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### Interactions in Binary N,N-Dimethylacetamide Ethanol and Ternary Lithium Nitrate N,N-Dimethylacetamide Ethanol Mixtures

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# INTERACTIONS IN BINARY *N,N*-DIMETHYLACETAMIDE + ETHANOL AND TERNARY LITHIUM NITRATE + *N,N*-DIMETHYLACETAMIDE + ETHANOL MIXTURES

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Excess volume ( $V^E$ ), excess viscosity ( $\eta^E$ ), excess free energy of activation of viscous flow ( $G^{*E}$ ), and Grunberg-Nissan interaction parameter ( $d$ ) of binary mixtures *N,N*-dimethylacetamide (DMA) + ethanol have been calculated from the viscosities ( $\eta$ ) measured at 298.15, 303.15, 308.15, 313.15 and 318.15 K over the whole composition range. All the excess functions studied are found to be negative over the entire range of composition indicating strong interaction between DMA and ethanol molecules. Densities ( $\rho$ ) and ultrasonic velocities ( $u$ ) of lithium nitrate in DMA + ethanol mixtures have been measured at above mentioned temperatures as function of DMA mol fraction. From these experimental data, isentropic compressibility ( $k_s$ ), intermolecular free length ( $L_f$ ), and relative association ( $R_A$ ) of  $\text{LiNO}_3$  + DMA + ethanol ternary mixtures have been computed. These properties are used to discuss ion-solvent interaction and selective solvation of ions by the component molecules of the liquid mixture.

**Keywords:** Thermodynamic functions; solvent–solvent; ion-solvent interactions

## 1. INTRODUCTION

The study of thermodynamic functions such as excess molar volume, excess viscosity, excess free energy of activation of viscous flow and interaction parameter of binary mixtures are useful in understanding the nature of intermolecular interactions between component mole-

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cules [1–4]. The non-aqueous binary mixtures of *N,N*-dimethylacetamide + ethanol covering the whole miscibility range have been chosen for the present investigation. Such binary liquid mixtures when mixed with suitable electrolytes are of considerable theoretical and industrial importance [5, 6]. The use of amides as reaction solvents and their close relationship to peptides and proteins have made these compounds very interesting. DMA is polar, aprotic solvent with large dipole moment and dielectric constant ( $\mu = 3.72$  D and  $\epsilon = 37.78$  at 298.15 K) [7], yet practically unassociated [8, 9] due to the absence of a proton donor group. Ethanol molecules, on the other hand, are highly associated through hydrogen bonds [7] though they have low values of dipole moment and dielectric constant ( $\mu = 1.69$  D and  $\epsilon = 24.55$  at 298.15 K) [7]. Therefore, DMA + ethanol will be an interesting binary solvent system for the study of intermolecular interactions. Furthermore, the study of the ternary mixtures  $\text{LiNO}_3$  + DMA + ethanol will be important in providing a better understanding of ion-solvent interactions and the possible selective solvation of cations and/or anions by either component of the solvent mixture.

In continuation of our recent studies [1, 2, 6, 10–12] on solvent–solvent and ion-solvent interactions in binary and ternary mixtures, we now report viscosities of DMA + ethanol binary mixtures together with the densities and ultrasonic velocities of  $\text{LiNO}_3$  + DMA + ethanol ternary mixtures at 298.15, 303.15, 308.15, 313.15, and 318.15 K, covering the whole miscibility range of DMA and ethanol. These properties are used to compute the excess molar volume, excess viscosity, excess free energy of activation of viscous flow and interaction parameter of binary DMA + ethanol mixtures; while isentropic compressibility, intermolecular free length and relative association are evaluated for  $\text{LiNO}_3$  + DMA + ethanol ternary mixtures. These derived parameters provide important informations regarding intermolecular and ion-solvent interactions and selective solvation of ions by the component molecules.

