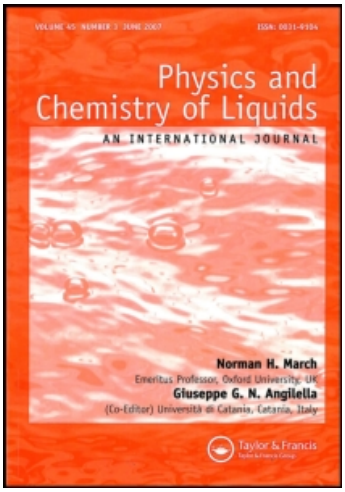

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Physico-Chemical Studies of Solvent-Solvent and Ion-Solvent Interactions in Solutions of Lithium Nitrate in Dimethyl-Sulphoxide Ethanol Mixtures

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PHYSICO-CHEMICAL STUDIES OF SOLVENT–SOLVENT AND ION-SOLVENT INTERACTIONS IN SOLUTIONS OF LITHIUM NITRATE IN DIMETHYL-SULPHOXIDE + ETHANOL MIXTURES

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Densities (ρ), viscosities (η), and ultrasonic velocities (u) through solutions of lithium nitrate in dimethylsulphoxide (DMSO) + ethanol mixtures have been measured as a function of electrolyte concentration and temperature. The suitability of various polynomial equations in reproducing the experimental values of ρ, η, and u was checked for the present system. The adiabatic compressibility (β), intermolecular free length (L_f), relative association (R_A), specific acoustic impedance (Z), molar sound velocity (R_m), enthalpy (ΔH^*) and entropy (ΔS^*) of activation of viscous flow have been computed. The results are explained in terms of solvent–solvent and ion-solvent interactions.

Keywords: Physico-chemical studies; solvent–solvent; ion-solvent interactions

1. INTRODUCTION

Recently much interest has been shown in electrolyte solutions in mixed aquo-organic solvents [1, 2]. However, very little work has been done so far on electrolytes mixed with non-aqueous binary solvent mixtures. Systems containing electrolytes in mixed solvents find applications in various technologies, as they offer a wide choice of solutions with appropriate properties. The present work is concerned with the study of $LiNO_3$ in DMSO + ethanol solvent mixtures.

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DMSO is called a "supersolvent", due to its wide range of applicability in chemical and biological processes, involving both plants and animals. It is aprotic, strongly associated solvent due to highly polar S=O group in the molecule [3] and has a large dipole moment and dielectric constant ($\mu = 3.96$ D and $\varepsilon = 46.6$ at 298.15 K) [4]. On the other hand, ethanol has a relatively low value of dipole moment and dielectric constant ($\mu = 1.69$ D and $\varepsilon = 24.55$ at 298.15 K) [4]; yet self-associated through hydrogen bonding into chain-like associates [5]. Hence, DMSO + ethanol will be an interesting solvent combination for the study of solvent–solvent and ion-solvent interactions in a ternary system containing $LiNO_3$.

In this paper we report densities, viscosities and ultrasonic velocities of 0.00, 0.25, 0.50, 0.75 and 1.00 M-$LiNO_3$ in 31.7, 58.3 and 80.7% (by weight) DMSO + ethanol binary mixtures at 298.15, 303.15, 308.15, 313.15 and 318.15 K. From these experimental data, adiabatic compressibility, intermolecular free length, relative association, specific acoustic impedance, molar sound velocity, enthalpy and entropy of activation of viscous flow have been computed. These thermodynamic functions have been used to study the solvent–solvent and ion-solvent interactions in $LiNO_3$ + DMSO + ethanol system.

2. EXPERIMENTAL

Ethanol (E. Merck, Germany) was purified as described in the literature [6]. DMSO (analytical grade) was further purified according to standard procedure [7]. $LiNO_3$ (E. Merck, Germany) was used without further purification, except for drying at 373.15 K for 24 hours, for preparing the solutions of different concentrations. DMSO + ethanol mixtures of varying compositions (31.7, 58.3 and 80.7 weight% of DMSO) as well as solutions of $LiNO_3$ in these binary solvent mixtures were prepared and stored in special airtight bottles.

Densities, viscosities and ultrasonic velocities were measured as described elsewhere [2, 8]. The experimental values of density and viscosity of pure DMSO at 298.15 K were compared with those reported earlier [9, 10] and were found to be in agreement within ± 0.01 and ± 0.1%, respectively. The ultrasonic velocity through DMSO at 298.15 K was 1485.8 ms^{-1} which compares well with the literature [7]

value $1485.8\,ms^{-1}$. The temperature of test liquids and their electrolyte solutions was maintained to an accuracy of $\pm 0.02\,K$ in a thermostatic water bath.

