

**Thermodynamic study of ion- association in  $\text{KNO}_3$  solution in the mixed solvent  
(water +methanol)**

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**ABSTRACT**

The solubility of  $\text{KNO}_3$  in the mixed solvent (water 85%+methanol 15%) were determined by using solvent evaporating method at different temperatures (25, 30, 40, 50, 60 °C). In addition the equilibrium constant of ion pair formation,  $K_{\text{IP}}$ , for  $\text{K}^+\text{NO}_3^-$  ion-pair on the basis of Fuoss contact ion pair model was calculated. Upon choosing the extended Debye-Hückel model for estimating the mean activity coefficient of ions in the saturated solution and using the iteration calculations, we estimated the ion association contribution to the solubility of considered ionic compound in the mixed solvent at various temperatures. The value of thermodynamic solubility product constant,  $K_{\text{sp}}$  (th),  $\Delta H_{\text{diss}}$ ,  $\Delta S_{\text{diss}}$  and  $\Delta G_{\text{diss}}$  of  $\text{KNO}_3$  in the mixed solvent (water 85%+methanol 15%) was calculated.

**Keywords:** Solubility product constant; Ion-association; Fuoss model; Mixed solvent

**INTRODUCTION**

Ion association is important in many phenomena. For example in sea water the percent of free  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  ions respect to the considered compound are approximately (70%, 50% and 10%) respectively and the remaining percent are as ion pairs or other kinds of ion-association. These values show clearly the role of ion association in geochemistry.

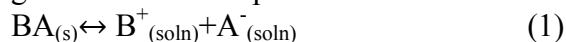
Ion-association phenomenon contributes in many other cases, such as the metal corrosion in aqueous media, the efficiency of Lithium batteries, electroplating, surfactants behaviour and so on [1-6]. So, the ion association phenomenon has been widely studied

experimentally and theoretically. Generally, the ion-association phenomenon has an important role in the extended of solubility of ionic compounds in different solvents and mixed solvents and the behaviour of considered electrolytic solutions [6-20].

The solubility of a given ionic compound depends on the dielectric constant,  $D$ , of the medium, temperature and some other factors. In thermodynamic view point, the extend of the solubility of a given ionic compound is related to its standard Gibbs free energy change,  $\Delta G_{\text{diss}}^0$ , associated to the dissolution of the considered ionic compound, such as, BA,

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that we can assume the following equilibrium in its saturated solution at a given constant temperature



while in this research  $BA_{(s)} \equiv KNO_3_{(s)}$ ,  $B^+ \equiv K^+$  and  $A^- \equiv NO_3^-$

As, we know from the chemical thermodynamics, the thermodynamic solubility product constant,  $K_{sp(th)}$ , of an ionic compound such as BA is written as:

$$K_{SP(th)} = a_B^+ a_A^- = [B^+][A^-] \gamma_{\pm}^2 = e^{\frac{-\Delta G_{diss}^0}{RT}} \quad (2)$$

where  $a_i$  represents the activity of species  $i$  in molarity,  $[i]$  is molarity of species  $i$  in solution and  $\gamma_{\pm}$  is mean activity coefficient. Now, if we denote the solubility of BA by  $s$  in  $\text{mol L}^{-1}$ , we could write

$$K_{SP(th)} = s^2 \gamma_+ \gamma_- = e^{\frac{-\Delta G_{diss}^0}{RT}} \quad (3)$$

So, knowing the values of  $s$  and  $\gamma_+$  and  $\gamma_-$  at a given condition, we can compute  $K_{sp(th)}$  and  $\Delta G_{diss}^0$ , or, viceversa.

We should pay appropriate attention to the fact that the fraction of ions that are involved in the ion association phenomenon do not contribute to the equilibrium (1) and equation (2). So, we should consider the ion association phenomenon in the context of studying ionic solution behavior along with the other affecting parameters.

The formation of ion-pair, ion-triplet and ... is due to the balance between electrostatic interaction of involved ions and their thermal agitation.

Bjerrum in his study of ion pair formation concluded that when the coulombic attraction energy between two ions of opposite charges is nearly to  $2kt$ , we may have an ion-pair ( $k$  is the Boltzmann constant and  $T$  is temperature in Kelvin)[15].

Alternatively, if the distance,  $r$ , between the center of two ions of opposite sign is less than  $q = \frac{Z_+ Z_- e^2}{8\pi D k T \epsilon_0}$ , we may have an ion-pair species [15].

$$r \leq q = \frac{Z_+ Z_- e^2}{8\pi D k T \epsilon_0} \quad (4)$$

where  $z_+$  and  $z_-$  are the electric charge of cation and anion respectively,  $e$  is absolute charge of electron,  $\epsilon_0$  is permittivity of vacuum,  $D$  is dielectric constant of the medium,  $k$  is the Boltzmann constant and  $T$  temperature in Kelvin.

