

## CHAPTER V

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# CONDUCTIVITY IS A CONTRIVANCE TO EXPLORE ION-PAIR AND TRIPLE ION STRUCTURE OF ETHANOATES IN TETRAHYDROFURAN, DIMETHYL SULPHOXIDE AND THEIR BINARIES

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### 5.1 Introduction

Studies of the transport properties of electrolytes in different solvent media are of considerable importance for the information they provide on the behaviour of ions in solution.

Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore the ion-ion and ion-solvent interactions can be better studied. Furthermore different quantities strongly influenced by solvent properties can be derived from concentration-dependence of the electrolyte conductivity. The conductometric method is well-suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions [1-6]. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions, which in its turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Thus extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years to examine the nature and magnitude of ion-ion and ion-solvent interactions.

Tetrahydrofuran (THF) is an important liquid which find a variety of applications in pharmaceuticals, cosmetics, etc. Dimethylsulphoxide (DMSO) is a powerful broad spectrum solvent for a wide variety of inorganic and organic reactants. Having low toxicity, DMSO can be used in biology and medicine, especially for low-temperature preservation. We have taken pure THF ( $\epsilon = 7.58$ ), DMSO ( $\epsilon = 46.7$ ) and their mixture for this study because we prefer non aqueous solvent which are nonprotic polar solvent and hydrogen bonding can be avoided. The experimental acetate salts are chosen as their charge densities are high and they form solvent-

separated ion pairs. Such studies have been assumed important because of their applications in modern technology [7]. This type of solvent mixture have applications in high energy batteries especially lithium batteries, in organic syntheses and cosmetics technology as manifested from the physicochemical studies in these media [8-10].

In this paper, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of some ethanoates in pure tetrahydrofuran (THF) and dimethylsulphoxide (DMSO) and their binary mixtures by using precise conductivity measurements at 298.15 K.

## 5.2 Experimental Section

Tetrahydrofuran,  $C_4H_8O$  (Merck, India) containing 0.1 % water and 0.005 % peroxide, was kept for several days over KOH, refluxed for 24 h, and distilled over  $LiAlH_4$  [8, 11-13].

Dimethyl sulfoxide (SRL Extra pure) was kept for several days over anhydrous  $CaSO_4$  and refluxed for 4 h over CaO. Finally, it was distilled according to the procedure described earlier [14]. Purity of the solvent checked by comparing their viscosity and density values with the literature values [15, 16].

The experimental ethanoates  $CH_3COOLi$ ,  $CH_3COOK$ ,  $CH_3COONH_4$  and  $CH_3COONa$  are 99 % pure (Merck) and they were purified by recrystallization twice from conductivity water. The samples were dried in vacuum and stored over  $P_2O_5$  under vacuum [17]. Tetrabutylammonium acetate ( $Bu_4NOAc$ ) was purified by recrystallization from acetone, and the crystallized salt was dried in vacuum for 48 hrs. Sodium tetraphenylborate ( $NaBPh_4$ ) was recrystallized three times from acetone and then dried under vacuum for 72 hrs [18]. Deionized water was used after further distillation having specific conductivity  $1.99 \times 10^{-6} \Omega^{-1}cm^{-1}$  at 298.15 K. The materials finally obtained were found to be > 99.5 % pure

Binary solvent mixtures were prepared by mixing a required volume of THF and DMSO with earlier conversion of required mass of each liquid into volume at 298.15 K using experimental densities. A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion

of molality into molarity was accomplished using density values. The uncertainty of molarity of different salt solutions is evaluated to  $\pm 0.0001 \text{ mol dm}^{-3}$ .

The value of the relative permittivity ( $\epsilon$ ) of the solvent mixtures was assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner [19]. The density ( $\rho$ ) was measured by means of vibrating-tube density-meter (Anton Paar, DMA 4500) which was calibrated with distilled water and air [18]. The uncertainty in the density measurement was  $\pm 0.0002 \text{ g cm}^{-3}$ .

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to  $\pm 0.01 \text{ K}$ . After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to  $\pm 0.1 \text{ s}$ . The uncertainty of viscosity values is  $\pm 0.003 \text{ cP}$ . The details of the methods and measurement techniques had been described elsewhere [20, 21].

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy  $\pm 0.01 \%$ ) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately ( $0.1 \pm 10 \%$ ). Measurements were made in a water bath maintained within  $T = (298.15 \pm 0.01) \text{ K}$  and the cell were calibrated by the method proposed by Lind et al [22]. The entire conductance data were reported at 1 KHz and were found to be  $\pm 0.3 \%$  precise.

## **5.3 Results and Discussion**

### **5.3.1 Electrical conductivity of ethanoates in pure DMSO and different binary mixtures of (THF + DMSO):**

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The experimental values of the molar conductance,  $\Lambda$  against the respective concentration,  $c$  for different electrolytes in pure THF ( $w_1$ ), DMSO ( $w_2$ ) and their different binary mixtures at 298.15 K are recorded in Table 2.

The conductance data for different electrolytes in pure DMSO and different binary mixtures having higher to moderate relative permittivity values ( $\epsilon = 46.70$ -

17.36), have been analyzed using the Fuoss conductance-concentration equation [23]. The conductance curves ( $\Lambda$  versus  $\sqrt{c}$ ) were linear and extrapolation of  $\sqrt{c} = 0$  evaluated the starting limiting molar conductances for the electrolytes. For a given set of conductivity values ( $c_j, \Lambda_j, j = 1, 2 \dots, n$ ), three adjustable parameters, i.e.,  $\Lambda^\theta, K_A$ , and  $R$  are derived from the Fuoss equation. Here  $\Lambda^\theta$  is the limiting molar conductance,  $K_A$  is the observed association constant, and  $R$  is the association distance, i.e., the maximum center to center distance between the ions in the solvent separated ion-pairs. There is no precise method [23] for determining the  $R$  value but in order to treat the data in our system,  $R$  value is assumed to be,  $R = a + d$ , where  $a$  is the sum of the crystallographic radii of the ions and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance,  $d$  is given by [24],

$$d = 1.183(M/\rho)^{1/3} \quad (1)$$

where  $M$  is the molecular weight and  $\rho$  is the density of the solvent. For mixed solvents,  $M$  is replaced by the mole fraction average molecular weight ( $M_{av}$ ) which is given by,

$$M_{av} = M_1 M_2 / (W_1 M_2 + W_2 M_1) \quad (2)$$

where  $W_1$  is the weight fraction of the first component of molecular weight  $M_1$ .

Thus the Fuoss conductance equation may be represented as follows:

$$\Lambda = p[\Lambda^\theta(1 + R_x) + E_L] \quad (3)$$

$$p = 1 - \alpha(1 - \gamma) \quad (4)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (5)$$

$$-\ln f = \beta k / 2(1 + k_R) \quad (6)$$

$$\beta = e^2 / \epsilon k_B T \quad (7)$$

$$K_A = K_R(1 + K_S) \quad (8)$$

where,  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $k^{-1}$  is the radius of the ion atmosphere,  $\epsilon$  is the relative permittivity of the solvent mixture,  $e$  is the electron charge,  $c$  is the molarity of the solution,  $k_B$  is the Boltzmann constant,  $K_S$  is the association constant of contact-pairs,  $K_R$  is the association constant of solvent-separated pairs,  $\gamma$  is the fraction of solute

present as unpaired ion,  $\alpha$  is the fraction of contact pairs,  $f$  is the activity coefficient,  $T$  is the absolute temperature and  $\beta$  is twice the Bjerrum distance.