3. RESULTS AND DISCUSSION

The experimental values of density, viscosity, and ultrasonic velocity of $LiNO_3$ in 31.7, 58.3 and 80.7 weight% of DMSO in DMSO + ethanol mixtures as functions of electrolyte concentration and temperature are given in Table I. The dependence of ρ on temperature was checked by a polynomial equation [11]

$$\rho(t) = \sum_{i=1}^{5} \rho_i t^{i-1}; \quad t/^{\circ}C \tag{1}$$

for each ternary mixture. The ρ_i coefficients were evaluated by means of least-squares method, using a multilinear regression package TSP [12], and standard deviations were calculated by using the relation

TABLE I-a Densities (ρ, 10^3 kg m^{-3}) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	*298.15*	*303.15*	*308.15*	*313.15*	*318.15*
			31.7% DMSO (by weight)		
0.00	0.8641	0.8598	0.8555	0.8512	0.8470
0.25	0.8778	0.8735	0.8693	0.8650	0.8607
0.50	0.8907	0.8865	0.8823	0.8781	0.8739
0.75	0.9041	0.8999	0.8958	0.8917	0.8876
1.00	0.9157	0.9117	0.9076	0.9036	0.8996
			58.3% DMSO (by weight)		
0.00	0.9422	0.9376	0.9331	0.9285	0.9241
0.25	0.9552	0.9509	0.9465	0.9422	0.9380
0.50	0.9678	0.9635	0.9592	0.9549	0.9507
0.75	0.9793	0.9750	0.9708	0.9666	0.9624
1.00	0.9904	0.9862	0.9819	0.9777	0.9735
			80.7% DMSO (by weight)		
0.00	1.0183	1.0136	1.0090	1.0043	0.9996
0.25	1.0311	1.0266	1.0222	1.0176	1.0131
0.50	1.0424	1.0381	1.0335	1.0290	1.0246
0.75	1.0535	1.0491	1.0447	1.0403	1.0359
1.00	1.0638	1.0594	1.0551	1.0508	1.0466

TABLE I-b Viscosities (η, 10^{-3} kg m^{-1} s^{-1}) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	298.15	303.15	308.15	313.15	318.15
			31.7% DMSO (by weight)		
0.00	1.0342	0.9553	0.8802	0.8192	0.7629
0.25	1.2793	1.1709	1.0746	0.9938	0.9209
0.50	1.5608	1.4182	1.2946	1.1911	1.0962
0.75	1.9306	1.7336	1.5639	1.4282	1.3127
1.00	2.3266	2.0632	1.8699	1.6897	1.5379
			58.3% DMSO (by weight)		
0.00	1.1763	1.0813	0.9979	0.9312	0.8665
0.25	1.4270	1.3035	1.1989	1.1103	1.0296
0.50	1.7254	1.5726	1.4403	1.3296	1.2304
0.75	2.0718	1.8650	1.7022	1.5559	1.4379
1.00	2.5006	2.2524	2.0395	1.8625	1.7039
			80.7% DMSO (by weight)		
0.00	1.4687	1.3427	1.2345	1.1450	1.0637
0.25	1.7975	1.6336	1.4899	1.3774	1.2708
0.50	2.1452	1.9410	1.7649	1.6220	1.4943
0.75	2.5712	2.3150	2.0931	1.9155	1.7618
1.00	3.0632	2.7372	2.4751	2.2505	2.0630

TABLE I-c Ultrasonic velocities (u, m s^{-1}) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	298.15	303.15	308.15	313.15	318.15
			31.7% DMSO (by weight)		
0.00	1233.0	1214.1	1199.1	1181.5	1165.2
0.25	1244.5	1229.5	1211.1	1194.4	1179.8
0.50	1255.7	1239.8	1223.1	1207.7	1191.8
0.75	1267.7	1251.4	1235.5	1219.7	1205.1
1.00	1275.0	1258.2	1244.1	1228.7	1213.3
			58.3% DMSO (by weight)		
0.00	1317.4	1301.1	1284.4	1268.1	1251.4
0.25	1331.1	1315.3	1297.7	1282.2	1267.2
0.50	1342.7	1325.5	1310.1	1295.1	1278.4
0.75	1354.3	1335.8	1317.4	1302.8	1287.4
1.00	1364.1	1345.7	1331.1	1314.4	1299.0
			80.7% DMSO (by weight)		
0.00	1406.1	1385.5	1368.4	1352.5	1336.3
0.25	1419.8	1399.7	1385.0	1371.1	1352.0
0.50	1429.4	1410.3	1393.1	1379.4	1363.7
0.75	1442.3	1425.4	1409.1	1393.4	1377.4
1.00	1451.1	1433.4	1416.4	1399.4	1386.2