## 2. EXPERIMENTAL

Ethanol was the same as in our previous study [1]. *N,N*-dimethylacetamide (s.d. fine, India) was purified as described in the literature

[13]. The purified liquids were stored in a dry atmosphere.  $\text{LiNO}_3$  was the same as in our earlier work [11]. The binary and ternary mixtures, DMA + ethanol and  $\text{LiNO}_3$  + DMA + ethanol, respectively, were prepared by weight and were kept in special airtight bottles. All the solutions were prepared in a dry box.

Viscosities of pure liquids, their binary mixtures while densities and ultrasonic velocities of  $\text{LiNO}_3$  in these binary mixtures were measured as described earlier [1, 2]. The experimental values of the viscosity and ultrasonic velocity of pure DMA were found to be  $8.78 \times 10^{-4} \text{ kg m}^{-1}\text{s}^{-1}$  and  $1462.0 \text{ ms}^{-1}$  at 303.15 and 298.15 K, respectively, which compare well with the literature values  $8.71 \times 10^{-4} \text{ kg m}^{-1}\text{s}^{-1}$  [14] and  $1462.6 \text{ ms}^{-1}$  [15]. The temperature of pure liquids and their binary and ternary mixtures was maintained to an accuracy of  $\pm 0.02 \text{ K}$  in a thermostatic water bath.

### 3. RESULTS AND DISCUSSION

The viscosity of pure DMA, ethanol and their nine binary mixtures whereas density and ultrasonic velocity of 1.0 M- $\text{LiNO}_3$  in DMA + ethanol mixtures as functions of mol fraction,  $x$  ( $0 \leq x \leq 1$ ) of DMA and temperature are listed in Table I. The viscosity and density [16] have been used to compute the excess volume ( $V^E$ ), excess viscosity ( $\eta^E$ ), excess free energy of activation of viscous flow ( $G^{*E}$ ), and Grunberg and Nissan [17] interaction parameter ( $d$ ) of DMA + ethanol binary mixtures with the help of the following relations

$$V^E = V - [(1-x)V_1 + xV_2] \quad (1)$$

$$\eta^E = \eta - [(1-x)\eta_1 + x\eta_2] \quad (2)$$

$$G^{*E} = RT[\ln \eta V - (1-x) \ln \eta_1 V_1 - x \ln \eta_2 V_2] \quad (3)$$

$$d = [\ln \eta - (1-x) \ln \eta_1 - x \ln \eta_2]/(1-x)x \quad (4)$$

The molar volumes ( $V$ ) of binary mixtures were calculated using the equation

$$V = [(1-x)M_1 + xM_2]/\rho \quad (5)$$

TABLE I-A Viscosities ( $\eta$ ,  $10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ) of DMA + ethanol binary mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	1.0957	0.9944	0.9015	0.8306	0.7648
0.0653	1.0400	0.9549	0.8702	0.8052	0.7371
0.1358	0.9918	0.9129	0.8423	0.7795	0.7160
0.2123	0.9588	0.8868	0.8171	0.7631	0.7077
0.2954	0.9368	0.8691	0.8034	0.7509	0.6996
0.3860	0.9289	0.8634	0.7995	0.7510	0.6999
0.4854	0.9280	0.8622	0.8019	0.7530	0.7022
0.5947	0.9232	0.8595	0.7991	0.7552	0.7034
0.7155	0.9273	0.8639	0.8093	0.7575	0.7108
0.8498	0.9421	0.8705	0.8100	0.7650	0.7156
1.0000	0.9437	0.8784	0.8164	0.7685	0.7245

TABLE I-B Densities ( $\rho$ ,  $10^3 \text{ kg m}^{-3}$ ) of  $\text{LiNO}_3$  in DMA + ethanol mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	0.8409	0.8370	0.8330	0.8291	0.8251
0.0616	0.8558	0.8519	0.8480	0.8441	0.8401
0.1279	0.8713	0.8673	0.8634	0.8594	0.8555
0.1993	0.8873	0.8832	0.8792	0.8751	0.8710
0.2767	0.9024	0.8983	0.8942	0.8900	0.8859
0.3602	0.9178	0.9136	0.9095	0.9054	0.9013
0.4513	0.9319	0.9278	0.9237	0.9195	0.9154
0.5508	0.9458	0.9417	0.9376	0.9334	0.9293
0.6599	0.9599	0.9558	0.9517	0.9476	0.9435
0.7802	0.9731	0.9689	0.9647	0.9605	0.9552
0.9133	0.9866	0.9823	0.9870	0.9738	0.9645