The computations are performed on a computer using the program suggested by Fuoss. The initial  $\Lambda^0$  values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [25, 26]. Now, we input for the program, the no. of data,  $n$ , followed by  $\varepsilon, \eta$  (viscosity of the solvent mixture), initial  $\Lambda^0$  value,  $T, \rho$  (density of the solvent mixture), mole fraction of the first component, molecular weights,  $M_1$  and  $M_2$  along with  $c_j, \Lambda_j$  values where  $j = 1, 2, \dots, n$  and an instruction to cover preselected range of  $R$  values.

In practice, calculations are performed by finding the values of  $\Lambda^0$  and  $\sigma$  which minimize the standard deviation,  $\sigma$ , whereby

$$\sigma^2 = \sum [\Lambda_{j(calc)} - \Lambda_{j(obs)}^0]^2 / n - 2 \quad (9)$$

for a sequence of  $R$  values and then plotting  $\sigma$  against  $R$ , the best-fit  $R$  corresponds to the minimum in  $\sigma$  versus  $R$  curve. So an approximate sum is made over a fairly wide range of  $R$  values using a 0.1 increment to locate the minimum, but no significant minima is found in the  $\sigma$ - $R$  curves for the salt studied here, thus  $R$  values are assumed to be  $R = a + d$ , with terms having usual significance [27]. Finally, the corresponding  $\Lambda^0$  and  $K_A$  values are obtained which are reported in Table 3, along with  $R$  and  $\sigma$  for the two binary mixtures of salts.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar salt conductance into their ionic components. In the absence of accurate transference data for these systems, we have used the "reference electrolyte" method. Sodium tetrphenyleborate ( $\text{NaBPh}_4$ ), tetrabutyleammonium acetate ( $\text{Bu}_4\text{NOAc}$ ) and sodium acetate ( $\text{NaOAc}$ ) were used to derive the  $\Lambda^0$  of tetrabutylammonium tetrphenyl borate ( $\text{Bu}_4\text{NBPh}_4$ ) as reference electrode following the Kohlrausch rule. The  $\Lambda^0$  ( $\text{Bu}_4\text{NBPh}_4$ ) was obtained from the  $\Lambda^0$  values of tetrabutylammonium acetate ( $\text{Bu}_4\text{NOAc}$ ), sodium tetrphenylborate ( $\text{NaBPh}_4$ ), and sodium acetate ( $\text{NaOAc}$ ) in the appropriate solvent mixture using the relation,

$$\Lambda^0(\text{Bu}_4\text{NBPh}_4) = \Lambda^0(\text{Bu}_4\text{NOAc}) + \Lambda^0(\text{NaBPh}_4) - \Lambda^0(\text{NaOAc}) \quad (10)$$

Ionic divisions were accomplished through the following relationships [28, 29]:

$$\Lambda^{\circ}(\text{Bu}_4\text{NBPh}_4) = \lambda^{\circ}(\text{Bu}_4\text{N}^+) + \lambda^{\circ}(\text{BPh}_4^-) \quad (11)$$

$$\lambda^{\circ}(\text{Bu}_4\text{N}^+) = 0.517 \Lambda^{\circ}(\text{Bu}_4\text{NBPh}_4). \quad (12)$$

The limiting ionic conductances calculated from the above equation are recorded in Table 4.

The limiting ionic conductance  $\lambda_{\pm}^{\circ}$  values were in turn utilized for the calculation of Stoke's hydrodynamic radii  $r_s$  according to the expression as modified by Gill [26] is given below.

$$r_s = \frac{F^2}{6\pi N_A \eta \lambda_{\pm}^{\circ}} \quad (13)$$

The Walden's product [30, 31],  $\Lambda^{\circ}\eta$  of an ion is also calculated for the various solvent compositions and the results have been given in Table 4.

The Gibbs' energy of ion-pair formation,  $\Delta G^{\circ}$  for the electrolytes in different binary mixtures studied here calculated by the following relationship [32],

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

Table 3 shows that the conductance of the electrolytes is observed to be lower when THF is present in lower proportion to the solvent mixtures of THF + DMSO considered. The increase in conductance with increase of concentration of THF in the mixture can probably be interpreted as a contraction of the solvent sheath (which envelops an ion and moves by ion-solvent interactions), whereas with increase of concentration of DMSO, the numbers of activated solvent molecules increase which forming the sheath. This trend also suggests predominance of the solvent viscosity ( $\eta_0$ ) over relative permittivity ( $\epsilon$ ) in effecting the electrolytic conductance in these media as with the increase of concentration of THF, both viscosity and permittivity of solvent mixtures decreases.

It also shows that the limiting equivalent conductivity for acetate salts of common anion follow the sequence:  $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$  in all the solvent mixtures studied here at the investigated temperature. The trend of variation of  $\Lambda^{\circ}$  values also indicates the relative actual sizes of these ions as they exist in solution. Thus the sizes of these cations as they exist in solution, follow the order:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ .

There is marked characteristic behaviour in the association constant  $K_a$  values. These electrolytes solutions, in general, show an increase in the  $K_a$  values

with an increase in mole fraction of THF in these solvent mixtures. This is expected as the relative permittivity ( $\epsilon$ ) decreases with the increase of THF.

The Walden products  $\Lambda^\circ\eta$  of the ions are usually employed to discuss the interactions of the ions with the solvent medium. From the Table 4, we see that the Walden product of cations decrease in the order,  $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ , and the Fig.1 also predicts that the electrolyte taken as a whole follows the same sequence. This is justified as the Walden product of an ion or solute is inversely proportional to the effective radius ( $r$ ) of the ion or solute in a particular solvent [33],

$$\Lambda^\circ\eta = 1/6\pi rT \quad (15)$$

This points out that the electrostatic ion-solvent interaction is strong in these cases, apparently due to the very high surface charge density on small ions [34]. Fig.1. indicates the variation of the Walden product with solvent composition due to preferential solvation of cations by THF and DMSO molecules respectively [34, 35]. The decrease in the Walden product with increase of concentration of THF in indicates the preferential solvation of cations by THF in (THF + DMSO) mixture. However this decrease may also probably be due to the Zwanzig [8] solvent relaxation effect.

The starting point for most evaluations of ionic conductances is Stokes' law that states that the limiting Walden product for any singly charged, spherical ion is a function of only the ionic radius and thus, under normal conditions, is a constant. In Table 4, we have calculated the Stokes' radii  $r_s$  of these ions in these different solvent mixtures.

Fig. 2 shows that the trend in ionic Walden products ( $\lambda^\circ\eta$ ) just mimics the trend in Walden product ( $\Lambda^\circ\eta$ ) for all electrolytes in these solvent mixtures and hence Stokes' radii also follow the same trend  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ . For lithium, sodium, potassium and ammonium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in these solvent mixtures. The Stokes' radius of the acetate ion is, however, found to be either very close to or slightly higher than their corresponding crystallographic radii indicating their low degree of solvation. This also supports our earlier contention, derived from the Walden products of those ions.

Fig. 3 points out the nature of curve for the Gibbs energy for ion-pair formation,  $\Delta G^\circ$  which clearly predicts that the tendency for ion-pair formation decreases significantly with an increase in the association factor for the ethanoates in different THF + DMSO mixtures. The  $\Delta G^\circ$  curve in Fig. 3 along with the other parameters mentioned above are quite in accordance with the results observed by Barthel et al. [32] and Hazra et al [34, 35].

The schematic representation of solvation of ions, at a particular concentration, in the solvent mixtures studied here in view of various derived parameters can be depicted in scheme I. Here the blue and red circles refer to THF ( $w_1$ ) and DMSO ( $w_2$ ) respectively.

**5.3.2. Electrical conductivity of ethanoates in pure THF:**

The experimental values of the molar conductances,  $\Lambda$  against the respective concentration,  $c$  of different acetate salts in pure THF ( $\epsilon = 7.58$ ) at 298.15 K are presented in Table 2. Here the conductance curves ( $\Lambda$  versus  $\sqrt{c}$ ) for all the electrolytes were follow the same trend, i.e.,  $\Lambda$  decreases with increasing concentration, reaches a minimum and then increases.