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

where Y is any physical property and n is the number of data points. The coefficients of Equation 1 along with the standard deviations $\sigma(\rho)$ for each concentration are listed in Table II. The goodness of this fit equation is ascertained by an average uncertainty of $\pm 5.69 \times 10^{-5}$ units of ρ. The dependence ρ of on concentration (C) of the electrolyte in ternary mixtures was established by the polynomial equation [11]

$$1/\rho(C) = \sum_{i=1}^{5} 1/\rho_i C^{i-1} \quad (3)$$

The results of this correlation procedure are given in Table III, along with the standard deviations $\sigma(1/\rho)$ at each investigated temperature. It is found that Equation 3 reproduces the experimental densities well within $\pm 1.04 \times 10^{-5}$ g cm^{-3} for the system under study.

The temperature dependence of η for ternary mixtures under investigation was modelled using a polynomial equation of the type

TABLE II Coefficients (ρ_i), of Equation 1 and standard deviation $\sigma(\rho)$ for $LiNO_3$ + DMSO + ethanol mixtures

C (M)	ρ_1	$\rho_2 \times 10^2$	$\rho_3 \times 10^4$	$\rho_4 \times 10^6$	$\rho_5 \times 10^8$	$\sigma(\rho) \times 10^5$
			31.7% DMSO (by weight)			
0.00	0.9781	−1.1870	4.8365	− 9.3043	6.6207	5.227
0.25	1.0569	−1.9569	8.1851	−15.6544	11.0579	7.617
0.50	0.9618	−0.6611	2.4468	−4.5345	3.1039	4.753
0.75	0.9995	−0.9534	3.7416	−7.0388	4.9001	4.160
1.00	1.0041	−0.8915	3.5561	−6.8293	4.8497	5.943
			58.3% DMSO (by weight)			
0.00	1.1285	−2.0304	8.4856	−16.2581	11.5206	7.786
0.25	0.9485	0.2463	−1.4345	2.6883	−1.8490	0.826
0.50	1.2241	−2.8747	12.2189	23.4318	16.6095	10.016
0.75	0.9407	0.6414	−3.2499	6.3519	−4.5755	4.210
1.00	1.0278	−0.2828	0.8938	−1.7679	1.2941	2.682
			80.7% DMSO (by weight)			
0.00	1.3018	−3.1842	13.5396	−25.9418	18.3595	10.128
0.25	1.0404	0.0617	−0.6483	1.2218	−0.8580	3.921
0.50	1.2605	−2.4360	10.3926	−20.1176	14.3817	10.739
0.75	1.2618	−2.2962	9.6537	−18.4641	13.0485	11.277
1.00	1.0521	0.3241	−1.8585	3.6574	−2.6405	2.511

TABLE III Coefficients $(1/\rho_i)$ of Equation 3 and standard deviations $\sigma(1/\rho)$ for $LiNO_3$ + DMSO + ethanol mixtures

T/K	ρ_1^{-1}	$\rho_2^{-1} \times 10$	$\rho_3^{-1} \times 10$	$\rho_4^{-1} \times 10$	$\rho_5^{-1} \times 10$	$\sigma(1/\rho) \times 10^6$
			31.7% DMSO (by weight)			
298.15	1.1573	−0.8259	0.6038	−0.9126	0.4827	6.852
303.15	1.1631	−0.8205	0.5249	−0.7861	0.4197	3.468
308.15	1.1689	−0.8323	0.5529	−0.8422	0.4507	4.106
313.15	1.1748	−0.8353	0.5183	−0.7862	0.4222	3.291
318.15	1.1806	−0.8428	0.5506	−0.8697	0.4720	1.796
			58.3% DMSO (by weight)			
298.15	1.0613	−0.5692	−0.0874	0.2810	−0.1405	6.318
303.15	1.0666	−0.3733	−1.6604	3.5271	−2.0194	7.105
308.15	1.0717	−0.6135	−0.0324	0.2527	−0.1398	0.737
313.15	1.0770	−0.6550	0.0904	0.0879	−0.0652	0.642
318.15	1.0821	−0.6790	0.1610	−0.0139	−0.0171	3.281
			80.7% DMSO (by weight)			
298.15	0.9820	−0.5572	0.3709	−0.4249	0.1911	0.415
303.15	0.9866	−0.5557	0.2829	−0.2605	0.1064	5.527
308.15	0.9911	−0.5996	0.4767	−0.5616	0.2515	8.331
313.15	0.9957	−0.6029	0.4450	−0.5005	0.2184	8.192
318.15	1.0004	−0.6220	0.4830	−0.5504	0.2404	2.555