TABLE I-C Viscosities ( $\eta$ ,  $10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ ) of  $\text{LiNO}_3$  in DMA + ethanol mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	2.3533	2.1119	1.8844	1.7065	1.5367
0.0616	2.3519	2.1188	1.9007	1.7310	1.5581
0.1279	2.3225	2.0972	1.8867	1.7060	1.5465
0.1993	2.2984	2.0704	1.8599	1.6940	1.5420
0.2765	2.2622	2.0715	1.8473	1.7048	1.5508
0.3602	2.2707	2.0830	1.8619	1.6993	1.5696
0.4513	2.2407	2.0452	1.8363	1.6899	1.5453
0.5508	2.2246	2.0031	1.8181	1.7011	1.5371
0.6599	2.2260	2.0159	1.8374	1.6858	1.5516
0.7802	2.2169	1.9868	1.8127	1.6615	1.5532
0.9133	2.2077	1.9929	1.8043	1.6556	1.5257

TABLE I-D Ultrasonic velocities ( $u$ ,  $\text{m s}^{-1}$ ) of  $\text{LiNO}_3$  in DMA + ethanol mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	1204.5	1185.0	1170.0	1152.9	1140.0
0.0616	1236.0	1217.1	1200.0	1185.3	1167.6
0.1279	1269.9	1251.0	1234.8	1217.1	1200.9
0.1993	1302.3	1281.3	1265.4	1252.5	1233.6
0.2765	1335.9	1316.4	1299.3	1282.5	1264.8
0.3602	1366.5	1350.9	1333.8	1317.3	1300.5
0.4513	1400.4	1383.0	1365.0	1347.9	1332.0
0.5508	1434.0	1415.2	1398.3	1380.6	1362.3
0.6599	1463.2	1446.7	1431.3	1411.3	1411.1
0.7802	1498.5	1479.3	1458.3	1440.3	1422.0
0.9133	1528.8	1504.1	1486.5	1466.6	1447.5

where suffixes 1 and 2 stand for ethanol and DMA;  $M_1$  and  $M_2$  are the molecular weight of ethanol and DMA, respectively;  $R$  is the gas constant and  $T$  is the absolute temperature.

The variations of  $V^E$ ,  $\eta^E$ , and  $G^{*E}$  with mol fraction of DMA are shown graphically in Figures 1–3. The excess functions were fitted with the equation

$$Y^E = x(1-x) \sum_{i=1}^5 A_i (1-2x)^{i-1} \quad (6)$$

where  $Y^E$  is  $V^E$  or  $\eta^E$  or  $G^{*E}$ . The values of the coefficients  $A_i$  of these fitting equations, together with the standard deviations  $\sigma(Y^E)$  calculated as

$$\sigma(Y^E) = \left[ \sum (Y_{\text{obs}}^E - Y_{\text{cal}}^E)^2 / (m-n) \right]^{1/2} \quad (7)$$

where  $m$  is the total number of experimental points and  $n$  is the number of  $A_i$  coefficients considered ( $n = 5$  in the present calculation), have been listed in Table II.

The excess volumes,  $V^E$  (Fig. 1) are negative over the entire range of mol fraction,  $x$ , and temperatures studied. Similar trends in  $V^E$  are also reported for benzyl alcohol + isoamyl, isopropyl alcohol [18] and *N*-methylacetamide + methanol, ethanol and 1-propanol [19] binary