The conductance data have been analyzed by the Fuoss-Kraus triple-ion theory [36] in the form as given below,

$$\Lambda g\sqrt{C} = \frac{\Lambda^\circ}{\sqrt{K_p}} + \frac{\Lambda^\circ_T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda^\circ}\right) C \tag{16}$$

$$g(c) = \frac{\exp\left\{-\frac{\beta'}{\sqrt{\Lambda^\circ}} \sqrt{(c\Lambda)}\right\}}{\left\{1 - \frac{S}{\Lambda^{3/2}} \sqrt{(c\Lambda)}\right\} \sqrt{\left(1 - \frac{\Lambda}{\Lambda^\circ}\right)}} \tag{17}$$

$$\beta' = \frac{1.8247 \times 10^6}{(\epsilon T)^{3/2}} \tag{18}$$

$$S = \alpha \Lambda^\circ + \beta = \frac{0.8206 \times 10^6}{(\epsilon T)^{3/2}} \Lambda^\circ + \frac{82.501}{\eta (\epsilon T)^{1/2}} \tag{19}$$

In the above equations,  $\Lambda^\circ$  is the sum of the molar conductances of the simple ions at infinite dilution,  $\Lambda^\circ_T$  is the sum of the values for the two kinds

of triple-ions,  $K_P$  and  $K_T$  are the ion-pair and triple-ion formation constants respectively,  $S$  is the limiting Onsager coefficient,  $\epsilon$  is the permittivity of the solvent,  $T$  is the absolute temperature. The symmetrical approximation of the two possible formation constant of triple ions equal to each other has been considered [37].  $g(c)$  is the factor which incorporates all interionic interaction terms [38].

Neglecting,  $\Lambda/\Lambda^0$ ,  $(S/\Lambda^{03/2})(c\Lambda)^{1/2}$  and assuming  $f_{\pm} = 1$ , lead to  $g(c) = 1$  in eq. 16, we get,

$$\Lambda\sqrt{C} = \frac{\Lambda^0}{\sqrt{K_P}} + \frac{\Lambda_T^0 K_T}{\sqrt{K_P}} C \quad (20)$$

$\Lambda^0$  is obtained by applying the Walden's rule [39] as suggested by the work of Krumgalz [31].  $\Lambda_T^0$  is calculated by setting the triple-ion conductance as equal to  $2/3 \Lambda^0$  [40]. On running the Fuoss-Kraus equation, we get  $K_P$ ,  $K_T$  from the slope and intercept. The results are listed in Table 5.

The limiting molar conductances of the simple ions,  $\Lambda^0$  and limiting molar conductances of the triple ions,  $\Lambda_T^0$  of the acetate salts in pure THF at 298.15 K follow the trend,

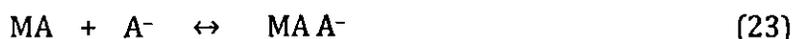


Increase in  $\Lambda^0$  significantly increase the mobility of ions due to lower solvation of the ions by the solvent molecules. Thus, the tendency of the ion-pair and triple-ion formation of electrolytes depends on the size and the charge distribution of the ions. Similar type of results has been reported earlier by Roy et al [21].

$K_P$  and  $K_T$  values predicts that major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions (neglecting quadruples). The values show that  $\text{CH}_3\text{COOLi}$  has the lowest  $K_P$  and highest  $K_T$  in pure THF as compared to the other salts. The tendency of triple-ion formation can be also judged from the  $K_T/K_P$  ratios, which is highest for  $\text{CH}_3\text{COOLi}$ . The large association between the ions may be due to the coulombic interactions as well as to covalent bonding forces, considering the ionic sizes of the species in the solution. The results are in good agreement with the works of Hazra and Muhuri [3].

At very low dielectric constant of the solvent, i.e.  $\epsilon < 10$ , electrostatic ionic interactions are very large. So the ion-pairs attract the free present in

the solution medium as the distance of the closest approach of the ions becomes minimum. This results in the formation of symmetrical triple-ions in addition to ion-pairs which acquire the charge of the respective ions in the solution [13, 41].



The effect of ternary association [21] is to remove some non-conducting species MA from the solution and replace them by triple ions which contribute to the conductance.

Schematically the triple-ion formation for lithium acetate (for example) in pure THF can be depicted in scheme II.

Furthermore, the ion-pair and triple-ion concentrations,  $C_p$  and  $C_T$  respectively of the electrolyte are also calculated at the highest concentration, using the following relations [21, 42],

$$\alpha = 1/K_p^{1/2} \cdot C^{1/2} \quad (24)$$

$$\alpha_T = (K_T/K_p^{1/2}) C^{1/2} \quad (25)$$

$$C_p = c(1 - \alpha - 3\alpha_T) \quad (26)$$

$$C_T = (K_T/K_p^{1/2}) C^{3/2} \quad (27)$$

Here,  $\alpha$  and  $\alpha_T$  are the fraction of ion-pairs and triple-ions and  $C_p$  and  $C_T$  are the concentration of ion-pair and triple-ion formation respectively. The  $C_p$  and  $C_T$  values show that, CH<sub>3</sub>COOLi has the highest value of  $C_T$  in pure THF as compared to the other salts whereas CH<sub>3</sub>COONH<sub>4</sub> has the highest value  $C_p$ . The results are in good agreement with the earlier conclusion and our results supports the general view that the tendency of ion-pair and triple-ion formation depends on the size and the charge distribution of the ions as well as on the solvent polarity. Similar type of work has been reported by Corti et al [43].

## 5.4 CONCLUSION

Through our work we have shown that the tendency of triple ion formation is proved in pure THF having low dielectric constant but that tendency has been diminished by the addition of DMSO. The electrolytes are remaining associated in solvent mixtures but the solvation of the ions weakened as soon as the ion pair is formed. The cations are found to be substantially solvated whereas the anions appear to have weak interactions with the solvent molecules. The coulombic force has a great effect on the association process.

### List of symbols

|             |   |
|-------------|---|
| $\rho$      | solution density                                |
| $\rho_0$    | solvent density                                 |
| $\eta$      | solution viscosity                              |
| $\eta_0$    | solvent viscosity                               |
| $\epsilon$  | relative permittivity                           |
| $c$         | molarity  |
| $m$         | molality  |
| $\Lambda$   | molar conductance                               |
| $\Lambda^0$ | limiting molar conductance                      |
| $K_A$       | association constant                            |
| $K_S$       | association constant of contact-pairs           |
| $K_R$       | association constant of solvent-separated pairs |
| $f_{\pm}$   | mean activity coefficient                       |
| $R_X$       | relaxation field effect                         |
| $E_L$       | electrophoretic counter current                 |
| $K_P$       | ion-pair formation constants                    |
| $K_T$       | triple-ion formation constants                  |
| $C_P$       | ion-pair concentrations                         |
| $C_T$       | triple-ion concentrations                       |
| $\gamma$    | fraction of solute present as unpaired ion      |
| $\beta$     | twice the Bjerrum distance                      |
| $\kappa$    | radius of ionic atmosphere                      |

- $e$  electric charge  
 $k_B$  Boltzmann constant  
 $R$  association distance or co-sphere diameter  
 $r_s$  Stoke's hydrodynamic radii  
 $\Delta G^0$  Gibbs energy of ion-association reaction  
 $\sigma$  standard deviation