$$\ln \eta = \sum_{i=1}^{5} \ln \eta_i \; T^{i-1}; \quad T/K \tag{4}$$

The coefficients $\ln \eta_i$; along with the standard deviations $\sigma(\ln \eta)$ for each salt concentration are presented in Table IV. Equation 4 reproduces the experimental viscosities with an average uncertainty of $\pm 1.55 \times 10^{-6}$ kg m^{-1}s^{-1}. The dependence of η on concentration (C) of the electrolyte in ternary mixtures was checked by using the polynomial equation

$$\eta(C) = \sum_{i=1}^{5} \eta_i C^{i-1} \tag{5}$$

Table V gives the η_i coefficients together with the standard deviations $\sigma(\eta)$ at each investigated temperature. It is found that Equation 5 reproduces the experimental viscosities with an average uncertainty of $\pm 8.26 \times 10^{-8}$ kg m^{-1}s^{-1} for the system under study.

The authors propose similar polynomial equations in order to model the dependence of ultrasonic velocity, u on composition of the

TABLE IV Coefficients ($\ln \eta_i$) of Equation 4 and standard deviations $\sigma(\ln \eta)$ for $LiNO_3$ + DMSO + ethanol mixtures

$C(M)$	$ln\eta_1$	$ln\eta_2 \times 10^2$	$ln\eta_3 \times 10^4$	$ln\eta_4 \times 10^6$	$ln\eta_5 \times 10^{10}$	$\sigma(ln\eta) \times 10^3$
			31.7% DMSO (by weight)			
0.00	4.5554	−0.2798	−0.3794	−0.1445	4.4489	1.246
0.25	5.3412	−0.3206	−0.4221	−0.1715	5.2645	0.676
0.50	5.7634	−0.3191	−0.4303	−0.1863	5.5642	0.967
0.75	8.4368	−0.7209	−0.6533	−0.2363	8.1525	0.894
1.00	7.7526	−0.4456	−0.5837	−0.2381	7.4875	2.925
			58.3% DMSO (by weight)			
0.00	5.3597	−0.3787	−0.4398	−0.1670	5.4005	1.592
0.25	5.8025	−0.3857	−0.4475	−0.1844	5.7806	1.016
0.50	6.2085	−0.4112	−0.4631	−0.1901	5.9699	0.727
0.75	7.9478	−0.7044	−0.5588	−0.2362	7.7304	1.393
1.00	6.9982	−0.3609	−0.5541	−0.1834	6.0501	0.860
			80.7% DMSO (by weight)			
0.00	6.1146	−0.4435	−0.4717	−0.1907	6.1266	0.946
0.25	6.6992	−0.4755	−0.4969	−0.2057	6.5493	1.696
0.50	7.2756	−0.5284	−0.5368	−0.2107	6.8604	0.975
0.75	7.8951	−0.3708	−0.6319	−0.2511	8.1339	0.943
1.00	8.2306	−0.3649	−0.6181	−0.2765	8.6058	0.975

TABLE V Coefficients (η_i) of Equation 5 and standard deviations $\sigma(\eta)$ for $LiNO_3$ + DMSO + ethanol mixtures

T/K	η_1	η_2	η_3	η_4	η_5	$\sigma(\eta) \times 10^6$
			31.7% DMSO (by weight)			
298.15	1.0342	1.0910	−0.9613	2.3797	−1.2170	6.114
303.15	0.9553	0.9382	−0.7018	1.8364	−0.9648	8.457
308.15	0.8842	0.7943	−0.2508	0.8333	−0.3870	0.977
313.15	0.8192	0.7076	−0.1901	0.6969	−0.3439	13.633
318.15	0.7629	0.6848	−0.4618	1.1499	−0.5979	18.386
			58.3% DMSO (by weight)			
298.15	1.1763	0.8739	0.6277	−0.5397	0.3623	7.060
303.15	1.0813	0.6688	1.2594	−1.7709	1.0137	13.870
308.15	0.9978	0.6224	1.0278	−1.4039	0.7953	12.727
313.15	0.9312	0.4855	1.3668	−2.0559	1.1349	5.556
318.15	0.8665	0.4528	1.1566	−1.6551	0.8830	1.982
			80.7% DMSO (by weight)			
298.15	1.4687	1.4277	−0.8468	1.7760	−0.7624	11.889
303.15	1.3427	1.2667	−0.7757	1.6378	−0.7340	18.503
308.15	1.2344	1.0611	−0.3588	0.8940	−0.3557	19.301
313.15	1.1450	0.9981	−0.5189	1.0963	−0.4700	1.804
318.15	1.0637	0.8707	−0.3699	0.9046	−0.4062	9.607

ternary mixtures. The dependence of u on concentration (C) of the electrolyte in ternary mixtures investigated was checked by a polynomial equation

$$\ln u(C) = \sum_{i=1}^{5} \ln u_i C^{i-1} \tag{6}$$

The results of this fit equation are listed in Table VI along with the standard deviations $\sigma(\ln u)$ at each investigated temperature. An average uncertainty of ± 0.0533 units of u envisages the usefulness of Equation 6. The significance of data fitting using similar polynomials in reproducing the experimental values of ρ and η has also been reported for N,N-dimethylformamide + 1,2-ethanediol [11] and formamide + ethanol [13] binary mixtures.

