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Physico-chemical studies of non-aqueous binary liquid mixtures at various temperatures

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Abstract

Densities, ρ, viscosities, η, and ultrasonic velocities, u, have been measured for pure *N*,*N*-dimethylformamide (DMF), ethanol and their binary mixtures at 298.15, 303.15, 308.15, 313.15 and 318.15 K over the whole mole fraction range. From these data adiabatic compressibilities, β, intermolecular free lengths, L_f, relative associations, R_A, excess adiabatic compressibilities, β^E, excess free lengths, L_f^E, excess molar volumes, V^E, excess viscosities, η^E, and excess free energies of activation of viscous flow, G^{*E}, have been calculated. All the excess functions studied were found to be negative over the entire range of mole fraction. These properties are used to explain the intermolecular interactions between the components. Furthermore, activation enthalpies, ΔH^* and entropies, ΔS^* of viscous flow have been evaluated and their variations with concentration discussed.

Keywords: Activation parameters; Excess functions; Non-aqueous mixtures; Physico-chemical studies

1. Introduction

The study of the solution properties of binary or ternary mixtures of polar solvents in which one of the components is highly associated is of considerable theoretical and industrial importance. The present investigation is concerned with the study of *N*,*N*-dimethylformamide (DMF)-ethanol mixtures covering the whole miscibility range. Ethanol is an interesting non-aqueous solvent, in particular because it is

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strongly self-associated through hydrogen bonding despite its low dipole moment and dielectric constant ($\mu = 1.69$ D and $\varepsilon = 24.55$ at 298.15 K) [1]. DMF, on the other hand, is highly polar ($\mu = 3.86$ D and $\varepsilon = 36.71$ at 298.15 K) [1], yet is practically unassociated [2], and behaves as a good solvent for many different groups of compounds. Moreover, DMF is reported to be a powerful breaker of polymerized structures of hydroxy compounds [3]. Numerous investigators have studied the thermodynamics of binary mixtures of amide–water [4–6], alcohol–water [7, 8], alcohol–alcohol [9, 10], and amides and alcohols mixed with other organic solvents [11] from the point of view of their ultrasonic and volumetric behaviour. However, to the best of our knowledge, relatively few data are available in the literature for amide–alcohol solvent systems [2, 3, 12]. Surprisingly there has been practically no study of amide–alcohol solvent systems from the point of view of their ultrasonic behaviour except the work of Rao and Reddy [13]. These authors studied only the excess volumes and excess isentropic compressibilities for mixtures of DMF with a branched alcohol at a single temperature, 303.15 K. However, a clear understanding of the solution structure of DMF–ethanol system is lacking.

In the present paper, we report densities, viscosities and ultrasonic velocities of mixtures of DMF with ethanol at 298.15, 303.15, 308.15, 313.15 and 318.15 K covering the whole miscibility range expressed by the mole fraction x of DMF ($0 \leqslant x \leqslant 1$). These properties have been used to compute adiabatic compressibility, excess intermolecular free length, excess molar volume, excess viscosity, excess free energy of activation, and enthalpy and entropy of activation for viscous flow. The significance of these parameters has been emphasized in understanding the intermolecular interactions between DMF and ethanol molecules.

2. Experimental

Ethanol (E. Merck, Germany) was purified by standard methods [14]. DMF (AnalaR grade) was purified as described in the literature [13]. All the mixtures were prepared by volume at 303.15 K.

The densities were measured with a single stem pycnometer of bulb capacity 8 cm^3. Viscosities were determined using an Ubbelohde viscometer. The experimental values of density and viscosity of DMF were compared with those reported earlier [3, 15] and were found to be in agreement within ±0.01 and ±0.1%, respectively. Ultrasonic velocities in pure liquids and their mixtures were measured using a single-crystal variable-path interferometer at 2 MHz with an accuracy of ±0.03%. The temperature of the solution was maintained to an accuracy of ± 0.05°C by circulating water through the brass jacket from a thermostatic water bath.

