Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 2 (1)
Science and Research Campus
ISSN: 1735-2126

Thermodynamics of the Solubility of Potassium Nitrate in the Mixed Solvent, Ethanol+ Water, and the related Ion- Association

M.Aghaie[1*], F.Ghaemi Amiri[2] and M. Giahi[3]

[1] Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemistry, Science and Research Campus, Islamic Azad University, Tehran, Iran
[3] Department of Chemistry, Lahijan Islamic Azad University, Lahijan, Iran

ABSTRACT

Using the evaporating method, the solubility of Potassium Nitrate was determined in various mixtures containing Water and Ethanol at 25°C. The results show that the solubility of KNO_3 decreases with increasing the mass percent of Ethanol in the mixtures. This trend is along with decreasing the dielectric constant of “Water + Ethanol” mixture. Moreover, it can be concluded that the total solubility of KNO_3 may be regarded as the sum of two contributions; one refering to the free ions in the solution and the other to K+NO3- ion- pairs which are formed in the saturated solution. Estimating the formation constant, KA, for the reaction K+(soln) + NO3-(soln) A K+NO3-(ion-pair) , upon Bjerrum or Fuoss models, then it is quite easy to evaluate the contributions of free ions and K+NO3-(ion- pair) to the total solubility.

Keywords: Solubility; Solubility product constant; Ion-association; Ion-pair, Mixed solvent; Dielectric constant

INTRODUCTION

The major physico- chemical properties of solutions is influenced by solvent dielectric constant. Indeed, in the context of solution chemistry, solvent polarity and solvent dielectric constant are of great interest and as a measure of the solvent ability to stabilize charges or dipoles. As an example, the dissolution of an ionic salt in a solvent depends on the dielectric constant and the polarity of the solvent and on the lattice energy. Of the many theories that have been applied to predict changes in solubility with variation of solvent, the majority are dependent upon changes in the electrostatic properties of the solvent. Numerous relations between solubility of electrolytes and various functions of the dielectric constant, ε, of the solvent have appeared in the litrature. The most commonly used equation is

$$\log s = A_1 + \frac{A_2}{\varepsilon} \qquad (1)$$

where s is the solubility, A_1 and A_2 are constants [1]. Nevertheless, it is easy to find a few exceptions to the rule(1). For instance, the solubility of NaF in water, Methanol and Ethanol at 25 ° C are 0.973 , 0.16 and 0.04 mol kg^{-1} respectively, while their dielectric constants are 78.54 , 32.6 and 24.3 respectively [1,2]. It is apparent, however, that the dielectric constant is not the main determinant of solubility, but rather ion solvation, which depends on the solvent base strength of the hydrogen- bonding capability. So, any improvement should be based on free energy calculation.

---

[*] Corresponding author

It is quite obvious that in the saturated solution of an ionic compound as BA, one can consider the following equilibrium

$$BA_{(s)} \rightleftharpoons B^{+}(soln) + A^{-}_{(soln)} \ ; \ K_a \tag{2}$$

$$K_a = a_{B^+} a_{A^-} \tag{3}$$

$$K_a = e^{-\Delta G^\circ diss/RT} \tag{4}$$

$$\Delta G^\circ diss = (\Delta G^\circ_{f(B^+,soln)} + \Delta G^\circ_{f(A^-,soln)}) - \Delta G^\circ_{f(BA,s)} \tag{5}$$

As it is obvious, if we know the standard Gibbs free energy of dissolution, ΔG°_{diss}, then, to estimate K_a is quite straightforward, or vice versa.

Now, it is worthwhile to consider the fact that the non-ideality of electrolyte solutions is due partly to the activity coefficient of ions in the solution and partly to the ion- association phenomenon [3-6]. Indeed, when two ions of opposite charges close enough one another, an ion-pair species may be formed due to the coulombic interactions [7-14]

$$B^{+}_{(soln)} + A^{-}_{(soln)} \rightleftharpoons B^{+}A^{-}(ion-pair) \ ; K_A \tag{6}$$

$$K_A = \frac{a_{i-p}}{a_{+}a_{-}} \tag{7}$$

where K_A is the assocition constant for the reaction(6) and a_i is respective activity. Atempts have been made to relate association constant to properties of the solvent and the solute, but all are limited in their application and can be used under restricted conditions if the results are to have any meaning [15,16].