**Tables:**

**Table 1. Physical properties of pure THF, DMSO and different binary mixtures of (THF + DMSO) at 298.15 K.**

| Mass % of<br>THF ( $w_1$ ) | $\rho \times 10^{-3}$ (kg m <sup>-3</sup> ) |             | $\eta$ (mPas) |            | $\epsilon$ |
|----------------------------|---|-------------|---------------|------------|------------|
|                            | Observed                                    | Literature  | Observed      | Literature |            |
| 0.00                       | 1.0958                                      | 1.0951 [15] | 1.9600        | 1.992 [15] | 46.70 [16] |
| 0.25                       | 1.0367                                      |             | 1.5234        |            | 36.92 [19] |
| 0.50                       | 0.9847                                      |             | 1.1125        |            | 27.14 [19] |
| 0.75                       | 0.9340                                      |             | 0.7376        |            | 17.36 [19] |
| 1.00                       | 0.8811                                      | 0.8811 [16] | 0.4630        | 0.463 [16] | 7.58 [16]  |

**Table 2. Molar conductivities and corresponding molarities of electrolytes in different binary mixtures of THF + DMSO at 298.15 K.**

| $c \times 10^4$<br>(mol dm <sup>-3</sup> ) | $\Lambda \times 10^4$<br>(S m <sup>2</sup> mol <sup>-1</sup> ) | $c \times 10^4$<br>(mol dm <sup>-3</sup> ) | $\Lambda \times 10^4$<br>(S m <sup>2</sup> mol <sup>-1</sup> ) | $c \times 10^4$<br>(mol dm <sup>-3</sup> ) | $\Lambda \times 10^4$<br>(S m <sup>2</sup> mol <sup>-1</sup> ) | $c \times 10^4$<br>(mol dm <sup>-3</sup> ) | $\Lambda \times 10^4$<br>(S m <sup>2</sup> mol <sup>-1</sup> ) |
|--|--|--|--|--|--|--|--|
| $W_1=0.00$                                 |  |  |  |  |  |  |  |
| CH <sub>3</sub> COONH <sub>4</sub>         |  | CH <sub>3</sub> COOLi                      |  | CH <sub>3</sub> COONa                      |  | CH <sub>3</sub> COOK                       |  |
| 29.226                                     | 24.85  | 39.312                                     | 21.72  | 29.636                                     | 24.26  | 45.187                                     | 23.41  |
| 37.344                                     | 24.14  | 47.174                                     | 21.23  | 37.868                                     | 23.65  | 54.224                                     | 22.78  |
| 44.813                                     | 23.39  | 54.432                                     | 20.91  | 45.442                                     | 23.06  | 62.566                                     | 22.39  |
| 51.707                                     | 22.57  | 61.152                                     | 20.42  | 52.433                                     | 22.67  | 70.290                                     | 21.74  |
| 58.091                                     | 21.94  | 67.392                                     | 20.20  | 58.907                                     | 22.11  | 77.463                                     | 21.21  |
| 64.018                                     | 21.67  | 73.201                                     | 19.90  | 64.917                                     | 21.64  | 84.141                                     | 20.89  |
| 69.537                                     | 21.12  | 78.624                                     | 19.34  | 70.514                                     | 21.32  | 90.373                                     | 20.52  |
| 74.688                                     | 20.68  | 83.696                                     | 19.17  | 75.737                                     | 20.89  | 96.204                                     | 20.11  |
| 79.507                                     | 20.22  | 88.452                                     | 18.86  | 80.623                                     | 20.48  | 101.670                                    | 19.70  |
| 84.024                                     | 19.75  | 92.919                                     | 18.69  | 85.204                                     | 20.13  | 106.805                                    | 19.32  |
| $W_1=0.25$                                 |  |  |  |  |  |  |  |
| CH <sub>3</sub> COONH <sub>4</sub>         |  | CH <sub>3</sub> COOLi                      |  | CH <sub>3</sub> COONa                      |  | CH <sub>3</sub> COOK                       |  |
| 59.859                                     | 26.07  | 13.236                                     | 23.49  | 14.664                                     | 26.56  | 14.960                                     | 28.82  |
| 63.184                                     | 25.75  | 16.913                                     | 23.11  | 18.737                                     | 25.89  | 19.116                                     | 28.07  |
| 64.725                                     | 25.59  | 23.417                                     | 22.32  | 22.484                                     | 25.34  | 22.939                                     | 27.24  |

|                                    |       |                       |       |                       |       |                      |       |
|------------------------------------|-------|-----------------------|-------|-----------------------|-------|----------------------|-------|
| 66.193                             | 25.36 | 28.993                | 21.63 | 25.944                | 24.67 | 26.468               | 26.72 |
| 67.592                             | 25.25 | 33.825                | 21.14 | 29.146                | 24.22 | 29.736               | 26.03 |
| 68.928                             | 25.14 | 38.053                | 20.64 | 32.121                | 23.70 | 32.770               | 25.34 |
| 71.426                             | 24.92 | 45.100                | 19.52 | 37.474                | 22.79 | 38.232               | 24.37 |
| 73.715                             | 24.64 | 50.738                | 18.86 | 39.892                | 22.16 | 40.698               | 24.10 |
| 75.821                             | 24.47 | 55.350                | 18.23 | 42.158                | 22.05 | 43.011               | 23.52 |
| 77.765                             | 24.30 | 59.194                | 17.89 | 44.287                | 21.67 | 45.183               | 23.12 |
| $W_1=0.50$                         |       |                       |       |                       |       |                      |       |
| CH <sub>3</sub> COONH <sub>4</sub> |       | CH <sub>3</sub> COOLi |       | CH <sub>3</sub> COONa |       | CH <sub>3</sub> COOK |       |
| 25.195                             | 29.23 | 16.467                | 23.89 | 17.028                | 26.55 | 9.605                | 30.55 |
| 26.595                             | 28.87 | 19.211                | 23.45 | 19.866                | 26.13 | 10.790               | 30.13 |
| 27.861                             | 28.57 | 23.731                | 22.61 | 22.349                | 25.53 | 11.891               | 29.72 |
| 28.450                             | 28.41 | 27.300                | 22.23 | 24.541                | 25.12 | 13.873               | 28.96 |
| 29.012                             | 28.26 | 30.189                | 21.78 | 26.488                | 24.62 | 14.768               | 28.63 |
| 29.550                             | 28.12 | 33.620                | 21.45 | 28.231                | 24.34 | 15.608               | 28.29 |
| 30.064                             | 28.01 | 36.288                | 20.83 | 29.799                | 23.93 | 16.396               | 28.04 |
| 30.556                             | 27.87 | 39.042                | 20.55 | 31.218                | 23.71 | 17.138               | 27.79 |
| 31.027                             | 27.76 | 41.167                | 20.27 | 32.508                | 23.54 | 18.498               | 27.28 |
| 31.914                             | 27.55 | 43.225                | 19.93 | 33.686                | 23.32 | 19.715               | 26.87 |
| $W_1=0.75$                         |       |                       |       |                       |       |                      |       |