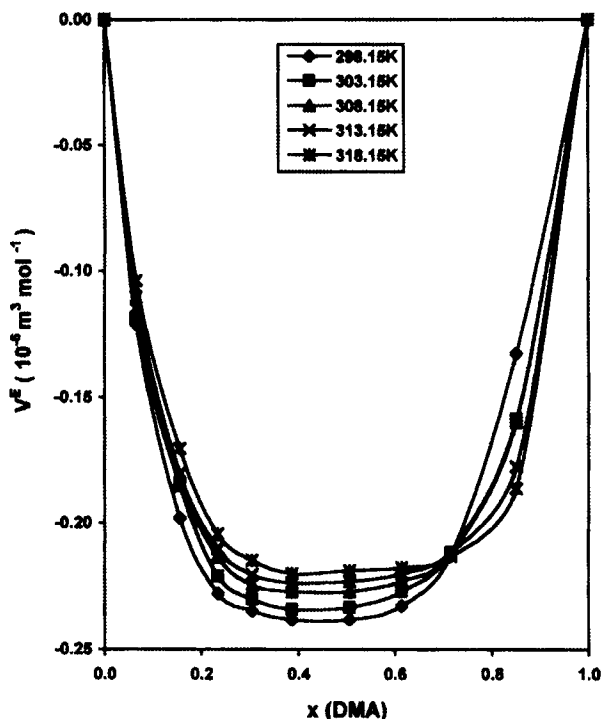


FIGURE 1 Variation of excess molar volume ( $V^E$ ) as function of mol fraction of DMA and temperature.

TABLE II Coefficients ( $A_i$ ) of eq. 6 and standard deviations  $\sigma(Y^E)$  for DMA + ethanol binary mixtures at various temperatures

$T/K$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$\sigma(Y^E)$
	$V^E(10^{-6} \text{ m}^3 \text{ mol}^{-1})$					
298.15	-0.9190	0.1029	-1.0525	-0.9980	0.5219	0.0029
303.15	-0.8908	0.0721	-1.0150	-0.5474	0.0342	0.0017
308.15	-0.8737	-0.0229	-1.1301	-0.3065	0.2243	0.0015
313.15	-0.8229	0.0402	-1.4341	-0.2170	0.3664	0.0024
318.15	-0.8156	-0.1397	-1.4547	0.6122	-0.0398	0.0026
	$\eta^E(10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$					
298.15	-0.3751	-0.2744	-0.3324	-0.1765	0.4043	0.0012
303.15	-0.2992	-0.2335	-0.2939	-0.0222	0.3247	0.0016
308.15	-0.2391	-0.2391	-0.0917	-0.1090	0.0140	0.0026
313.15	-0.1877	-0.1952	-0.1549	0.0276	0.1559	0.0010
318.15	-0.1712	-0.1342	-0.1195	-0.0666	0.0024	0.0013
	$G^{*E} \text{ (kJ mol}^{-1})$					
298.15	-0.6976	-0.6278	-0.8260	-0.4119	1.1170	0.0031
303.15	-0.5909	-0.5921	-0.7629	-0.0250	0.8876	0.0043
308.15	-0.4754	-0.6589	-0.5138	0.2653	0.5223	0.0073
313.15	-0.3694	-0.5829	-0.7290	0.0511	0.8998	0.0031
318.15	-0.3742	-0.4443	-0.5034	-0.2160	0.0766	0.0046