The ion-pair concept was introduced by Bjerrum when he considered the probability of finding two ions of opposite charges at a distance, r, from each other [7]. The resulting distribution function has a minimum at a characteristic distance, q,

$$q = \frac{|z_{+}z_{-}|e^2}{2\varepsilon\kappa T} \tag{8}$$

where κ and e are the Boltzmann constant and the charge of electron. Bjerrum proposed that an ion located at a distance r<q from the reference ion of opposite charge tends to form an ion-pair, whereas any other one outside a sphere of radius q would be considered as being free. Then the association constant was obtained from the calculation fraction of paired ions:

$$K_A = \frac{4\pi N}{1000}\left(\frac{z^2e^2}{\varepsilon\kappa T}\right)^3 Q(b) \tag{9}$$

where Q(b) is a function that has been computed by Bjerrum for 1<b<15

$$Q(b) = \int_2^b e^x x^{-4} dx \tag{10}$$

$$b = z^2e^2/a\varepsilon\kappa T \ ; \ x = z^2e^2/r\varepsilon\kappa T \tag{11}$$

where a is the distance of closest approach, or mean ionic diameter.

A different approach has been proposed by Fuoss [16]. He obtained the following expression for the association constant of the contact ion-pair:

$$K_A = \frac{4\pi N a^3}{3000} e^{z^2e^2/\varepsilon a\kappa T} \tag{12}$$

It is useful to consider the definition of ion-pairs as given by Griffiths and Symons:

1. Complexes; two or more ions held in contact by covalent bonds.
2. Contact ion-pairs; ions in contact that do not present any covalent bonding.
3. Solvent- shared ion-pairs; pairs of ions linked electrostatically by a single oriented solvent molecule.
4. Solvent-separated ion-pair; pairs of ions linked electrostatically but separated by more than one solvent molecule.

EXPERIMENTAL

KNO_3 and other chemicals were purchased from Merck Company with high degree of purity and used without further purification. The mixed solvent, Water+ Ethanol, at various mass percents of Ethanol (%3, %5, %10, %20, %30, %40, %50, %60) were prepared from deionized Water and Ethanol. Then, the solubility of KNO_3 in each mentioned mixture was determined by the solvent evaporating method at 25.0°C (table 1).

DISCUSSION

The experimental results (table 1) show that the solubility of KNO_3 in the mixed solvent, Water + Ethanol, decreases with increasing the mass percent of Ethanol. This trend is along with decreasing the dielectric constant of the mixed solvent which can be estimatied by the following approximation:

$$\varepsilon_{m-s} = X_w\varepsilon_w + X_e\varepsilon_e \tag{13}$$

where subscripts m-s, w and e refer to mixed solvent, water and ethanol respectively and X is mole fraction. The dielectric constants which are estimated upon eq.(13) are summarized in table 2.

Table 1. Solubility, s, $molL^{-1}$, of KNO_3 in the mixed solvent, Water+ Ethanol, at 25.0°C

Mass percent of Ethanol	Iterat ion	1	2	3	4
%3	$S/molL^{-1}$	2.890	2.878	2.887	2.870
	$\bar{S}/molL^{-1}$	2.881 ± 0.014			
%5	:	2.646	2.646	2.650	2.647
	$\bar{s}$ =	2.647 ± 0.001			
%10	:	2.110	2.126	2.122	
	$\bar{s}$ =	2.119 ± 0.001			
%20	:	1.387	1.377	1.368	
	$\bar{s}$ =	1.377 ± 0.02			
%30	:	0.9007	0.901	0.898	
	$\bar{s}$ =	0.900 ± 0.002			
%40	:	0.617	0.620	0.611	
	$\bar{s}$ =	0.616 ± 0.011			
%50	:	0.401	0.399	0.403	
	$\bar{s}$ =	0.401 ± 0.004			
%60	:	0.2415	0.243	0.243	
	$\bar{s}$ =	0.2425 ± 0.002			