| CH <sub>3</sub> COONH <sub>4</sub> |       | CH <sub>3</sub> COOLi |       | CH <sub>3</sub> COONa |       | CH <sub>3</sub> COOK |       |
|------------------------------------|-------|-----------------------|-------|-----------------------|-------|----------------------|-------|
| 6.268                              | 38.36 | 4.133                 | 28.31 | 4.048                 | 31.50 | 3.450                | 33.98 |
| 6.732                              | 37.94 | 5.281                 | 27.97 | 4.723                 | 31.15 | 3.981                | 33.46 |
| 7.574                              | 37.38 | 6.337                 | 27.56 | 5.313                 | 30.87 | 4.473                | 33.11 |
| 8.316                              | 36.88 | 7.312                 | 27.24 | 5.834                 | 30.56 | 4.929                | 32.80 |
| 8.976                              | 36.32 | 9.053                 | 26.62 | 6.297                 | 30.31 | 5.751                | 32.12 |
| 9.567                              | 35.89 | 10.562                | 26.20 | 8.008                 | 29.10 | 6.469                | 31.47 |
| 10.098                             | 35.53 | 11.883                | 25.84 | 9.108                 | 28.61 | 7.104                | 31.00 |
| 10.579                             | 35.21 | 14.083                | 25.10 | 9.875                 | 28.08 | 7.667                | 30.65 |
| 11.416                             | 34.53 | 15.843                | 24.53 | 10.440                | 27.89 | 8.626                | 29.85 |
| 12.118                             | 34.08 | 17.284                | 24.12 | 10.874                | 27.57 | 9.410                | 29.42 |
| <i>w</i> <sub>1</sub> =1           |       |                       |       |                       |       |                      |       |
| CH <sub>3</sub> COONH <sub>4</sub> |       | CH <sub>3</sub> COOLi |       | CH <sub>3</sub> COONa |       | CH <sub>3</sub> COOK |       |
| 0.820                              | 10.89 | 0.559                 | 12.76 | 0.405                 | 22.71 | 0.254                | 40.40 |
| 0.946                              | 10.24 | 0.645                 | 10.65 | 0.517                 | 16.43 | 0.352                | 29.30 |
| 1.171                              | 9.67  | 0.798                 | 8.75  | 0.716                 | 10.28 | 0.435                | 21.50 |
| 1.366                              | 9.56  | 1.048                 | 8.35  | 0.887                 | 7.55  | 0.480                | 18.40 |
| 1.537                              | 9.74  | 1.323                 | 12.41 | 1.164                 | 8.48  | 0.677                | 10.60 |
| 1.821                              | 10.32 | 1.464                 | 16.50 | 1.278                 | 11.73 | 0.762                | 10.00 |
| 2.049                              | 11.13 | 1.579                 | 20.35 | 1.471                 | 19.71 | 0.831                | 11.73 |

|                    |       |                      |       |                    |       |                      |       |
|--------------------|-------|----------------------|-------|--------------------|-------|----------------------|-------|
| 2.235              | 11.71 | 1.676                | 24.37 | 1.626              | 30.46 | 0.889                | 13.70 |
| 2.459              | 13.05 | 1.759                | 28.86 | 1.755              | 39.78 | 0.938                | 16.21 |
| 2.634              | 14.34 | 1.831                | 32.39 | 1.863              | 49.62 | 0.998                | 20.72 |
| $w_1=0.25$         |       |                      |       | $w_1=0.50$         |       |                      |       |
| NaBPh <sub>4</sub> |       | Bu <sub>4</sub> NOAc |       | NaBPh <sub>4</sub> |       | Bu <sub>4</sub> NOAc |       |
| 13.75              | 24.11 | 14.74                | 24.77 | 18.58              | 24.21 | 17.25                | 24.81 |
| 17.56              | 23.76 | 18.83                | 24.21 | 22.30              | 23.75 | 18.04                | 24.65 |
| 21.08              | 23.41 | 22.60                | 23.55 | 25.73              | 23.34 | 18.77                | 24.47 |
| 24.32              | 23.17 | 26.07                | 23.10 | 28.91              | 22.85 | 19.47                | 24.35 |
| 27.32              | 22.89 | 29.29                | 22.64 | 31.86              | 22.53 | 20.12                | 24.26 |
| 30.11              | 22.64 | 32.28                | 22.23 | 34.61              | 22.12 | 20.75                | 24.14 |
| 32.704             | 22.46 | 35.06                | 21.73 | 37.17              | 21.78 | 21.34                | 24.05 |
| 35.127             | 22.22 | 37.66                | 21.42 | 41.82              | 21.41 | 21.90                | 23.92 |
| 37.393             | 22.03 | 40.09                | 21.07 | 43.93              | 21.15 | 22.43                | 23.80 |
| 39.517             | 21.84 | 42.37                | 20.71 | 45.92              | 21.00 | 22.94                | 23.71 |
| $w_1=0.75$         |       |                      |       |                    |       |                      |       |
| NaBPh <sub>4</sub> |       | Bu <sub>4</sub> NOAc |       |                    |       |                      |       |
| 2.786              | 28.34 | 2.419                | 29.90 |                    |       |                      |       |
| 3.070              | 28.19 | 2.666                | 29.75 |                    |       |                      |       |
| 3.582              | 27.87 | 3.110                | 29.44 |                    |       |                      |       |

|       |       |       |       |
|-------|-------|-------|-------|
| 4.030 | 27.62 | 3.311 | 29.14 |
| 4.425 | 27.42 | 3.499 | 29.06 |
| 4.776 | 27.27 | 3.676 | 28.98 |
| 5.091 | 27.08 | 3.842 | 28.91 |
| 5.373 | 26.86 | 3.999 | 28.68 |
| 5.629 | 26.74 | 4.147 | 28.53 |
| 5.862 | 26.61 | 4.287 | 28.38 |

**Table 3. Derived conductance and thermodynamic parameters for different electrolytes in different binary mixtures of THF + DMSO at 298.15 K.**

| Electrolytes                       | $\Lambda^{\circ} \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> ) | $K_A$ (dm <sup>3</sup> mol <sup>-1</sup> ) | $R$ (Å) | $\sigma$ (%) | $\Lambda^{\circ} \eta \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> Pa s) | $\Delta G^{\circ}$ (kJ mol <sup>-1</sup> ) |
|------------------------------------|---|--|---------|--------------|--|--|
| $w_1=0.00$                         |   |  |         |              |  |  |
| CH <sub>3</sub> COONH <sub>4</sub> | 32.75 ± 0.71  | 148.08 ± 13                                | 8.63    | 0.20         | 0.642  | -12.38                                     |
| CH <sub>3</sub> COOLi              | 27.22 ± 0.47  | 84.11 ± 07                                 | 7.79    | 0.14         | 0.534  | -10.98                                     |
| CH <sub>3</sub> COONa              | 29.80 ± 0.50  | 94.58 ± 08                                 | 8.15    | 0.18         | 0.584  | -11.27                                     |
| CH <sub>3</sub> COOK               | 31.90 ± 0.80  | 118.01 ± 12                                | 8.52    | 0.18         | 0.625  | -11.82                                     |
| NaBPh <sub>4</sub>                 | 24.15 ± 0.21  | 49.48 ± 03                                 | 10.67   | 0.10         | 0.473  | -9.67                                      |
| Bu <sub>4</sub> NOAc               | 28.89 ± 0.56  | 108.52 ± 09                                | 12.13   | 0.18         | 0.566  | -11.61                                     |
| $w_1=0.25$                         |   |  |         |              |  |  |
| CH <sub>3</sub> COONH <sub>4</sub> | 44.86 ± 0.75  | 258.94 ± 14                                | 8.68    | 0.03         | 0.683  | -13.77                                     |

