified as follows:

$$K_A = 2.522 \cdot 10^{21} a^3 \exp(1.674 \cdot 10^{-3} z^2 / aDT) \quad (22)$$

where a is in centimeters. Replacing a by $3.55 \cdot 10^{-8}$ cm[7] gives

$$K_A = 7.25 \quad (23)$$

As it is clear, the estimated value of K_A is considerably greater than its experimental value. The reason could come from the fact that Fuoss model deals with very dilute ionic solution and contact ion-pairs, while these conditions are not completely obeyed in the saturated solution under our research. In addition there are some uncertainties in Rysselberghe−Eisenberg model: the ion size and other affecting factors.

Conclusion

The solubility of K_2SO_4 in the mixed solvent, (water (1) + ethanol (2)) with $w_1 = 0.9$ increases linearly with the increasing ionic strength in a wide range of $NaNO_3$ from (0.1 to 0.7) $mol \cdot L^{-1}$ of the background salt concentrations. The value of the thermodynamic solubility product constant of K_2SO_4 in the mentioned mixed solvent could be estimated on the value of the solubility of the considered ionic compound at zero ionic strength upon the extrapolating method. The saturated solution of K_2SO_4 in the mixed solvent with the presence of $NaNO_3$ is highly nonideal. The nonideality 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 activity coefficient and using the iteration calculations, the activity coefficient contribution and ion association contribution to the solubility of the considered ionic compound in the considered solvent and desired temperature are evaluated.

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