The reaction of  $B^+A^-$  ion pair formation from  $B^+$  and  $A^-$  ions is written as



where  $a$  is activity in  $\text{mol L}^{-1}$

## EXPERIMENTAL

$KNO_3$  and other chemicals were purchased from Merck Company with high degree of purity and used without further purification.

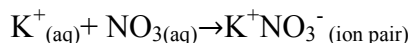
The mixed solvent (water deionized 85% + methanol 15%) was prepared. Then, the solubility of  $KNO_3$  was determined by the solvent evaporating method at different temperatures (288, 298, 308, 318, 328, 338, 348 K) and the results are given in table (1).

**Table 1.** Solubility,  $s$ ,  $\text{mol L}^{-1}$ , of  $KNO_3$  in the mixed solvent, (water 85% + methanol 15%) at different temperature

$T/K$	$s/\text{mol L}^{-1}$
288	0.761
298	1.651
308	1.879
318	2.719
328	3.609
338	4.697
348	5.790

## RESULT AND DISCUSSION

We can consider the,  $K^+_{(aq)} + NO_3^-_{(aq)} \rightarrow K^+NO_3^-_{(ion\ pair)}$  equilibrium when an ion – pair species is formed [12-15] in the mixed solvent, (water 85%+ methanol 15%)



$$K_{IP} = \frac{a_{IP}}{a_{K^+} a_{NO_3^-}} \quad (6)$$

where  $a$  is activity in molarity .

The contact ion pair formation constant can be estimated by Fuoss model:

$$K_{IP} = 2.522 \times 10^{21} a^3 \exp(1.674 \times 10^3 z^2 / TaD) \quad (7)$$

where here  $a$  is the ion size in centimeters,  $T$  in Kelvin, and  $K_{IP}$  in  $L.mol^{-1}$  and  $D$  is the dielectric constant of the mixed solvent. The dielectric constant of the mixed solvent  $D_{mix}$  can be estimated by the following equation

$$D_{m-s} = x_w D_w + x_m D_m \quad (8)$$

$D_w$  and  $D_m$  represent the dielectric constant of water and methanol respectively.

The estimated values of  $K_{IP}$  upon eq. (7) at various temperatures are gathered in table 2.

**Table 2.** The values of  $K_{IP}$ , of dissolving KNO3 in the mixed solvent (water 85%+ methanol 15%) at different temperatures

$T/K$	$K_{IP}$
288	0.9232
298	0.8458
308	0.7797
318	0.7219
328	0.6717
338	0.6278
348	0.2882

Considering only the ion-pair formation in the saturated solution and neglecting the other kinds of ion association formation and denoting the

molarity of ion-pair species in the saturated solution by  $x$  and the molarity of other considered ions by  $[...]_{free}$ , we may rewrite eq.(7) as follow:

$$K_{IP} = \frac{x}{(s-x)^2 \gamma_{\pm}^2} \quad (8)$$

where  $x = [IP] \cong a_{IP}$  and  $(s-x) = [K^+]_{free} = [NO_3^-]_{free}$  and  $\gamma_{\pm}$  = mean activity coefficient for  $K^+$  and  $NO_3^-$  ions.

Or:

$$x^2 - (2s + \frac{1}{K_A \gamma_{\pm}^2}) x + s^2 = 0 \quad (9)$$

By solving eq. (9), we can obtain the value of  $x$ , but we should firstly calculate  $\gamma_{\pm}$  by using the extended Debye –Huckle law (eq.10)

$$\log \gamma_{\pm} = - \frac{A' |Z_+ Z_-| ([I])^{\frac{1}{2}}}{1 + aB'([I])^{\frac{1}{2}}} \quad (10)$$

The value of  $A$  and  $B$  respect to water at 298 K is 0.509, and , 0.328  $A^{\circ-1}$  and  $d$  represents the density of the solvent in terms of ( $g\ cm^{-3}$ ).  $A'$  and  $B'$  for the mixed solvent can be calculated at the same temperature, as follow:

$$A' = \frac{A(d_{ms}/d_{water})^{\frac{1}{2}}}{(D_{ms}/D_{water})^{\frac{3}{2}}} \quad B' = \frac{B}{(D_{ms}/D_{water})^{\frac{1}{2}}} \quad (11)$$

$A'$  and  $B'$  refer to the mixed solvent at the same temperature and  $a$  is the parameter of ion size.

In order to calculate  $x$  upon equation (9), at the first approximation we assumed  $I=s$ , and found the first approximate values of  $\gamma_{\pm}$  and  $x$ , say  $x_1$ .