|                                    |              |             |       |      |       |        |
|------------------------------------|--------------|-------------|-------|------|-------|--------|
| CH <sub>3</sub> COOLi              | 28.70 ± 0.80 | 185.28 ± 25 | 7.84  | 0.40 | 0.437 | -12.94 |
| CH <sub>3</sub> COONa              | 33.35 ± 0.69 | 216.53 ± 21 | 8.20  | 0.24 | 0.508 | -13.32 |
| CH <sub>3</sub> COOK               | 36.94 ± 0.78 | 243.23 ± 23 | 8.57  | 0.25 | 0.563 | -13.61 |
| NaBPh <sub>4</sub>                 | 26.55 ± 0.09 | 71.28 ± 02  | 10.72 | 0.05 | 0.404 | -10.57 |
| Bu <sub>4</sub> NOAc               | 30.11 ± 0.40 | 177.82 ± 12 | 12.18 | 0.15 | 0.459 | -12.84 |
| w <sub>1</sub> =0.50               |              |             |       |      |       |        |
| CH <sub>3</sub> COONH <sub>4</sub> | 47.66 ± 0.49 | 511.36 ± 18 | 8.73  | 0.02 | 0.530 | -15.45 |
| CH <sub>3</sub> COOLi              | 30.88 ± 0.50 | 250.05 ± 19 | 7.89  | 0.15 | 0.344 | -13.68 |
| CH <sub>3</sub> COONa              | 35.99 ± 0.58 | 316.95 ± 23 | 8.25  | 0.11 | 0.400 | -14.27 |
| CH <sub>3</sub> COOK               | 38.98 ± 0.37 | 391.27 ± 19 | 8.62  | 0.09 | 0.434 | -14.79 |
| NaBPh <sub>4</sub>                 | 30.19 ± 0.25 | 179.73 ± 07 | 10.77 | 0.08 | 0.336 | -12.86 |
| Bu <sub>4</sub> NOAc               | 31.44 ± 0.21 | 223.68 ± 08 | 12.23 | 0.02 | 0.350 | -13.40 |
| w <sub>1</sub> =0.75               |              |             |       |      |       |        |
| CH <sub>3</sub> COONH <sub>4</sub> | 50.64 ± 0.60 | 756.75 ± 46 | 8.79  | 0.12 | 0.374 | -16.42 |
| CH <sub>3</sub> COOLi              | 32.50 ± 0.29 | 310.47 ± 24 | 7.95  | 0.18 | 0.240 | -14.22 |
| CH <sub>3</sub> COONa              | 37.87 ± 0.37 | 556.71 ± 38 | 8.31  | 0.16 | 0.279 | -15.66 |
| CH <sub>3</sub> COOK               | 40.85 ± 0.33 | 681.74 ± 36 | 8.68  | 0.13 | 0.301 | -16.17 |
| NaBPh <sub>4</sub>                 | 31.54 ± 0.11 | 364.73 ± 15 | 10.83 | 0.05 | 0.233 | -14.62 |
| Bu <sub>4</sub> NOAc               | 33.56 ± 0.24 | 491.77 ± 38 | 12.29 | 0.07 | 0.248 | -15.36 |

**Table 4. Limiting ionic conductance, ionic Walden product, Stoke's radii ( $r_s$ ) and crystallographic radii ( $r_c$ ) in different binary mixtures of THF+DMSO at 298.15 K**

| Ions                             | $\lambda_{\pm}^0 \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> ) | $\lambda_{\pm}^0 \eta \times 10^4$ (S m <sup>2</sup> mol <sup>-1</sup> Pa s) | $r_s$ (Å) | $r_c$ (Å) |
|----------------------------------|---|--|-----------|-----------|
| $w_1=0.00$                       |   |  |           |           |
| CH <sub>3</sub> COO <sup>-</sup> | 16.87   | 0.331  | 2.48      | 2.28      |
| NH <sub>4</sub> <sup>+</sup>     | 15.87   | 0.312  | 2.63      | 1.44      |
| Li <sup>+</sup>                  | 10.35   | 0.203  | 4.04      | 0.60      |
| Na <sup>+</sup>                  | 12.93   | 0.254  | 3.23      | 0.96      |
| K <sup>+</sup>                   | 15.02   | 0.295  | 2.78      | 1.33      |
| BPh <sub>4</sub> <sup>-</sup>    | 11.23   | 0.220  | 3.72      | 4.80      |
| Bu <sub>4</sub> N <sup>+</sup>   | 12.02   | 0.236  | 3.48      | 4.94      |
| $w_1=0.25$                       |   |  |           |           |
| CH <sub>3</sub> COO <sup>-</sup> | 18.06   | 0.275  | 2.98      | 2.28      |
| NH <sub>4</sub> <sup>+</sup>     | 26.80   | 0.408  | 2.01      | 1.44      |
| Li <sup>+</sup>                  | 10.64   | 0.162  | 5.06      | 0.60      |
| Na <sup>+</sup>                  | 15.29   | 0.233  | 3.52      | 0.96      |
| K <sup>+</sup>                   | 18.88   | 0.288  | 2.85      | 1.33      |
| BPh <sub>4</sub> <sup>-</sup>    | 11.26   | 0.172  | 4.78      | 4.80      |
| Bu <sub>4</sub> N <sup>+</sup>   | 12.05   | 0.184  | 4.47      | 4.94      |
| $w_1=0.50$                       |   |  |           |           |
| CH <sub>3</sub> COO <sup>-</sup> | 18.18   | 0.202  | 4.05      | 2.28      |
| NH <sub>4</sub> <sup>+</sup>     | 29.47   | 0.328  | 2.50      | 1.44      |
| Li <sup>+</sup>                  | 12.70   | 0.141  | 5.80      | 0.60      |
| Na <sup>+</sup>                  | 17.81   | 0.198  | 4.14      | 0.96      |
| K <sup>+</sup>                   | 20.80   | 0.231  | 3.54      | 1.33      |
| BPh <sub>4</sub> <sup>-</sup>    | 12.38   | 0.138  | 5.95      | 4.80      |
| Bu <sub>4</sub> N <sup>+</sup>   | 13.25   | 0.147  | 5.56      | 4.94      |
| $w_1=0.75$                       |   |  |           |           |
| CH <sub>3</sub> COO <sup>-</sup> | 19.48   | 0.144  | 5.71      | 2.28      |
| NH <sub>4</sub> <sup>+</sup>     | 31.16   | 0.230  | 3.57      | 1.44      |
| Li <sup>+</sup>                  | 13.01   | 0.096  | 8.54      | 0.60      |
| Na <sup>+</sup>                  | 18.39   | 0.136  | 6.04      | 0.96      |
| K <sup>+</sup>                   | 21.36   | 0.158  | 5.20      | 1.33      |
| BPh <sub>4</sub> <sup>-</sup>    | 13.15   | 0.097  | 8.45      | 4.80      |
| Bu <sub>4</sub> N <sup>+</sup>   | 14.08   | 0.104  | 7.90      | 4.94      |

**Table 5. Calculated limiting molar conductance of ion pair and triple ions, slope and intercepts and ion pair and triple ion formation constant for different electrolytes in pure THF at 298.15 K.**

| Electrolytes                      | $\Lambda^0 \times 10^4$<br>( $\text{Sm}^2\text{mol}^{-1}$ ) | $\Lambda^0_{\text{T}} \times 10^4$<br>( $\text{S m}^2\text{mol}^{-1}$ ) | Slope<br>$\times 10^3$ | Intercept<br>$\times 10^3$ | $K_{\text{P}} \times 10^{-9}$<br>( $\text{mol dm}^{-3}$ ) <sup>-1</sup> | $K_{\text{T}}$<br>( $\text{mol dm}^{-3}$ ) <sup>-1</sup> | $K_{\text{T}}/K_{\text{P}}$<br>$\times 10^9$ |
|-----------------------------------|---|---|------------------------|----------------------------|---|--|--|
| H <sub>3</sub> COONH <sub>4</sub> | 192.44  | 128.29  | 1.37                   | -2.83                      | 4.611   | 0.725  | 0.157  |
| H <sub>3</sub> COOLi              | 145.26  | 96.84   | 3.29                   | -4.43                      | 1.075   | 1.111  | 1.034  |
| H <sub>3</sub> COONa              | 156.38  | 104.25  | 2.58                   | -3.59                      | 1.895   | 1.076  | 0.568  |
| H <sub>3</sub> COOK               | 174.27  | 116.18  | 2.17                   | -3.43                      | 2.583   | 0.947  | 0.367  |