3. Results and discussion

The experimental results of measurements of density, ρ, viscosity, η, and ultrasonic velocity, u, of the pure liquids and their binary mixtures as a function of concentration and temperature are listed in Table 1. The ultrasonic velocity was used to calculate the

Table 1
Density, $\rho/(\mathrm{kg\,m^{-3}})$, viscosity, $\eta \times 10^3/(\mathrm{N\,m^{-2}\,s})$ and ultrasonic velocity, $u/(\mathrm{m\,s^{-1}})$ of binary mixtures at various temperatures

x (DMF)	Temperature/K				
	298.15	303.15	308.15	313.15	318.15
			ρ		
0.0000	785.8	781.8	777.6	773.5	769.3
0.0777	802.1	798.0	793.9	789.7	785.6
0.1593	821.1	816.7	812.2	807.7	803.4
0.2452	838.3	833.7	829.1	824.5	820.0
0.3357	853.4	848.7	844.1	839.4	834.6
0.4312	868.2	863.5	858.8	854.0	849.3
0.5320	883.1	878.6	874.2	869.6	865.0
0.6388	898.6	894.4	890.2	885.9	849.3
0.7520	913.6	909.1	904.6	899.9	895.3
0.8721	930.1	925.5	920.9	916.2	911.6
1.0000	944.6	940.1	935.7	931.1	926.6
			η		
0.0000	1.0957	0.9944	0.9097	0.8306	0.7648
0.0777	0.9871	0.9119	0.8361	0.7704	0.7111
0.1593	0.9169	0.8499	0.7835	0.7278	0.6761
0.2452	0.8731	0.8125	0.7510	0.7003	0.6534
0.3357	0.8350	0.7800	0.7257	0.6804	0.6357
0.4312	0.8165	0.7620	0.7115	0.6687	0.6268
0.5320	0.8063	0.7557	0.7053	0.6640	0.6259
0.6388	0.8051	0.7548	0.7073	0.6678	0.6284
0.7520	0.8058	0.7564	0.7078	0.6708	0.6371
0.8721	0.8095	0.7594	0.7113	0.6727	0.6377
1.0000	0.8130	0.7654	0.7194	0.6816	0.6446
			u		
0.0000	1152.4	1132.2	1117.0	1102.8	1083.7
0.0777	1188.2	1171.1	1152.8	1132.6	1119.4
0.1593	1220.0	1203.1	1188.8	1172.0	1151.0
0.2452	1254.0	1238.0	1219.4	1204.2	1183.4
0.3357	1288.8	1268.2	1256.2	1234.8	1218.0
0.4312	1315.7	1300.8	1281.1	1262.5	1244.0
0.5320	1348.0	1330.0	1312.0	1294.2	1273.7
0.6388	1380.5	1359.4	1342.8	1326.2	1310.8
0.7520	1407.4	1392.8	1372.8	1358.0	1336.5
0.8721	1434.2	1416.0	1400.8	1379.4	1361.1
1.0000	1468.0	1447.7	1428.5	1410.2	1392.0

adiabatic compressibility, β, intermolecular free length, L_f and relative association, R_A, as a function of concentration and temperature using the following relationships [16].

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

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

$$R_A = \rho/\rho_0(u_0/u)^{1/3} \tag{3}$$

where K is a temperature-dependent constant $(=(93.875+0.375\,T)\times 10^{-8})$ and ρ_0 and u_0 are the density and ultrasonic velocity of pure solvent (ethanol).