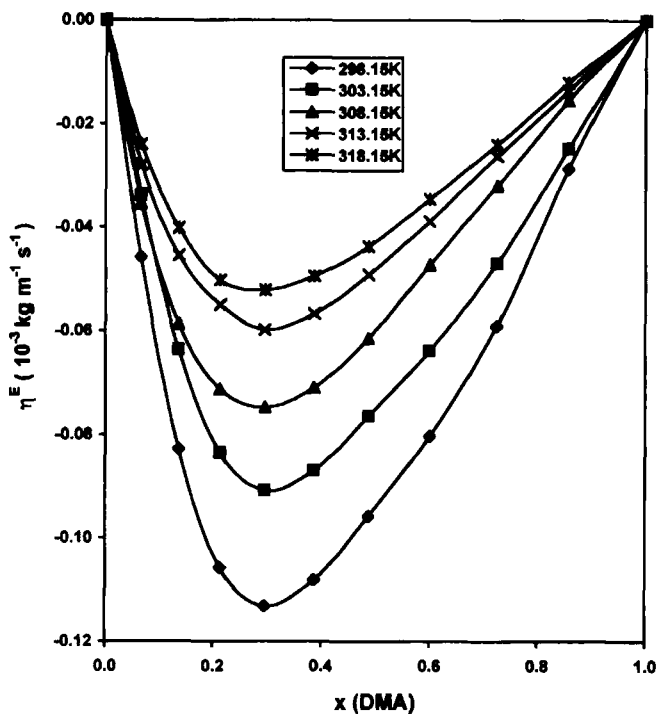


FIGURE 2 Variation of excess viscosity ( $\eta^E$ ) as function of mol fraction of DMA and temperature.

mixtures. Negative values of  $V^E$  are indicative of strong interaction between the component molecules. Mixing of DMA with ethanol will induce the dissociation of ethanol-ethanol associates [20] with subsequent formation of DMA-ethanol hydrogen bonding between unlike molecules. The former effect contributes to positive values while the latter has a negative contribution to excess volume. The observed negative values of  $V^E$  over the whole composition range of binary mixtures DMA + ethanol suggest that the main contribution to  $V^E$  is the decrease in the volume due to hydrogen bond formation between DMA and ethanol molecules. It has been suggested [20, 21] that DMA has strong proton-accepting ability; as a result the formation of hydrogen bonds between oxygen of C=O group of DMA and hydrogen atom of H—O— group of ethanol molecules is obvious. In fact, carbonyl bond in DMA is said to be highly polar with high



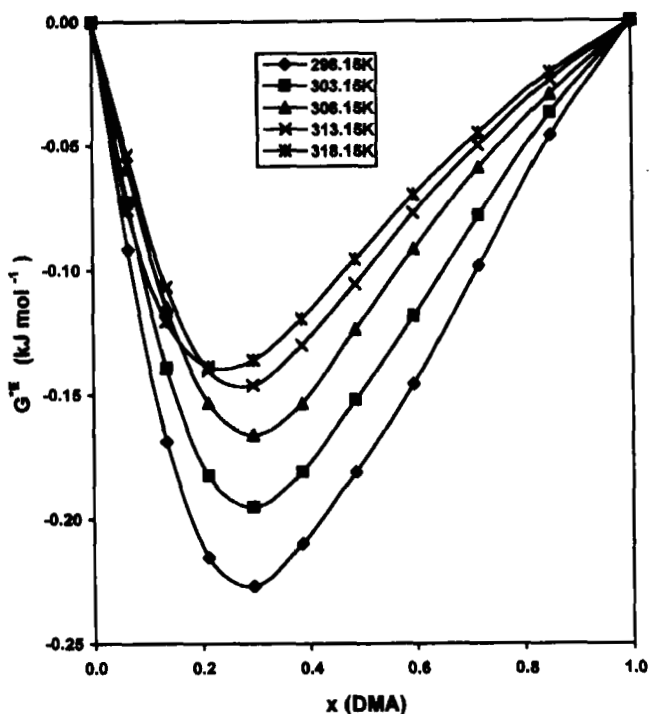


FIGURE 3 Variation of excess free energy of activation of viscous flow ( $G^E$ ) as function of mol fraction of DMA and temperature.

percentage of ionic character [22] making oxygen of C=O group strongly negative, hence, strong proton-acceptor. Moreover, the negative values of  $V^E$  may be, partly, due to the difference in size of the component molecules in the mixture. The molar volumes of DMA and ethanol at 298.15 K are  $8.78 \times 10^{-5}$  and  $5.86 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ , respectively, which might allow the component molecules to fit into each other's structure [23], thereby, reducing the volume of the mixture. Ali and coworkers [1], and also Pikkarainen [24], considered the difference in size of the component molecules to explain the negative  $V^E$  values for *N,N*-dimethylformamide + ethanol and DMA/*N,N*-dimethylmethanesulfonamide + aliphatic alcohols. As the temperature of the system increases the value of  $V^E$  extrema decreases, implying that the system tends towards ideal condition in which  $V^E$  should be zero. This suggests that the interaction between component

molecules is temperature sensitive and becomes less strong as a consequence of rise in temperature.