**Table 6. Maximum concentration, the ion pair fraction ( $\alpha$ ), triple ion fraction ( $\alpha_{\text{T}}$ ), ion pair concentration ( $C_{\text{P}}$ ) and triple ion concentration ( $C_{\text{T}}$ ) for different electrolytes in pure THF at 298.15 K.**

| Electrolytes                       | $C_{\text{max}} \times 10^4$<br>( $\text{mol dm}^{-3}$ ) | $\alpha \times 10^5$ | $\alpha_{\text{T}} \times 10^5$ | $C_{\text{P}} \times 10^4$<br>( $\text{mol dm}^{-3}$ ) | $C_{\text{T}} \times 10^9$<br>( $\text{mol dm}^{-3}$ ) |
|------------------------------------|--|----------------------|---------------------------------|--|--|
| CH <sub>3</sub> COONH <sub>4</sub> | 2.634  | 0.024                | 0.017                           | 2.571  | 0.046  |
| CH <sub>3</sub> COOLi              | 1.831  | 0.041                | 0.046                           | 1.755  | 0.084  |
| CH <sub>3</sub> COONa              | 1.863  | 0.031                | 0.034                           | 1.804  | 0.063  |
| CH <sub>3</sub> COOK               | 0.998  | 0.020                | 0.019                           | 0.979  | 0.019  |

Figures:

Figure 1: Plots of Walden product ( $\lambda^0\eta$ ) of  $\text{CH}_3\text{COONH}_4$  (x),  $\text{CH}_3\text{COOK}$  (◻),  $\text{CH}_3\text{COONa}$  (■) and  $\text{CH}_3\text{COOLi}$  (▲) in different THF + DMSO binary mixtures containing 0, 25, 50, and 75 mass % of THF at 298.15 K.

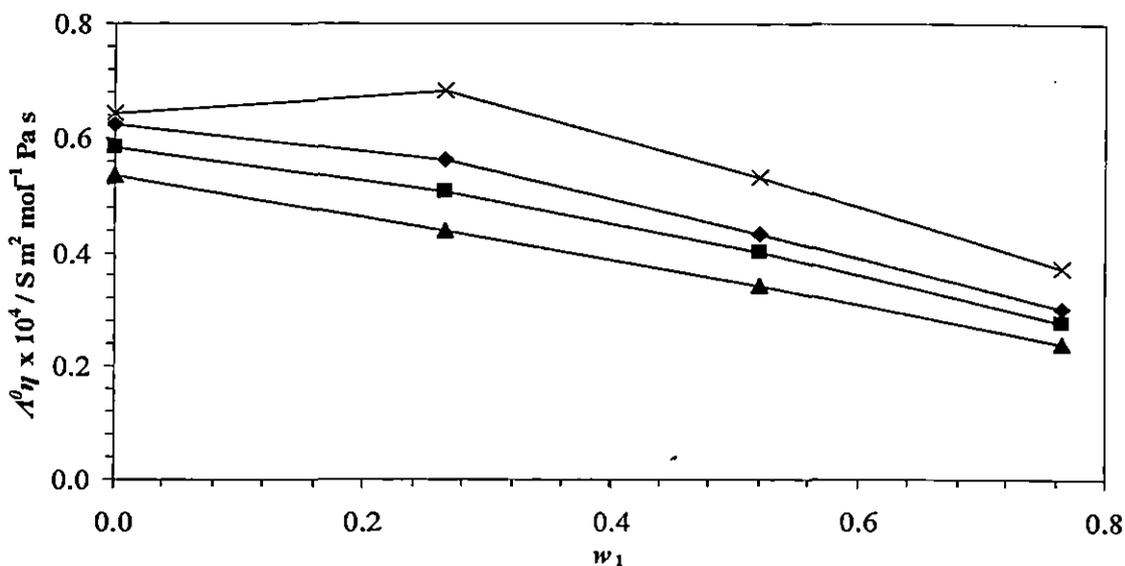
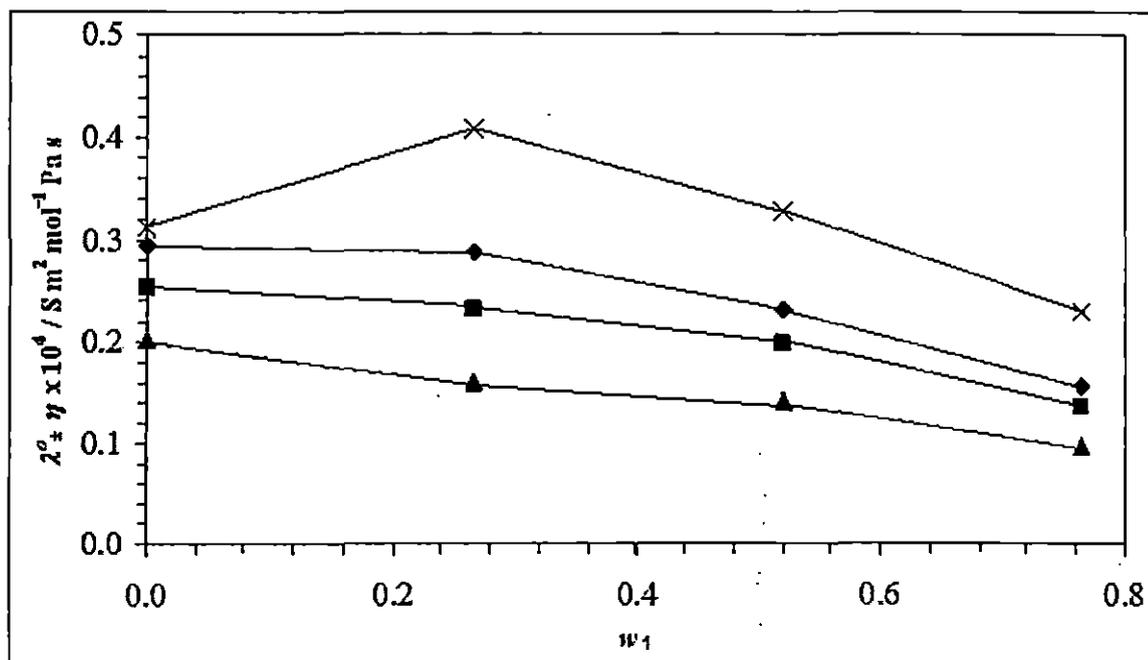
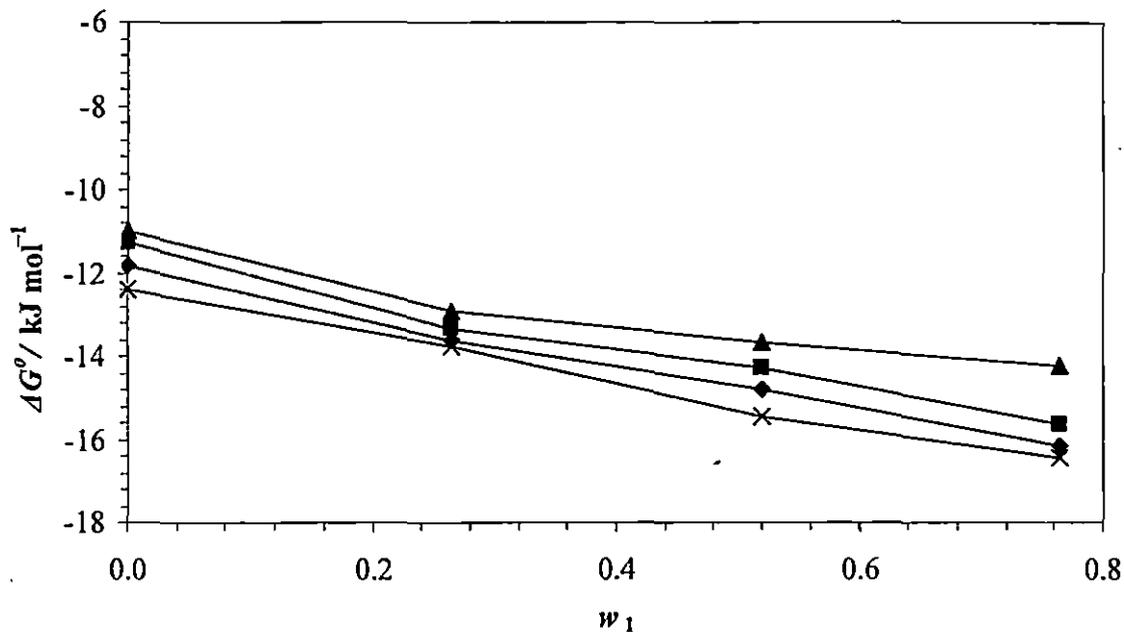