The variations of β, L_f and R_A with mole fraction of DMF and temperature have been presented in Table 2. The variation of u through the mixtures depends upon the value of L_f. The increase in the value of u and corresponding decrease in L_f observed in

Table 2
Adiabatic compressibility, $\beta/(\mathrm{m}^2\,N^{-1})\times 10^{10})$, intermolecular free length, $L_f/\mathrm{m}\times 10^{11}$, and relative association, R_A of binary mixtures at various temperatures

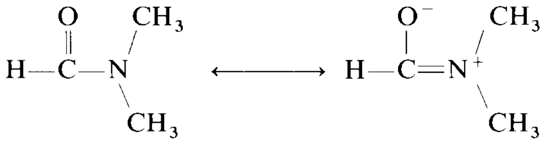
x (DMF)	Temperature/K				
	298.15	303.15	308.15	313.15	318.15
			β		
0.0000	9.5826	9.9783	10.3070	10.6300	11.0680
0.0777	8.8306	9.1371	9.4782	9.8715	10.3230
0.1593	8.1825	8.4593	8.7120	9.0135	9.3954
0.2452	7.5859	7.8262	8.1115	8.3640	8.7081
0.3357	7.0547	7.3261	7.5074	7.8134	8.0766
0.4312	6.6537	6.8441	7.0948	7.3465	7.6085
0.5320	6.2318	6.4344	6.6454	6.8656	7.1261
0.6388	5.8393	6.0503	6.2300	6.4180	6.6009
0.7520	5.5260	5.6704	5.8658	6.0257	6.2531
0.8721	5.2270	5.3889	5.5340	5.7363	5.9213
1.0000	4.9125	5.0754	5.2372	5.4006	5.5697
			L_f		
0.0000	6.0901	6.2691	6.4269	6.5832	6.7748
0.0777	5.8463	5.9990	6.1631	6.3439	6.4904
0.1593	5.6277	5.7722	5.9087	6.0619	6.2419
0.2452	5.4186	5.5520	5.7015	5.8394	6.0092
0.3357	5.2254	5.3717	5.4850	5.6439	5.7872
0.4312	5.0748	5.1920	5.3322	5.4727	5.6170
0.5320	4.9112	5.0342	5.1606	5.2905	5.4360
0.6388	4.7541	4.8816	4.9967	5.1152	5.2319
0.7520	4.6248	4.7259	4.8484	4.9564	5.0922
0.8721	4.4979	4.6071	4.7093	4.8359	4.9552
1.0000	4.3605	4.4711	4.5813	4.6923	4.8059
			R_A		
0.0000	–	–	–	–	–
0.0777	1.0312	1.0323	1.0318	1.0301	1.0323
0.1593	1.0650	1.0660	1.0664	1.0656	1.0655
0.2452	1.0973	1.0973	1.0979	1.0977	1.0976
0.3357	1.1273	1.1274	1.1289	1.1269	1.1280
0.4312	1.1548	1.1568	1.1561	1.1550	1.1559
0.5320	1.1841	1.1858	1.1862	1.1858	1.1866
0.6388	1.2145	1.2159	1.2173	1.2179	1.2211
0.7520	1.2427	1.2460	1.2461	1.2470	1.2480
0.8721	1.2732	1.2754	1.2771	1.2762	1.2785
1.0000	–	–	–	–	–

the present system supports the view proposed by Eyring and Kincaid [17] according to which the ultrasonic velocity increases with decrease in free length, and vice versa. The pronounced decrease in L_f with x signifies the strong interaction between DMF and ethanol molecules. The variation of u with concentration, c, of DMF can be expressed as

$$\mathrm{d}u/\mathrm{d}c = -u/2[1/\rho(\mathrm{d}\rho/\mathrm{d}c) + 1/\beta(\mathrm{d}\beta/\mathrm{d}c)] \tag{4}$$

The data (Tables 1 and 2) indicate that β decreases as ρ increases along with the concentration. The term $1/\beta(\mathrm{d}\beta/\mathrm{d}c)$ is greater than $1/\rho(\mathrm{d}\rho/\mathrm{d}c)$, $\mathrm{d}u/\mathrm{d}c$ is positive and hence u increases with the concentration of DMF which is in good agreement with the results reported for water–formamide [6] and aniline–alcohol [16] binary mixtures. The decrease in u with temperature is manifested in the increase in L_f.