The values of excess viscosity,  $\eta^E$  are negative over the whole composition range and at all temperatures (Fig. 2). Negative deviations in  $\eta^E$  are found to occur where dipole-forces are primarily responsible for interaction between the component molecules [25]. As mentioned earlier, addition of DMA in ethanol disrupts the associated structure in the latter causing more free ethanol molecules. These free ethanol molecules may interact through dipole-dipole forces, in addition to hydrogen bonding, with DMA molecules in the mixture. Some authors [26, 27] have suggested that negative  $\eta^E$  values may also be due to the difference in size of the component molecules, as in our case. Ritzoulis [28] and Fort and Moore [26] have explained the negative deviations in  $\eta^E$  for dimethylsulphoxide + isopropanol and dimethylsulphoxide + acetonitrile, + methanol by considering the differences in molecular size of the components of the binary mixture. It is observed that the values of  $\eta^E$  become less negative and tend towards zero as the temperature of the system increases (Fig. 2). This again supports our view that the system tends towards ideal behaviour as a result of rise in temperature.

The variation of excess free energy of activation of viscous flow,  $G^{*E}$  with mol fraction of DMA and temperature is shown graphically in Figure 3. All the values of  $G^{*E}$  are found to be negative over the entire range of mol fraction and temperature. The negative values of  $G^{*E}$  suggest that the complex formed between DMA and ethanol molecules is thermodynamically stable and this stability decreases with increase in temperature of the system. This is supported by the fact that the minimum in  $G^{*E}$  vs.  $x$  curves (Fig. 3) becomes less negative as the temperature of the system increases. A similar trend in  $G^{*E}$  vs.  $x$  plots was also observed for *N,N*-dimethylformamide + 1,2-ethanediol [29] and ethyl acetate + cyclohexane [30] binary mixtures. The interaction parameter,  $d$ , a measure of the strength of interaction between the component molecules of the mixture, is found to increase at a given temperature (Tab. III) as the mol fraction of DMA in the mixture increases. This may be attributed to the increased interaction involving dipole-dipole/hydrogen-bonding between DMA and ethanol molecules in the mixture.

TABLE III Grunberg-Nissan interaction parameters ( $d$ ) for DMA + ethanol binary mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	–	–	–	–	–
0.0653	–0.6953	–0.5318	–0.4728	–0.4265	–0.5472
0.1358	–0.6764	–0.5845	–0.4640	–0.4510	–0.4992
0.2123	–0.6090	–0.5276	–0.4619	–0.4080	–0.3951
0.2954	–0.5412	–0.4712	–0.4128	–0.3745	–0.3512
0.3860	–0.4537	–0.3940	–0.3450	–0.2984	–0.2860
0.4854	–0.3751	–0.3303	–0.2761	–0.2419	–0.2369
0.5947	–0.3422	–0.2986	–0.2557	–0.2031	–0.2135
0.7155	–0.2952	–0.2550	–0.1813	–0.1793	–0.1697
0.8498	–0.1891	–0.2164	–0.1782	–0.1274	–0.1602
1.0000	–	–	–	–	–

It is worth to mention that the compositions at which the excess thermodynamic functions exhibit maxima or minima indicate strong interaction between the component molecules leading to the formation of the complexes [23]. Figures 2 and 3 show that both  $\eta^E$  and  $G^{*E}$  reach a well-defined minimum at  $x \sim 0.30$ , hence, the complex likely to be formed between the component molecules is of the type DMA: 2 (ethanol). However, the minimum in case of  $V^E$  vs.  $x$  curves occurs in the concentration range  $0.33 < x < 0.48$  which supports that the maximum stability of the structure is reached in this concentration range.