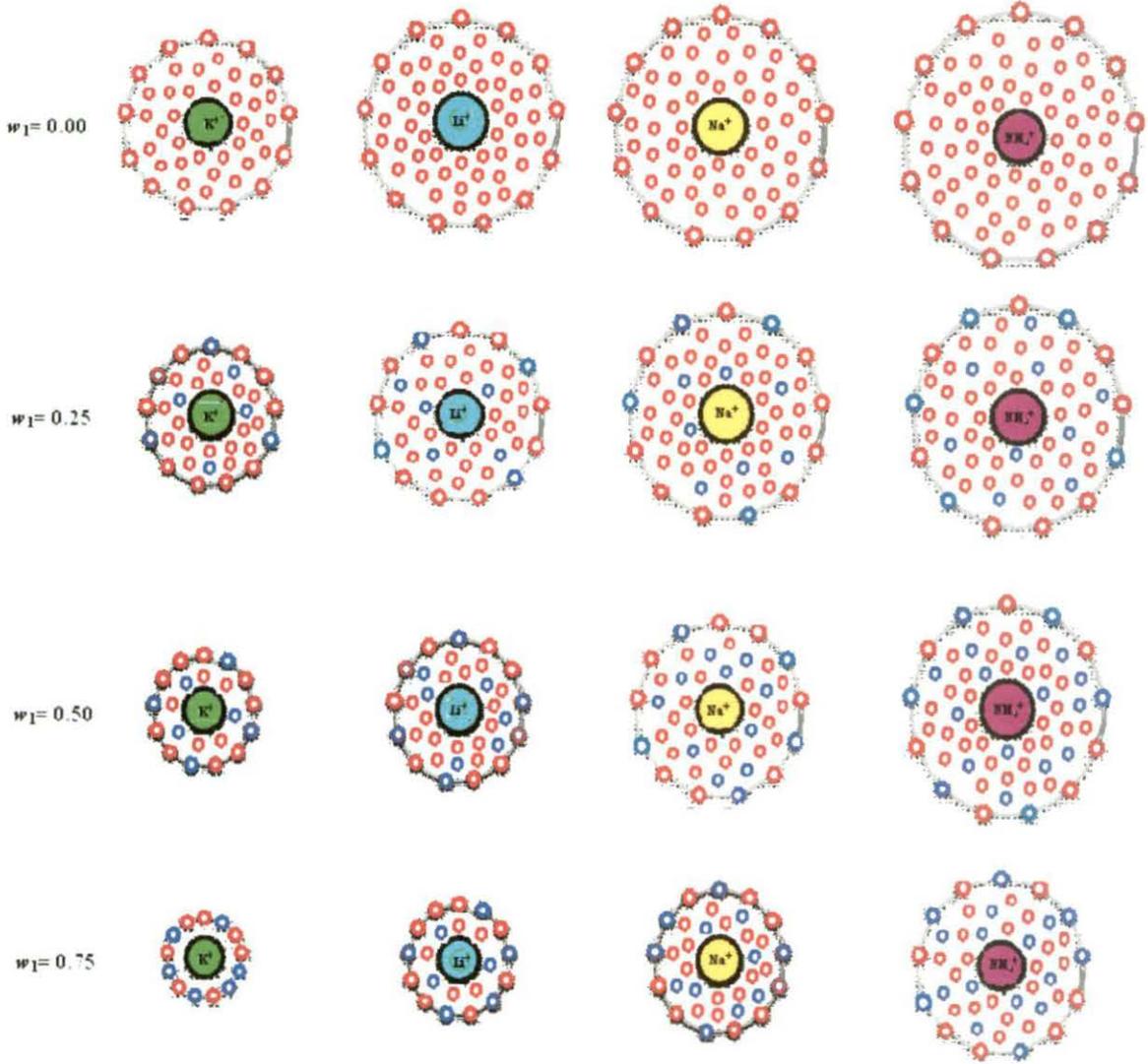
Figure 2: Plots of Ionic Walden product ( $\lambda^{\circ\pm}\eta$ ) of  $\text{NH}_4^+$ (x),  $\text{K}^+$  (◆),  $\text{Na}^+$ (■) and  $\text{Li}^+$ (▲) in different THF + DMSO binary mixtures containing 0, 25, 50, and 75 mass % of THF at 298.15 K



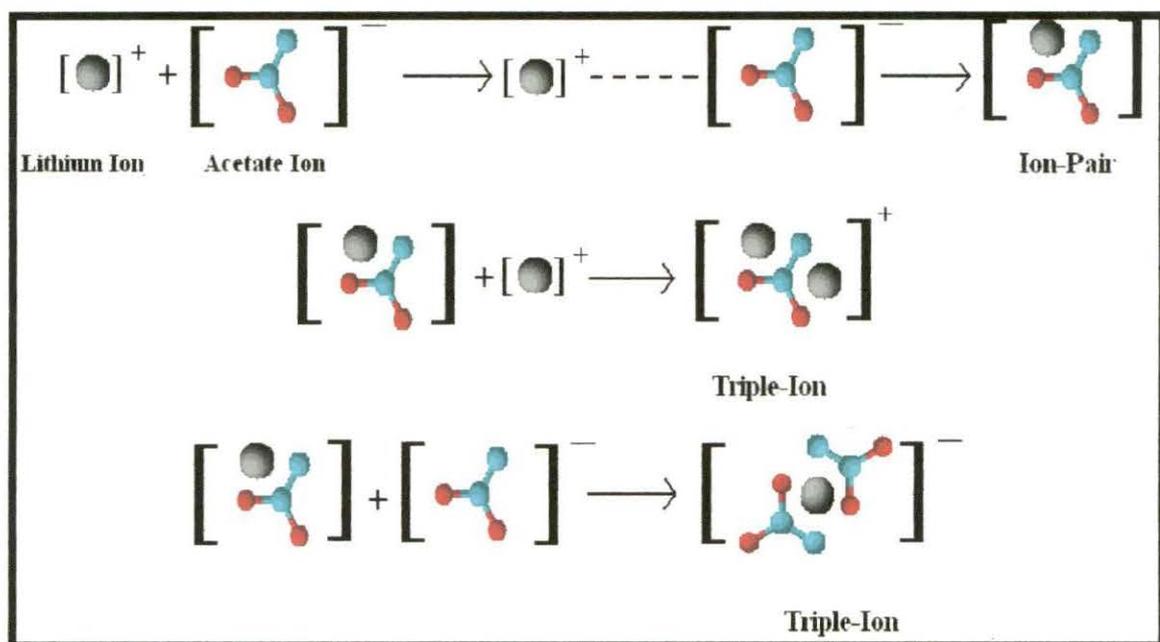
**Figure 3:** Plots of Gibbs energy of ion-pair formation ( $\Delta G^\circ$ ) of  $\text{CH}_3\text{COONH}_4$  (x),  $\text{CH}_3\text{COOK}$  ( $\blacklozenge$ ),  $\text{CH}_3\text{COONa}$  ( $\blacksquare$ ) and  $\text{CH}_3\text{COOLi}$  ( $\blacktriangle$ ) in different THF + DMSO binary mixtures containing 0, 25, 50, and 75 mass % of THF at 298.15 K.



Schemes:



SCHEME I



SCHEME II