As expected, the adiabatic compressibility, β, decreases while relative association, R_A, increases with increase in x (Table 2), suggesting interaction between DMF and ethanol molecules. Such trends in the variations of β and R_A have also been reported by others [16, 18] during ultrasonic study of binary mixtures. The added DMF tends, for one thing, to occasion breaking of associates present in the ethanol molecules with a consequent increase in β and L_f and a decrease in R_A. But, because of simultaneous formation of strong hydrogen bonding between the unlike molecules there is a compensating effect resulting in an overall decrease in β and L_f, and a reverse trend in R_A with x is observed. The strong hydrogen bonding between DMF and ethanol molecules may be attributed to the presence of two unshared electron pairs on the oxygen atom of the C=O group of DMF represented by the two sp^2-hybridized orbitals. If one of these orbitals may be considered to be colinear with the –OH···O axis there is maximum interaction between the –OH group of ethanol and the oxygen atom of carbonyl group. This is because the dipole moment of the DMF–ethanol complex thus formed would be enhanced due to a moment induced by the –OH bond in the highly polarizable lone pair. The observed trends in the variations of β, L_f and R_A with x (Table 2) reinforce the above view. A similar explanation was suggested [19] in order to explain the hydrogen bonding between *n*-butanol and acetone–cyclohexanone. The strength of hydrogen bonding (C=O···HO–) between the oxygen atom of DMF and ethanol may be further enhanced by the nitrogen atom of DMF due to the following resonance structure of the DMF molecule,



as considered by Rajashekhar and Reddy [4] for the study of excess thermodynamic properties of DMF–water mixtures at 303.15 K. Furthermore, the existence of specific acid–base interaction between DMF and ethanol molecules can be assumed by considering ethanol as a Lewis acid and DMF as a Lewis base. Recently, Ho-Nam Tran [12] emphasized the importance of acid–base interaction between *tert*-butyl alcohol and DMF–dimethylacetamide in order to evaluate the interaction energy in alcohol-amide systems.

Perusal of Fig. 1 reveals that the viscosity, η decreases sharply with the increase in mole fraction of DMF up to $x \simeq 0.50$ then increases slightly, i.e., the quantity $d\eta/dc$ which is negative in the ethanol-rich region becomes less negative and finally slightly positive as the mole fraction of DMF in the mixture increases. This may be attributed to the breaking of associated structure of ethanol by DMF at lower DMF concentrations. As the mole fraction of DMF increases the formation of hydrogen bonds between DMF and ethanol molecules overrides the dissociative effect.

In the next part of the investigation the authors intend to deal with the excess thermodynamic properties such as β^E, L_f^E, V^E, η^E and G^{*E}. These properties have been evaluated using the following relationships:

$$\beta^E = \beta - [(1-x)\beta_1 + x\beta_2] \tag{5}$$

$$L_f^E = L_f - [(1-x)L_{f1} + xL_{f2}] \tag{6}$$

$$V^E = V - [(1-x)V_1 + xV_2] \tag{7}$$

$$\eta^E = \eta - [(1-x)\eta_1 + x\eta_2] \tag{8}$$

$$G^{*E} = RT[\ln \eta V - (1-x)\ln \eta_1 V_1 - x \ln \eta_2 V_2] \tag{9}$$

The molar volumes of the binary mixtures were calculated using the equation

$$V = [(1-x)M_1 + xM_2]/\rho \tag{10}$$

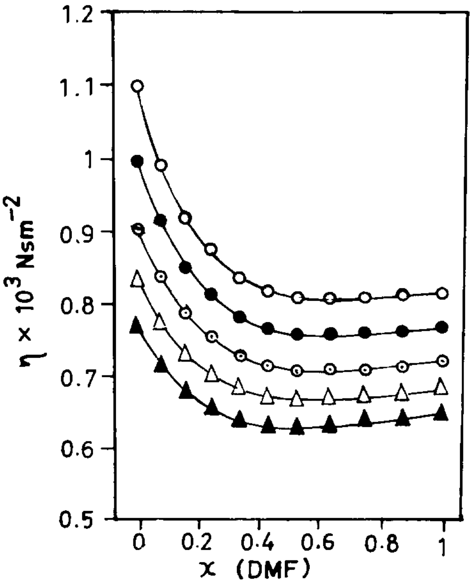


Fig. 1. Viscosity, η, as a function of mole fraction of DMF and temperature. (○) 298.15 K, (●) 303.15 K, (⊙) 313.15 K, (△) 308.15 K and (▲) 318.15 K.