The experimental values of density and ultrasonic velocity of ternary mixtures  $\text{LiNO}_3 + \text{DMA} + \text{ethanol}$  were used to calculate the different thermodynamic parameters such as isentropic compressibility ( $k_s$ ), intermolecular free length ( $L_f$ ), and relative association ( $R_A$ ) as function of DMA mol fraction and temperature, using the relations described earlier [1, 6]. The calculated parameters are presented in Table IV. The variation of ultrasonic velocity with concentration,  $x$  of DMA can be expressed as

$$du/dx = -(u/2)[1/\rho(d\rho/dx) + 1/k_s(dk_s/dx)] \quad (8)$$

The data (Tabs. I and IV) show that at each investigated temperature  $k_s$  decreases as  $\rho$  increases along with the mol fraction,  $x$  of DMA. The term  $(dk_s/dx)$  is negative, but greater in magnitude than  $(d\rho/dx)$  which

TABLE IV-A Isentropic compressibilities ( $k_s$ ,  $10^{-10} \text{ m}^{-2} \text{ N}^{-1}$ ) of  $\text{LiNO}_3$  in DMA + ethanol binary mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	8.1968	8.5082	8.7697	9.0742	9.3257
0.0616	7.6488	7.9243	8.1892	8.4324	8.7313
0.1279	7.1169	7.3674	7.5962	7.8551	8.1052
0.1993	6.6452	6.8967	7.1032	7.2843	7.5445
0.2765	6.2094	6.4240	6.6244	6.8312	7.0562
0.3602	5.8349	5.9979	6.1804	6.3649	6.5601
0.4513	5.4718	5.6351	5.8104	5.9859	6.1572
0.5508	5.1416	5.3021	5.4548	5.6208	5.7983
0.6599	4.8659	4.9989	5.1291	5.2998	5.4581
0.7802	4.5765	4.7164	4.8743	5.0188	5.1237
0.9133	4.3367	4.4999	4.6273	4.7743	4.9484

TABLE IV-B Intermolecular free lengths ( $L_f$ ,  $10^{-11} \text{ m}$ ) of  $\text{LiNO}_3$  in DMA + ethanol binary mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	5.6326	5.7889	5.9283	6.0823	6.2187
0.0616	5.4410	5.5867	5.7287	5.8632	6.0172
0.1279	5.2485	5.3868	5.5174	5.6590	5.7975
0.1993	5.0715	5.2119	5.3354	5.4495	5.5934
0.2765	4.9024	5.0301	5.1524	5.2773	5.4093
0.3602	4.7523	4.8604	4.9767	5.0940	5.2157
0.4513	4.6020	4.7112	4.8254	4.9400	5.0530
0.5508	4.4610	4.5699	4.6755	4.7870	4.9035
0.6599	4.3398	4.4373	4.5337	4.6483	4.7575
0.7802	4.2087	4.3100	4.4197	4.5233	4.6311
0.9133	4.0970	4.2100	4.3063	4.4118	4.5299

TABLE IV-C Relative associations ( $R_f$ ) of  $\text{LiNO}_3$  in DMA + ethanol mixtures as function of mol fraction of DMA and temperature

$X$ (DMA)	$T/K$				
	298.15	303.15	308.15	313.15	318.15
0.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.0616	1.0265	1.0269	1.0266	1.0275	1.0263
0.1279	1.0546	1.0551	1.0553	1.0554	1.0550
0.1993	1.0830	1.0830	1.0834	1.0850	1.0838
0.2765	1.1108	1.1115	1.1116	1.1123	1.1115
0.3602	1.1383	1.1402	1.1406	1.1416	1.1414
0.4513	1.1653	1.1671	1.1674	1.1683	1.1685
0.5508	1.1921	1.1937	1.1945	1.1955	1.1952
0.6599	1.2180	1.2205	1.2219	1.2226	1.2227
0.7802	1.2446	1.2464	1.2363	1.2477	1.2462
0.9133	1.2703	1.2707	1.2716	1.2726	1.2658

is positive, therefore,  $du/dx$  is positive, hence  $u$  increases with concentration of DMA. This is in good agreement with the results of other workers [31, 32] reported for solutions of electrolytes in binary solvent mixtures.