The experimental values of density, ultrasonic velocity and viscosity have been used to calculated different thermodynamic parameters such as adiabatic compressibility (β), intermolecular free length (L_f), relative association (R_A), specific acoustic impedance (Z) and molar sound velocity (R_m) as function of electrolyte concentration and temperature, using the following relations [8, 14, 15] in order to have an

TABLE VI Coefficients ($\ln u_i$) of Equation 6 and standard deviations $\sigma(\ln u)$ for $LiNO_3$ + DMSO + ethanol mixtures

T/K	$\ln u_1$	$\ln u_2 \times 10$	$\ln u_3 \times 10$	$\ln u_4 \times 10$	$\ln u_5 \times 10$	$\sigma(\ln u) \times 10^5$
			31.7% DMSO (by weight)			
298.15	7.1172	0.4647	−0.6077	1.1418	−0.6638	3.574
303.15	7.1017	0.7657	−1.5317	2.2224	−1.1003	5.455
308.15	7.0893	0.4718	−0.4611	0.8698	−0.5114	8.901
313.15	7.0745	0.3969	0.2138	−0.2863	0.0673	3.110
318.15	7.0605	0.6887	−1.1428	1.8168	−0.9576	2.277
			58.3% DMSO (by weight)			
298.15	7.1834	0.5106	−0.5390	0.7297	−0.3524	3.033
303.15	7.1709	0.6278	−1.0639	1.3974	−0.6241	7.663
308.15	7.1579	0.2831	0.9833	−2.1172	1.2089	11.670
313.15	7.1453	0.3051	0.9629	−2.0188	1.1085	6.794
318.15	7.1320	0.5900	−0.3413	−0.0576	0.1829	4.171
			80.7% DMSO (by weight)			
298.15	7.2486	0.6241	−1.4385	2.2544	−1.1249	2.280
303.15	7.2338	0.6661	−1.6306	2.7380	−1.4336	7.001
308.15	7.2214	1.0383	−3.3687	5.3431	−2.6670	4.752
313.15	7.2097	1.0907	−3.2287	4.8559	−2.3768	4.702
318.15	7.1977	0.6673	−1.2310	1.9042	−0.9745	1.841

insight on solvent–solvent and ion-solvent interactions in the present system:

$$\beta = u^{-2}\rho^{-1} \tag{7}$$

$$L_f = K/u\rho^{1/2} \tag{8}$$

$$R_A = (\rho/\rho_o)(u_o/u)^{1/3} \tag{9}$$

$$Z = u\rho \tag{10}$$

$$R_m = u^{1/3}V \tag{11}$$

where ρ_o and u_o are the density and ultrasonic velocity of pure solvent; V is the molar volume of the mixture; K is the temperature dependent Jacobson's constant [16] [$=(93.875 + 0.3757) \times 10^{-8}$].

The concentration and temperature dependence of β, L_f, R_A, Z and R_m are presented in Table VII. It is evident from the Tables I and VIIb that the increase in u and a corresponding decrease in L_f with the molar concentration of $LiNO_3$ in DMSO + ethanol mixtures is in accordance with the view proposed by Eyring and Kincaid [17]; according to which the ultrasonic velocity increases with decrease in the free length and vice-versa.

It should be noted that the values of β and L_f are found to decrease linearly with the concentration of $LiNO_3$ in all the three solvent mixtures (Tab. VIIa and b) with no maxima or minima such as those associated with electrolytes in dimethylformamide + water [18] and acetone + water [19] systems. This suggests the absence of complex formation in $LiNO_3$ + DMSO + ethanol system. A similar conclusion was arrived at by Osinska *et al.* [18] from the viscosity study of NaI in formamide + water mixtures and also by Ali and Nain [2] during the ultrasonic study of KBr + formamide + water system.