where x, as mentioned earlier, is the mole fraction of DMF; M_1, the molecular weight of ethanol; M_2, the molecular weight of DMF; and suffixes 1 and 2 stand for ethanol and DMF, respectively. The variations in β^E, L_f^E, V^E, η^E and G^{*E} with mole fraction, x, of DMF are shown graphically in Figs. 2–6. The excess functions were fitted with the equation

$$Y^E = x(1-x)\sum_{i=1}^{n} A_i(1-2x)^{i-1} \tag{11}$$

where Y^E is β^E, L_f^E, V^E, η^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

$$\sigma(Y^E) = [\sum(Y^E_{obs} - Y^E_{cal})^2/(m-n)]^{1/2} \tag{12}$$

where m is the total number of data points and n is the number of coefficients considered ($n = 5$ in the present calculation), have been listed in Table 3.

The values of excess adiabatic compressibility, β^E and excess intermolecular free length, L_f^E are found to be negative (Figs. 2 and 3) over the entire range of mole fraction of DMF, indicating the presence of AB-type interactions [20]. Negative excess adiabatic compressibilities have also been reported for *tert*-butanol–water [21], *n*-butanol–cyclohexane, acetone and choloroform [19] and mixtures of *iso*-propyl, *iso*-amyl and *n*-butylalcohol with aniline [16]. The pronounced minimum in β^E and also in L_f^E at $x \simeq 0.35$ may be attributed to strong AB-type interaction which eventually results in complexation [6]. As the temperature of the mixtures increases there is partial breaking of DMF-ethanol interactions making β^E and L_f^E more negative.

The negative values of excess volume, V^E, like β^E and L_f^E, over the whole composition range (Fig. 4) further support the presence of AB-type interactions. Negative V^E values reported for DMF–toluene, bromobenzene [22] and DMF–water [4] reinforce the above view. Although a major part of the negative contribution may be attributed to the formation of hydrogen bonds and specific acid–base interactions between DMF and ethanol molecules, there may be another source of negative contribution due to the different sizes and shapes of the component molecules of the mixtures. The molar volumes of DMF and ethanol at 298.15 K are 7.74×10^{-5} and 5.86×10^{-5} m^3 mol^{-1}, respectively, which might allow the component molecules to fit into each others' structures thereby reducing the volume of the mixture. Assarson and Eirich [23] explained the negative volume change for DMF–water mixtures by assuming that small water molecules occupy the void space available in DMF. A similar explanation for the negative excess volume for mixtures of *N*,*N*-dimethylacetamide or *N*,*N*-dimethylmethanesulfonamide with aliphatic alcohols has also been proposed by Pikkarainen [24]. It is interesting to point out the common intersection in the excess molar volume at $x \simeq 0.53$, suggesting the temperature-independent nature of V^E at this unique composition of the mixture. The phenomenon of the common intersection in ultrasonic velocity (hence, adiabatic compressibility) and relative viscosity has been observed for aqueous solutions of amides [5] and NaI–water–formamide and or DMF [25] systems. Endo [26] has argued that this phenomenon is due to the clathrate formation. However, the evidence of clathrate formation corresponding to the concentration of common intersection has been questioned [5].