Table IV indicates that the values of  $k_s$  and  $L_f$  for ternary mixtures decrease monotonically with the mol fraction of DMA in the solvent mixtures. It is interesting to note the absence of minima in these properties for  $\text{LiNO}_3 + \text{DMA} + \text{ethanol}$  mixtures unlike those associated with excess functions for  $\text{DMA} + \text{ethanol}$  binary mixtures. This suggests the absence of complex formation in the ternary mixtures. Similar result were also reported for  $\text{NaCl} + N,N\text{-dimethylformamide} + \text{water}$  [32] and  $\text{KBr} + \text{formamide} + \text{water}$  [6] ternary mixtures. As mentioned above DMA and ethanol molecules, in the absence of  $\text{LiNO}_3$ , interact with each other through hydrogen bonding/dipole-dipole forces forming associated species. The added electrolyte,  $\text{LiNO}_3$  splits into  $\text{Li}^+$  and  $\text{NO}_3^-$  ions which initially break the DMA-ethanol associated structure with a consequent increase in  $k_s$  and  $L_f$ . But, because of simultaneous solvation of these ions by the free solvent molecules there is a compensating effect resulting in an overall decrease in  $k_s$  and  $L_f$ , supporting strong ion-solvent interactions.

The dielectric constant of a medium plays an important role in deciding the strength of ion-solvent interaction in that medium. As the dielectric constant of DMA is greater than that of ethanol at a given temperature, the dielectric constant of their mixtures would increase with the increase of DMA concentration in the mixture. The calculated dielectric constants, as described in the literature [33], are found to be 25.36, 27.19, 29.31, 31.84, 34.87 and 36.63 at 298.15 K for 6.16, 19.33, 36.02, 55.08, 78.02, and 91.33% (by weight) DMA + ethanol mixtures. Hence, the electrostatic effect of the solvent (DMA + ethanol) on  $\text{Li}^+$  and  $\text{NO}_3^-$  ions is increased with the increasing concentration of DMA in  $\text{LiNO}_3 + \text{DMA} + \text{ethanol}$  mixture. The pronounced decrease in  $k_s$  and  $L_f$  with the increase in DMA content in the mixture (Tab. IV) at each investigated temperature reinforces the above view. Table IV indicates that the values of  $k_s$  and  $L_f$  both increase as the temperature of the system increases. The rise in temperature dissociates DMA-ethanol aggregated resulting in an increase in  $k_s$  and  $L_f$  values which is not compensated by the ion-solvent interaction. The relative association,  $R_A$  (Tab. IV) is found to

increase as the concentration of DMA in  $\text{LiNO}_3 + \text{DMA} + \text{ethanol}$  mixture increases. This is attributed to the increased ion-solvent interaction with the increasing concentration of DMA in the mixture. A similar explanation has been suggested in order to explain the variation of  $R_A$  with composition for monochloroacetic acid + nitrobenzene + ethanol [34] ternary system.

Furthermore, it is interesting to discuss the selective solvation of  $\text{Li}^+$  and/or  $\text{NO}_3^-$  ions by the component molecules of the solvent mixture. The more pronounced decrease in the values of  $k_s$  and  $L_f$  while an appreciable increase in the values of  $R_A$  for the DMA rich mixtures (Tab. IV) suggests a certain tendency for selective solvation of  $\text{Li}^+$  ion by DMA molecules and possibly  $\text{NO}_3^-$  ion by ethanol molecules. This is supported by the fact that n.m.r. studies of ion-solvent interactions [3, 5] suggest that relatively long-lived and strong cation ( $\text{Li}^+$ )-DMA species are formed, but not with ethanol. Moreover, if we consider the acidic nature of  $\text{Li}^+$  ion [6], selective solvation of this ion by DMA, a Lewis-base, can be assumed by the existence of specific acid-base interaction [36]. Cox *et al.* [37] observed that anions, like  $\text{NO}_3^-$ , interact more strongly with the protic solvents such as ethanol than with dipolar aprotic solvents such as DMA.

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