In the second step we set  $I=s-x_1$  and calculated the value of  $\gamma_{\pm}$  and  $x$  by resolving eq.(9) to obtain the next value of

$x(x_2)$ . We repeated the procedure up to achieving to the reliable value for  $x$  (table3) at every experimental temperature.

Now, equation (2) respect to  $KNO_3$  may be rewritten as:

$$K_{sp(th)} = [K^+]_{free} [NO_3^-]_{free} \gamma_{\pm}^2 \quad (12)$$

and calculate the value of  $K_{sp(th)}$  at the desired temperature(see table4).

Using Van't Hoff equation (plot of  $\ln K_{sp(th)}$ ), we can obtain the value of  $\Delta H^\circ$  and  $\Delta S^\circ$  related to the dissolving  $KNO_3$  in

the considered mixed solvent (water 85%+ methanol 15%) from the slope and intercept of the plot.

$$\ln K_{th} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{RT} \quad (13)$$

The obtained values are summarized in table 5.

In addition the values of  $\Delta G^\circ_{diss}$  at experimental temperatures can be obtained from the following equation and the results are given in table 6

$$\Delta G^\circ = -RT \ln K_{th} \quad (14)$$

**Table 3.** The values of ion pair concentrations obtained upon cyclic calculations in the mixed solvent (water85% + methanol 15%) at different temperatures

T/K	$\gamma_{\pm}$	$X_1$	$\gamma_{\pm}$	$X_2$	$\gamma_{\pm}$	$X_3$
288	0.557	0.118	0.571	0.122	0.572	0.122
298	0.493	0.347	0.5115	0.365	0.5126	0.365
308	0.484	0.398	0.502	0.418	0.503	0.419
318	0.458	0.647	0.476	0.678	0.477	0.681
328	0.439	0.927	0.458	0.927	0.459	0.976
338	0.423	1.295	0.442	1.359	0.444	1.365
348	0.4111	1.080	0.4226	1.114	0.4230	1.114

**Table 4.** The values of  $s$ ,  $I$ ,  $K_{IP}$ ,  $K_{th}$ ,  $\ln K_{th}$  of dissolving  $KNO_3$  in the mixed solvent (water 85%+ methanol 15%) at different temperatures

$T$	$s/(\text{mol/L})$	$I$	$K_{IP}$	$\ln K_{th}$	$K_{th}$
288	0.761	0.639	0.9232	-2.017	0.133
298	1.651	1.286	0.8458	-0.837	0.433
308	1.879	1.461	0.7797	-0.618	0.539
318	2.719	2.041	0.7219	-0.056	0.945
328	3.609	2.637	0.6717	0.378	1.460
338	4.697	3.330	0.6278	0.782	2.188
348	5.79	4.675	0.2882	1.364	3.912

**Table 5.** The values of  $\Delta H^\circ_{diss}$  and  $\Delta S^\circ_{diss}$  of dissolving  $KNO_3$  in the mixed solvent (water85%+methanol 15%)

$\Delta H^\circ_{diss}/\text{J/mol}$	$\Delta S^\circ_{diss}/\text{J/molK}$
45707.87	142.53

**Table 6.** The values of  $\Delta G^\circ_{\text{diss}}$  of dissolving  $\text{KNO}_3$  in the mixed solvent (water 85%+methanol 15%) at different temperatures

T/K	288	298	308	318	328	338	348
$\Delta G^\circ_{\text{diss}}$ J/mol	4829.569	2073.728	1582.52	149.3776	-1030.8	-2197.52	-3946.42

## CONCLUSION

The solubility of  $\text{KNO}_3$  in the mixed solvent (water 85% + methanol 15%) increased by increasing in temperature. The formation constant of ion pair,  $\text{K}^+\text{NO}_3^-$  was estimated by fuoss model. Then, the concentrations of  $\text{K}^+\text{NO}_3^-$  ion-pair in the mixed solvent at various temperatures, were evaluated upon  $\text{KNO}_3$  solubilities,  $s$ , and estimated mean activity coefficient of ions,  $\gamma_{\pm}$ .

Using the solubility of  $\text{KNO}_3$  at a given temperature and related  $\text{K}^+\text{NO}_3^-$  ion-pair concentration and estimated,  $\gamma_{\pm}$ , we calculated  $K_{\text{sp(th)}}$  for  $\text{KNO}_3$  dissolution in the mixed solvent at the related temperature.

In addition the variation of  $\ln K_{\text{sp(th)}}$  versus  $\frac{1}{T}$  was drawn (Van t Hoff plot) and  $\Delta H^\circ_{\text{diss}}$  and  $\Delta S^\circ_{\text{diss}}$  were determined by the slope and intercept of the plot. Both  $\Delta H^\circ_{\text{diss}}$  and  $\Delta S^\circ_{\text{diss}}$  are positive.

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