Table 3
Coefficients A_i of Eq. (11) and standard deviations $\sigma(Y^E)$ for excess functions of binary mixtures at various temperatures

T/K	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
			$\beta^E/(m^2\,N^{-1})$			
298.15	−3.5803	−1.2772	−1.5213	−0.9602	−1.7613	0.0110
303.15	−3.9822	−1.7040	−0.6221	−0.7036	−0.4346	0.0119
308.15	−3.9792	−1.7515	−2.0428	−0.2186	1.8387	0.0248
313.15	−3.9325	−1.5384	−4.0831	−0.1565	6.5115	0.0070
318.15	−4.2720	−1.0009	−2.6795	−2.1863	3.1202	0.0124
			L_f^E/m			
298.15	−1.0672	−0.3062	−0.4948	−0.3482	0.7111	0.0041
303.15	−1.1559	−0.4595	−0.1632	−0.1948	−0.0603	0.0042
308.15	−1.1716	−0.4567	−0.6486	−0.0338	0.6784	0.0089
313.15	−1.1402	−0.3567	−1.3284	−0.0869	2.2630	0.0025
318.15	−1.2244	−0.1419	−0.9681	−0.8046	1.3194	0.0049
			$V^E/(m^3\,mol^{-1})$			
298.15	−1.0628	−1.6874	1.0848	2.1689	–	0.0065
303.15	−1.0260	−1.2792	1.1258	1.5530	–	0.0061
308.15	−1.0106	−0.9248	1.0800	0.8548	–	0.0056
313.15	−0.9929	−0.5579	1.1478	0.3028	–	0.0059
318.15	−0.9689	−0.1344	1.0801	−0.5156	–	0.0074
			$\eta^E/(N\,m^{-2}\,s)$			
298.15	−0.5863	−0.4074	−0.0293	−0.1315	−0.3596	0.0020
303.15	−0.4934	−0.3496	−0.0383	0.0158	−0.2016	0.0019
308.15	−0.4130	−0.2995	−0.0573	0.0685	−0.1020	0.0009
313.15	−0.3625	−0.2625	−0.0113	0.0314	−0.2079	0.0002
318.15	−0.3179	−0.2244	−0.0076	−0.0282	−0.1807	0.0001
			$G^{*E}/K\,J$			
298.15	−1.4685	−1.0604	−0.1119	−0.0368	−0.5275	0.0053
303.15	−1.3599	−0.9990	−0.1555	0.2917	−0.2373	0.0055
308.15	−1.2531	−0.9428	−0.2544	0.4014	0.0028	0.0026
313.15	−1.1954	−0.8984	−0.1610	0.2538	−0.3403	0.0011
318.15	−1.1394	−0.8277	−0.2062	−0.0331	−0.2367	0.0030

The expected negative values of excess viscosity, η^E over the entire range of mole fraction of DMF (Fig. 5) indicate that the dispersive forces are dominant [9, 20]. The value of η^E passes through a minimum at $x \simeq 0.35$ which suggests complex formation between DMF and ethanol molecules [23, 27]. It is observed that with the increase in temperature the value of η^E decreases indicating that the system under study tends towards ideal behaviour. The variation of excess free energy of activation of viscous flow, G^{*E}, with mole fraction of DMF and temperature has been displayed in Fig. 6 where a minimum is located at $x \simeq 0.35$. It is observed that all the values of G^{*E}

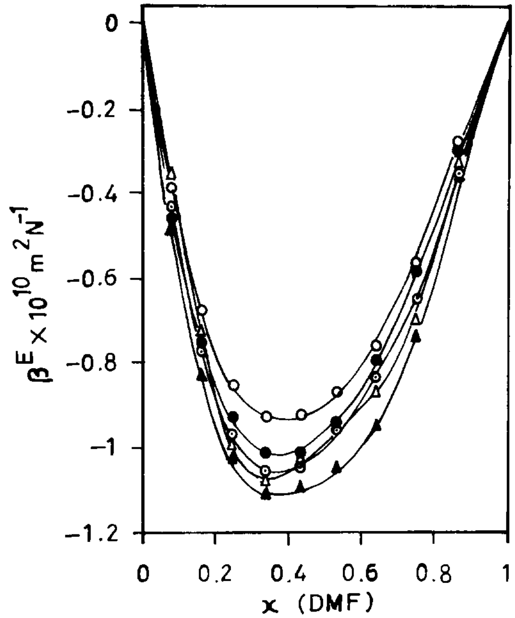


Fig. 2. Excess adiabatic compressibility, β^E, as a function of mole fraction of DMF and temperature. The symbols are the same as in Fig. 1.