The decrease in β and L_f on going from 31.7 to 80.7% (by weight) DMSO + ethanol mixtures in the absence of $LiNO_3$ is interesting. Addition of DMSO to ethanol dissociates ethanol–ethanol aggregates [20] thereby increasing β and L_f values. But, due to simultaneous formation of hydrogen bond between DMSO and ethanol molecules [21] through oxygen atom of highly polar S=O group of DMSO and hydrogen atom of –OH group of ethanol there is compensating effect

TABLE VII-a Adiabatic compressibility (β, 10^{-10} m^2 N^{-1}) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	298.15	303.15	308.15	313.15	318.15
			31.7% DMSO (by weight)		
0.00	7.6122	7.8903	8.1296	8.4159	8.6959
0.25	7.3555	7.5732	7.8428	8.1037	8.3470
0.50	7.1203	7.3387	7.5763	7.8080	8.0562
0.75	6.8826	7.0960	7.3131	7.5383	7.7578
1.00	6.7178	6.9287	7.1186	7.3305	7.5512
			58.3% DMSO (by weight)		
0.00	6.1154	6.3003	6.4964	6.6975	6.9102
0.25	5.9086	6.0788	6.2738	6.4557	6.6391
0.50	5.7313	5.9073	6.0741	6.2436	6.4361
0.75	5.5674	5.7479	5.9352	6.0953	6.2693
1.00	5.4262	5.5994	5.7479	5.9202	6.0876
			80.7% DMSO (by weight)		
0.00	4.9670	5.1395	5.2928	5.4433	5.6023
0.25	4.8111	4.9720	5.0999	5.2274	5.4000
0.50	4.6952	4.8433	4.9857	5.1075	5.2482
0.75	4.5630	4.6915	4.8209	4.9510	5.0882
1.00	4.4642	4.5942	4.7243	4.8596	4.9724

resulting in an overall decrease in β and L_f. However, the decrease in β and L_f values with increase in DMSO content, principally in DMSO rich mixture (80.7% DMSO, Tab. VII a and b), may be due to hydrogen bonding between the component molecules and dipole–dipole interactions between DMSO molecules. As it has been suggested that in DMSO rich mixtures, its molecules tend to preserve their structural order [3] thereby partly contributing in lowering β and L_f values through dipole–dipole interactions.

Since the dielectric constant of DMSO is higher than that of ethanol at a given temperature, it may be assumed that the dielectric constant of their mixture would increase with increasing amount of DMSO in the mixture. Similar assumption was made by Moore [22] who calculated the "approximated dielectric constant" (ADC) of a mixture of two or more liquids using the relation.

$$\text{ADC} = [(\%\ \text{solvent}_1)(\varepsilon_1) + (\%\ \text{solvent}_2)(\varepsilon_2) + \ldots$$

$$\ldots + (\%\ \text{solvent}_x)(\varepsilon_x)]/100 \qquad (12)$$

TABLE VII-b Intermolecular free length (L_f, 10^{-11} m) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	*298.15*	*303.15*	*308.15*	*313.15*	*318.15*
			31.7% DMSO (by weight)		
0.00	5.4280	5.5747	5.7078	5.8575	6.0050
0.25	5.3357	5.4616	5.6062	5.7478	5.8833
0.50	5.2497	5.3763	5.5102	5.6420	5.7799
0.75	5.1613	5.2867	5.4136	5.5437	5.6718
1.00	5.0992	5.2240	5.3411	5.4667	5.5958
			58.3% DMSO (by weight)		
0.00	4.8652	4.9815	5.1024	5.2254	5.3530
0.25	4.7822	4.8931	5.0142	5.1302	5.2470
0.50	4.7099	4.8236	4.9337	5.0452	5.1662
0.75	4.6421	4.7581	4.8770	4.9849	5.0988
1.00	4.5828	4.6962	4.7994	4.9128	5.0243
			80.7% DMSO (by weight)		
0.00	4.3846	4.4992	4.6055	4.7108	4.8199
0.25	4.3153	4.4253	4.5208	4.6164	4.7321
0.50	4.2630	4.3676	4.4699	4.5631	4.6651
0.75	4.2025	4.2986	4.3954	4.4927	4.5934
1.00	4.1568	4.2538	4.3511	4.4510	4.5409

Thus, the calculated ADCs for 31.7, 58.3 and 80.7% (by wright) DMSO + ethanol mixtures are found to be 29.30, 34.50 and 40.24. As a result, the electrostatic effect of the solvent on the dissolved electrolyte is increased; it can be inferred that electrolyte-solvent interaction increases with the increase in DMSO concentration in the mixture. The progressive decrease in β and L_f on going from 31.7 to 80.7% DMSO + ethanol mixture at each electrolyte concentration supports the above view. It has been assumed that the "solvated" solvent molecules are fully compressed by the electrical forces of the ions [2]. Hence, a fraction of the solvent molecules is rendered incompressible and thus the compressibility of the solution is mainly due to the free solvent molecules. As the concentration of $LiNO_3$ in the mixture increases, more and more solvent molecules get solvated resulting in a decrease in β and L_f. The trend is the same in all the three solvent mixtures. At almost all the concentrations of $LiNO_3$ studied, increase in temperature increases the value of β and L_f. This may be mainly due to the dissociation of DMSO-ethanol aggregates which seem to be temperature sensitive and is not compensated by the solvation of the ions.