Table 2. Solubility of KNO_3 in various “Water + Ethanol” mixtures at 25.0°C as a function of dielectric constant of the mixture

Mass percent of Ethanol	$X_{ethanol}$	$\varepsilon_{mixture}$	$s/molL^{-1}$
%0	-0-	78.54	3.302 ± 0.01
%3	0.01196	77.89	2.881 ± 0.014
%5	0.02018	77.74	2.647 ± 0.001
%10	0.04167	76.28	2.119 ± 0.001
%20	0.0891	73.71	1.377 ± 0.02
%30	0.1436	70.75	0.900 ± 0.002
%40	0.2069	67.32	0.616 ± 0.011
%50	0.2813	63.28	0.401 ± 0.004
%60	0.3699	58.48	0.2425 ± 0.002
%100	1	24.3	-

On the basis of eq.(12), one can estimate the ion- association constant, K_A, of the reaction $K^+_{(soln)} + NO^-_{3(soln)} \rightleftharpoons K^+NO^-_{3(ion-pair)}$ related to each “$H_2O + C_2H_5OH + KNO_3$” saturated solution system given in table 2 and then express the concentration of $K^+NO_3^-$ ion-pair in terms of K_A and activities of free ions, a_+ and a_-,

$$[IP] = K_A a_{K^+} a_{NO_3^-} =$$

$$K_A f_{\pm}^2 [KNO_3]^2_{free} \qquad (14)$$

where $[KNO_3]$ represents the fraction of the total molarity of potasium nitrate that contributes to the free ions in the saturated solution. In fact, the total solubility, s, of KNO_3 may be regarded as the sum of two contributions; one corresponding to the free state, s', and the other to the ion-pair state, s'' ,. So, $s = s' + s''$.Or

$$s'' = s - s' \qquad (15)$$

It is clear that the left sides of equations (14) and (15) are the same, therefore

$$s - s' = K_A f_{\pm}^2 s'^2$$

Or

$$K_A f_{\pm}^2 s'^2 + s' - s = 0 \qquad (16)$$

Now, if we estimate the value of K_A upon eq.(12) and also compute the value of $f_{\pm}$ upon a suitable model and then insert them into the eq.(16), we will conclude the values of s' and s'' related to the corresponding saturated solution. Finally, the thermodynamic solubility product constant, $K_{sp(th)}$, of the following equilibrium can be evaluated for each saturated solution

$$KNO_{3(s)} \rightleftharpoons K^{+}_{(soln)free} + NO^{-}_{3(soln)free} : K_{sp(th)}$$

$$\begin{aligned} K_{sp(th)} &= a_{K^+} a_{NO_3^-} \\ &= [K^+][NO_3^-]f_{\pm}^2 \\ &= s'^2 f_{\pm}^2 \end{aligned} \tag{17}$$

The results of such calculations are given in table 3. The formula of Van Rysselberghe-Eisenberg has been used for estimating the values of f± [17]

$$\log f_{\pm} = -\frac{A\sqrt{c}}{1 + a\sqrt{c}/3.042} + 2.206 \times 10^{-3} a^3 c + 26.27 \times 10^{-7} a^6 c^2 \tag{18}$$

where c and a represent the concentration in mol L^{-1} and the ion-size parameter in angstrom respectively and the parameter A that has the value of 0.5059 for water at $25^{o}C$ has been corrected for each "Water + Ethanol" mixture by multiplying it by $(\varepsilon_{water} / \varepsilon_{mixture})^{3/2}$ factor. The value of the ion-size parameter for KNO_3 is taken equal to $3.2^{o}A$[18]. Moreover, it is taken $c = s$ in order to compute $f_{\pm}$ upon eq (18) at the first approximation. Then, $s'_{(1)}$ is calculated upon eq.(16). Now we take $c = s'_{(1)}$ and recalculate $f_{\pm}$. The new $f_{\pm}$ is inserted into the eq.(16) to obtain $s'_{(2)}$. This procedure is iterated until the difference between two successive s' becomes less than %1. The final values of $f_{\pm}$ and s' that are given in table 3 have been obtained by the mentioned procedure.