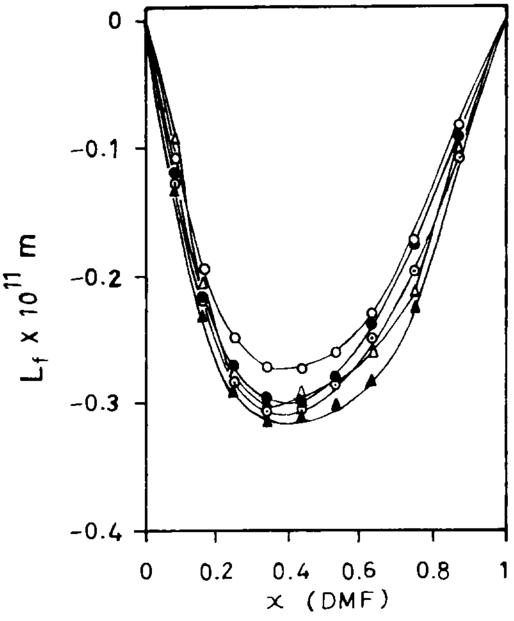


Fig. 3. Excess intermolecular free length, L_f^E, as a function of mole fraction of DMF and temperature. The symbols are the same as in Fig. 1.

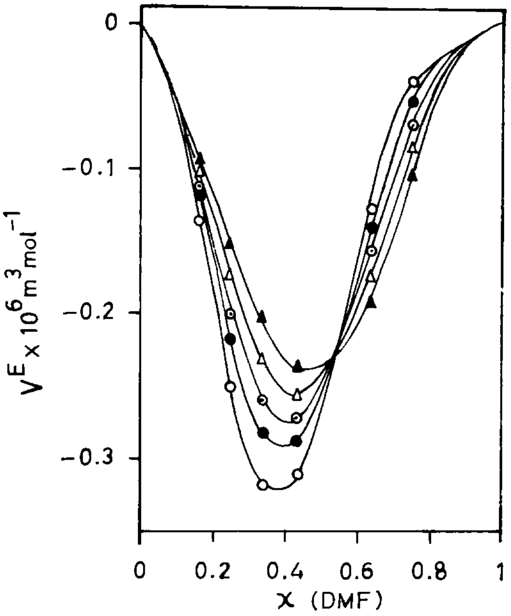


Fig. 4. Excess volume, V^E, as a function of mole fraction of DMF and temperature. The symbols are the same as in Fig. 1.

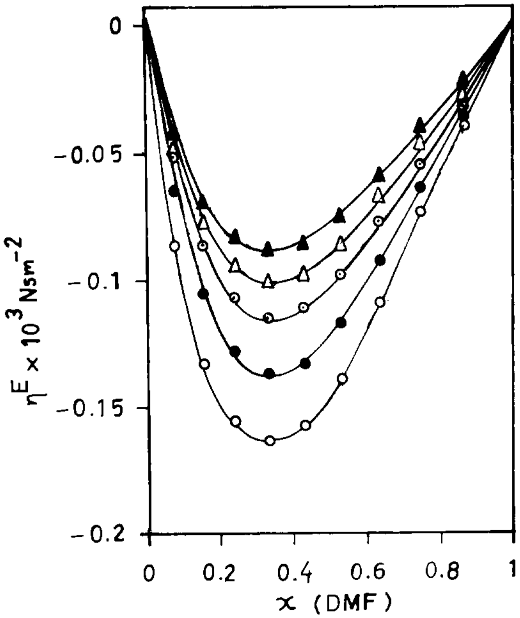


Fig. 5. Excess viscosity, η^E, as a function of mole fraction of DMF and temperature. The symbols are the same as in Fig. 1.