In the present investigation, relative association (R_A) is found to increase with the concentration of $LiNO_3$ and temperature in all the three DMSO + ethanol mixtures (Tab. VII c). R_A is found to be influenced by two opposing factors: the breaking up of the solvent aggregates (DMSO-ethanol) on addition of electrolyte; and subsequent solvation of ions by the solvent molecules. The former effect results in a decrease while the latter increases the value of R_A. The increase in R_A with electrolyte concentration for each solvent mixture indicates that the ion-solvent interaction predominates over the breaking up of the DMSO-ethanol aggregates. Increase in the temperature provides more free solvent molecules due to the dissociation of DMSO-ethanol aggregates, resulting enhanced solvation of ions by the solvent molecules leading to an increase in R_A with temperature. Similar behaviour in R_A has also been reported by Nikam and Hiray [23] for binary solvent mixtures containing electrolyte.

The value of specific acoustic impedance (Z) is found to increase with molar concentration of $LiNO_3$ in DMSO + ethanol mixtures (Tab. VII d). It is obvious that the linear increase in Z in all three solvent mixtures is in agreement with the theoretical requirement

TABLE VII-c Relative association (R_A) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	*298.15*	*303.15*	*308.15*	*313.15*	*318.15*
			31.7% DMSO (by weight)		
0.00	1.0000	1.0000	1.0000	1.0000	1.0000
0.25	1.0190	1.0202	1.0195	1.0199	1.0204
0.50	1.0371	1.0383	1.0382	1.0392	1.0396
0.75	1.0560	1.0572	1.0576	1.0588	1.0598
1.00	1.0716	1.0730	1.0740	1.0755	1.0765
			58.3% DMSO (by weight)		
0.00	1.0000	1.0000	1.0000	1.0000	1.0000
0.25	1.0173	1.0179	1.0178	1.0185	1.0193
0.50	1.0337	1.0340	1.0348	1.0357	1.0361
0.75	1.0490	1.0491	1.0492	1.0504	1.0513
1.00	1.0634	1.0637	1.0649	1.0657	1.0666
			80.7% DMSO (by weight)		
0.00	1.0000	1.0000	1.0000	1.0000	1.0000
0.25	1.0158	1.0163	1.0172	1.0179	1.0175
0.50	1.0293	1.0302	1.0304	1.0313	1.0320
0.75	1.0434	1.0449	1.0455	1.0462	1.0468
1.00	1.0557	1.0571	1.0578	1.0583	1.0599

TABLE VII-d Specific acoustic impedance (Z, 10^6 kg m^{-2} s^{-1}) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
$C(M)$	*298.15*	*303.15*	*308.15*	*313.15*	*318.15*
			31.7% DMSO (by weight)		
0.00	1.0654	1.0439	1.0258	1.0057	0.9869
0.25	1.0924	1.0740	1.0528	1.0332	1.0155
0.50	1.1185	1.0991	1.0791	1.0605	1.0415
0.75	1.1461	1.1261	1.1068	1.0876	1.0696
1.00	1.1675	1.1471	1.1291	1.1103	1.0915
			58.3% DMSO (by weight)		
0.00	1.2413	1.2199	1.1985	1.1774	1.1564
0.25	1.2715	1.2507	1.2283	1.2081	1.1886
0.50	1.2995	1.2771	1.2566	1.2367	1.2154
0.75	1.3263	1.3024	1.2789	1.2593	1.2390
1.00	1.3510	1.3271	1.3070	1.2851	1.2646
			80.7% DMSO (by weight)		
0.00	1.4318	1.4043	1.3807	1.3583	1.3358
0.25	1.4640	1.4369	1.4157	1.3952	1.3697
0.50	1.4900	1.4640	1.4398	1.4194	1.3972
0.75	1.5195	1.4954	1.4721	1.4496	1.4268
1.00	1.5437	1.5185	1.4944	1.4705	1.4508

because u and ρ both increase with the molar concentration of $LiNO_3$. The value of Z increases as the amount of DMSO in the mixture increases suggesting that Z varies directly with the dielectric constant of the medium. A linear increase in Z with electrolyte concentration has also been reported for aqueous and non-aqueous solutions of lithium salts in ethanol, acetone and methylethyl ketone [24]. The decrease in Z with increase in temperature is due to the corresponding decrease in u and ρ with temperature. The molar sound velocity (R_m) increases with the increase in DMSO% in DMSO + ethanol mixture (Tab. VII e). This is expected, since the values of molar volume (V) and that of u both increase with the increasing amount of DMSO in the mixture. It is interesting to note that the value of R_m decreases with increase in the concentration of $LiNO_3$ in DMSO + ethanol mixtures. It is due to the fact that the decrease in V dominates over the corresponding increase in u as the concentration of electrolyte in all the three mixtures $LiNO_3$ + DMSO + ethanol increases. The molar sound velocity (R_m), as expected, is found to be nearly temperature independent for the present system.