Table 3. The estimated values of K_A, $s' / molL^{-1}$ and $K_{sp(th)}$ related to the saturated solutions given in table2

Ethanol% by mass	ε	**s/molL^{-1}**	**s'/molL^{-1}**	**$f_{\pm}$**	**K_A**	**$K_{sp(th)}$**
%0	78.54	3.302	1.199	0.681	3.15	0.639
%3	77.89	2.881	1.111	0.673	3.17	0.559
%5	77.74	2.647	1.060	0.667	3.19	0.500
%10	76.28	2.119	0.927	0.656	3.23	0.370
%20	73.71	1.377	0.705	0.637	3.34	0.202
%30	70.75	0.900	0.526	0.624	3.47	0.108
%40	67.32	0.616	0.398	0.613	3.65	0.060
%50	63.28	0.401	0.285	0.605	3.90	0.030
%60	58.48	0.2425	0.188	0.602	4.27	0.013
%100	24.3	-	-	-	23.04	-

CONCLUSION

The solubility of KNO_3 in the mixed solvent "Water + Ethanol" at constant temperature decreases with increasing the mass percent of Ethanol. The trend is along with decreasing the dielectric constant of the mixed solvent. The total solubility of KNO_3 can be considered as the sum of two contributions; one corresponding to the free ions in the saturated solution and the other to the ion-association.

The formation constant of $K^{+}NO_3^{-}$ ion-pair can be estimated upon Bjerrum or Fuoss models and then, the evaluation of the free ions and ion-association contributions to the total solubility of KNO_3 will be quite straightforward.

REFERENCES

1. Water and Aqueous Solutions, Edited by Horne,R.A., (1972)P. 114,116.
2. Chemistry Data Book, by Stark, J.G. and Wallace, H.G., 2nd. Ed.(1990) P.62.
3. Margaret, R.W., Lain, L.J.P., Kenneth, D.M.H., J.Chem. Ed. 75/ 3(1998)352.
4. Zhong,E.C., Friedman, H.L.,J. Phys. Chem. 92 (1988) 1685.
5. Smith, D.E., Kalyuzhnyi, Y.V., Haymet, A.D.J., J.Chem.Phys. 95 (1991) 9165.
6. Ion Association, by Davies, C.W., (1962).
7. Bjerrum, N., K. Danske Vidensk. Selsk (Math. fys. Medd.) 7 (1926)No.9.
8. Guggenheim,E.A.,Disc. Faraday Soc. 21(1957) 53.
9. Fuoss,R.M.,J.Amer. Chem. Soc. 80 (1958) 5059.
10. Eblig,W.,Z. Physik. Chem. (Leipzig), 238 (1968)400.
11. Yokoyama, H., Yamatera, H., Bull. Chem. Soc. Jpn. 48 (1975) 1770.
12. Fialkov, Yu. Ya., Gorbachev, V. Yu., Journal of Molecular Liquids 102/1-3 (2003) 277.

13. Takayanagi, T., Analytical Science February 2004, Vol.20, The Japan Society for Analytical Chemistry.
14. Kalhori, S. , Thomas, R., Al-Khalili, A., Ehlerding, A., Hellbery, F., Neau, A., Larsson, M., Physical Review, A69 (2004) 022713, The American Physical Society.
15. Petit, L.D., Bruckenstein, S., J. Amer.Chem. Soc. 88(1966)4783.
16. Fuoss, R.M., Trans. Faraday Soc. 30 (1934) 967.
17. Van Rysselberghe, P.,Eisenberg, S., J.Am. Chem. Soc. 61(1939)3030.
18. Fundamental of Analytical Chemistry, by Skoog, D.A., West, D.M., Third Ed. (1976).