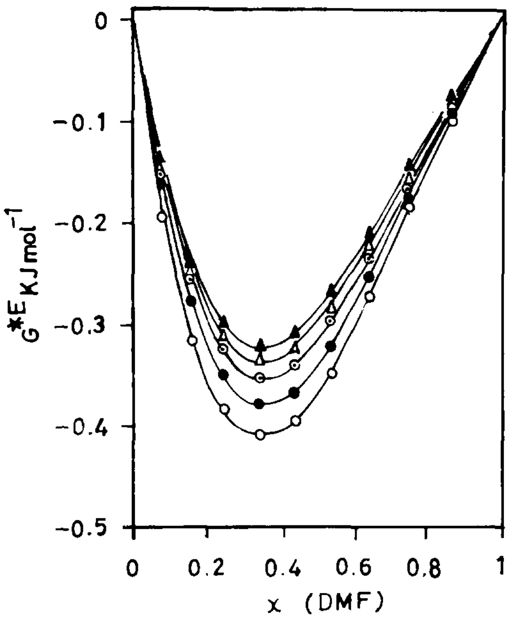


Fig. 6. Excess free energy of activation of viscous flow, G^{*E}, as a function of mole fraction of DMF and temperature. The symbols are the same as in Fig. 1.

are negative at the investigated temperatures. The negative values suggest the strong interaction between DMF and ethanol molecules. Similar trends in G^{*E} have also been reported for benzyl alcohol–isoamylalcohol [9] and 1,2-ethane diol–DMF [3] binary mixtures.

It is worth mentioning that the optimum concentration (in the present study, $x \simeq 0.35$) at which the excess functions exhibit minima indicates strong interaction between DMF and ethanol molecules, leading to the formation of a DMF–ethanol complex. Along this line of argument, we suggest a 2 (ethanol)–DMF–type complex where two ethanol molecules are associated strongly with the two unshared pairs of electrons on the carbonyl oxygen of DMF.

Furthermore, while studying the ultrasonic and excess properties of the DMF–ethanol system, it is equally useful to discuss the activation parameters of viscous flow. Eyring's viscosity equation [28],

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

when combined with

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

yields the equation

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

Table 4
Enthalpy, ΔH^*/(k J mol^{-1}); entropy, ΔS^*/(J mol^{-1} K^{-1}); and linear correlation factor, f, of viscous flow for binary mixtures from 298.15 to 318.15 K

x(DMF)	ΔH^*	ΔS^*	f
0.0000	13.3508	2.5600	0.9991
0.0777	12.1845	−0.7362	0.9996
0.1593	11.1951	−3.6044	0.9998
0.2452	10.6388	−5.2653	0.9997
0.3357	9.8837	−7.6543	0.9998
0.4312	9.5336	−8.6622	0.9999
0.5320	9.2186	−10.0619	0.9996
0.6388	8.9993	−11.0267	0.9998
0.7520	8.5138	−12.8988	0.9980
0.8721	8.6289	−12.7999	0.9990
1.0000	8.3942	−13.9127	0.9997

where h is Planck's constant, N the Avogadro number, R the gas constant, ΔG^* the free energy, ΔS^* the entropy and ΔH^* the enthalpy of activation of viscous flow. Plots of $R \ln(\eta V)$ against $1/T$ for each binary mixture were found to be linear, indicating that the ΔH^* values are constant in the temperature range 298.15 to 318.15 K.

The values of the slopes, ΔH^* and the intercepts, ΔS^* obtained from the above plots, together with the linear correlation factor, f of Eq. (15) are given in Table 4. The values of ΔH^* are positive and decrease with mole fraction of DMF. This indicates that the formation of activated species necessary for viscous flow appears quite easy in the DMF-rich region and becomes difficult as the ethanol mole fraction increases. The values of ΔS^* are found to decrease and become more negative as the mole fraction of DMF in the mixture increases. This suggests that during viscous flow the liquid is more structured, as a result of the formation of activated species, than it is in the initial state. Similar trends in the variation of ΔH^* and ΔS^* have also been reported [3] for 1,2-ethanediol–DMF binary mixtures.

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