TABLE VII-E Molar sound velocity (R_m, 10^{-4} m^3 mol^{-1} $(m\ s^{-1})^{1/3}$) of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration and temperature

	T/K				
C(M)	298.15	303.15	308.15	313.15	318.15
	317% DMSO (by weight)				
0.00	6.5729	6.5718	6.5775	6.5783	6.5803
0.25	6.5200	6.5257	6.5243	6.5265	6.5322
0.50	6.4736	6.4767	6.4782	6.4818	6.4842
0.75	6.4258	6.4280	6.4299	6.4318	6.4357
1.00	6.3835	6.3832	6.3880	6.3897	6.3912
	58.3% DMSO (by weight)				
0.00	7.0432	7.0485	7.0520	7.0568	7.0592
0.25	6.9868	6.9905	6.9915	6.9953	6.9992
0.50	6.9307	6.9318	6.9358	6.9403	6.9409
0.75	6.8835	6.8822	6.8801	6.8844	6.8871
1.00	6.8369	6.8350	6.8400	6.8405	6.8431
	80.7% DMSO (by weight)				
0.00	7.5782	7.5759	7.5790	7.5849	7.5900
0.25	7.5084	7.5056	7.5114	7.5200	7.5182
0.50	7.4439	7.4413	7.4439	7.4518	7.4553
0.75	7.3876	7.3895	7.3923	7.3959	7.3987
1.00	7.3311	7.3315	7.3321	7.3326	7.3388

The next part of the present work deals with the thermodynamic properties of viscous flow of the system under investigation. By combining Eyring's viscosity equation [25]

$$\eta = (hN/V)\exp(\Delta G^*/RT) \tag{13}$$

with the relation

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{14}$$

one gets the relation

$$R\ln(\eta V) = [R\ln(hN) - \Delta S^*] + \Delta H^*/T \tag{15}$$

where h is the Planck's constant, N is the Avogadro's number, V is the molar volume of the mixtures, ΔG^* is the free energy, ΔH^* is the

enthalpy and ΔS^* is the entropy of activation of viscous flow. The plots of $R \ln(\eta V)$ against $1/T$ for each binary mixture were found to be linear, suggesting that ΔH^* values are constant in the temperature range 298.15 to 318.15 K.

The values of the slopes (ΔH^*) and intercepts (ΔS^*) obtained from the above plots, together with the linear correlation factor (f) of Equation 15 are given in Table VIII. The values of ΔH* and ΔS* are found to increase with the concentration of electrolyte in all the three solvent mixtures. The behaviour of ΔH^* and ΔS^* with concentration of the electrolyte may be explained assuming that the flow process involves the co-operative movement of dislocations or discontinuities in the fluid layers created by the statistical fluctuations of local density [25]. Therefore, ΔH^* may be viewed as a measure of the degree of co-operation between the species taking part in viscous flow. In the low temperature range, as well as for highly structured system, one may expect a considerable degree of order, so that transport phenomena take place co-operatively, as a result great heat of activation

TABLE VIII Enthalpy (ΔH^*, kJ mol^{-1}), entropy (ΔS^*, JK^{-1} mol^{-1})and linear correlation factor (f) of viscous flow of $LiNO_3$ in DMSO + ethanol mixtures as function of electrolyte concentration from 298.15 to 318.15 K

$C(M)$	ΔH^*	ΔS^*	f
	31.7% DMSO (by weight)		
0.00	11.24	−4.44	0.9997
0.25	12.19	−2.92	0.9997
0.50	13.15	−1.24	0.9997
0.75	14.51	1.65	0.9987
1.00	15.52	3.55	0.9991
	58.3% DMSO (by weight)		
0.00	11.24	−5.88	0.9993
0.25	12.11	−4.45	0.9995
0.50	12.62	−4.25	0.9995
0.75	13.70	−2.03	0.9988
1.00	14.43	−1.11	0.9997
	80.7% DMSO (by weight)		
0.00	11.97	−5.69	0.9992
0.25	12.94	−4.00	0.9991
0.50	13.57	−3.30	0.9992
0.75	14.26	−2.38	0.9989
1.00	14.93	−1.51	0.9990

associated to a relatively high value of flow entropy is observed. The progressive increase in ΔH^* and ΔS^* values with $LiNO_3$ concentration in all the three DMSO + ethanol mixtures may be due to the increasing structuredness of the system as a result of strong ion-solvent interaction.

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