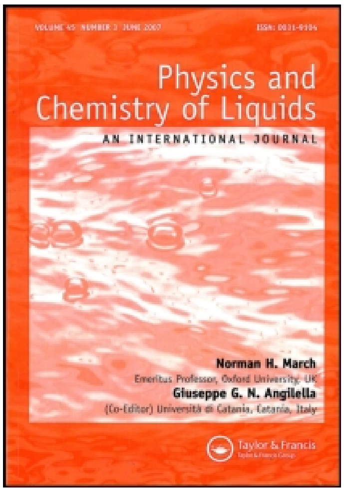

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STUDY OF INTERMOLECULAR INTERACTION IN DIMETHYLSULPHOXIDE + 1-ALKANOLS (1-BUTANOL, 1-HEXANOL, 1-OCTANOL) AT 303.15 K

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The ultrasonic velocity, u, viscosity, η, and density, ρ of dimethylsulphoxide (DMSO), 1-butanol, 1-hexanol, 1-octanol, and of their binary mixtures, where DMSO is common component, have been measured at 303.15 K. From the experimental data, excess isentropic compressibility, K_s^E, excess intermolecular free length, L_f^E, excess velocity, u^E, excess acoustic impedance, Z^E, excess viscosity, η^E, excess free energy of activation of viscous flow, G^{*E}, and excess rheochore, $[R^E]$ have been calculated. The behaviours of excess functions with composition of the mixtures suggest that the structure-breaking effect dominates over the interaction effect between the component molecules. Furthermore, the experimental values of u and η were fitted by empirical equations stating their dependence on composition of the mixtures. The experimental values of u have been compared with those calculated by using Nomoto and Van Dael relations.

Keywords: Ultrasonic velocity; viscosity; excess functions; binary mixtures; molecular interactions

1. INTRODUCTION

The studies of molecular interactions in mixed solvent systems is of great significance owing to the practical applications of these systems

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in various technologies, as they provide a wide choice of solutions with appropriate properties. In continuation of our earlier work on the study of intermolecular interaction in non-aqueous binary liquid mixtures [1 – 3], we report the results of the ultrasonic and viscosity study of molecular interactions in DMSO + 1-butanol, + 1-hexanol, and + 1-octanol mixtures at 303.15 K covering the whole composition range (expressed in terms of the mole fraction, x of DMSO). DMSO is a versatile compound, especially in its wide range of applicability as solvent, plasticizer, chemical intermediate, and in biological processes involving both plants and animals [4]. It is highly polar, strongly associated aprotic solvent due to S$=$O group in the molecule [5, 6]. It has a large dipole moment and dielectric constant ($\mu = 3.96\,\mathrm{D}$ and $\varepsilon = 46.6$ at 298.15 K) [7]. Alkanols, on the other hand, have relatively low values of dipole moment and dielectric constant, yet self associated through hydrogen bonding [7]. DMSO + 1-alkanols will be interesting binary solvent systems for the study of intermolecular interactions as both the component liquids (DMSO and 1-alkanol) are also used in the process of extraction for many metal ions, *viz*., uranium (VI), thorium (IV), actinides, lanthanides and various other metals [3]. Therefore, a deeper knowledge of the solution properties of DMSO + 1-alkanols mixtures will be important in providing a better understanding of many chemical and biological processes in these media.

The experimental values of u, η, and ρ of pure DMSO, 1-butanol, 1-hexanol, 1-octanol, and those of their binary mixtures have been used to compute the values of K_s^E, L_f^E, u^E, Z^E, η^E, G^{*E}, and $[R^E]$ as a function of the mole fraction, x of DMSO. The significance of these parameters has been emphasized in understanding the interactions between DMSO and 1-alkanol molecules.

2. EXPERIMENTAL

DMSO, 1-butanol, 1-hexanol, and 1-octanol (all of analytical grade) were purified as described in the literature [8, 9]. All the chemicals were stored over molecular sieve type 4A to remove any trace of water, and degassed just before use.

The ultrasonic velocities of pure liquids and their mixtures were measured using single crystal variable path interferometer at 3 MHz by the method of Subrahmanyam and Murthy [10] with an accuracy of ±0.02%. Viscosities were determined using Cannon Ubbelhode viscometer [11]. The densities were measured using a single-capillary pyknometer made of Pyrex glass (capacity $15 \times 10^{-6}\,m^3$) with a graduated stem of about $5 \times 10^{-8}\,m^3$ divisions. The marks on the stem were calibrated with deionised double distilled water with an accuracy of 3 parts per 10^5. All the masses were measured by an electric balance precisely up to 0.0001 gm. The temperature of the test liquids and their mixtures was maintained to an accuracy of ± 0.01°C in a thermostatic water bath. The experimental values of ultrasonic velocities, viscosities and densities of pure liquids at 298.15/303.15 K were found to be in close agreement with those reported in the literature [9, 12, 13].

3. RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity, u, viscosity, η and density, ρ of pure liquids and their binary mixtures as a function of the mole fraction, x of DMSO at 303.15 K are given in Table I. The derived parameters from ultrasonic velocity and viscosity such as isentropic compressibility, K_s, intermolecular free length, L_f, acoustic impedance, Z, and rheochore, $[R]$, were obtained using the standard relations [2, 14].

Excess properties such as $K_s^E, L_f^E, u^E, Z^E, \eta^E, G^{*E}$, and $[R^E]$ have been calculated by using the general equation

$$Y^E = Y_{\text{mixture}} - [xY_1 + (1-x)Y_2] \tag{1}$$

where Y_1 is the property (K_s, L_f, Z, u, η, G^*, and $[R]$) for DMSO and Y_2 is the same property for the other components; x is the mole fraction of DMSO. All the excess properties were fitted to a Redlich-Kister type equation

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

The values of the coefficients A_i evaluated by the method of least-squares are given in Table II along with the standard deviations $\sigma(Y^E)$. The variations in $K_s^E, L_f^E, u^E, Z^E, \eta^E, G^{*E}$, and $[R^E]$ with mole fraction, x of DMSO are shown graphically in Figures 1–7. The

TABLE I Ultrasonic velocities, u, viscosities, η and densities, ρ of binary mixtures at 303.15 K

x (DMSO)	u ($m s^{-1}$)	η ($10^{-3} kg m^{-1} s^{-1}$)	ρ ($kg m^{-3}$)
	DMSO + 1-Butanol		
0.0000	1232.0	2.1205	802.0
0.1941	1262.8	1.6983	847.5
0.3691	1296.2	1.5276	892.2
0.5276	1328.1	1.4975	935.7
0.6718	1363.2	1.5058	978.4
0.8037	1402.1	1.5432	1021.0
0.9297	1448.8	1.6716	1065.9
1.0000	1490.9	1.7004	1094.9
	DMSO + 1-Hexanol		
0.0000	1282.0	3.8068	811.8
0.1907	1311.1	2.8313	848.4
0.3639	1332.5	2.2879	888.1
0.5220	1356.5	2.0885	932.1
0.6669	1379.2	1.8982	974.9
0.8002	1405.1	1.7392	1016.9
0.9231	1450.5	1.7223	1061.1
1.0000	1490.9	1.7004	1094.9
	DMSO + 1-Octanol		
0.0000	1329.0	6.5132	817.5
0.1888	1334.2	4.2667	843.0
0.3612	1348.6	3.2957	875.3
0.5190	1366.5	2.5932	933.3
0.6642	1385.6	2.2596	996.7
0.7982	1412.1	1.9646	1035.2
0.9223	1450.2	1.7567	1071.0
1.0000	1490.9	1.7004	1094.9

non-linear decrease or increase of u, K_s, L_f, Z, and η values with the change in composition of the mixture in each system indicate the presence of molecular interaction [15].

The variation of u through the mixtures depends on the increase or decease of L_f. The observed increase in u and corresponding decrease in L_f with x in the present systems is in accordance with the view proposed by Eyring and Kincaid [16].

It may qualitatively be explained that mixing of DMSO with 1-alkanols will induce (i) the breaking up of hydrogen bonds (in the 1-alkanols) and loss of dipolar association (in DMSO molecules), (ii) the possibility of formation of hydrogen bond between S = O group of DMSO and —OH group of alkanols (>S=O----H—O—), dipole–dipole interaction between unlike molecules, and interstitial

TABLE II Coefficients A_i of Equation 2 and standard deviations $\sigma(Y^E)$ of binary mixtures at 303.15 K

Y^E	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
			DMSO + 1-Butanol			
K_s^E $(10^{-11}\,m^2\,N^{-1})$	0.1602	−5.0033	−2.6172	1.3040	17.0755	0.0040
L_f^E $(10^{-12}\,m)$	3.0260	−2.6569	−0.1275	−0.1677	6.6015	0.0012
u^E $(m\,s^{-1})$	−163.21	98.6422	61.5148	−6.6267	−306.76	0.0255
Z^E $(10^5\,kg\,m^{-2}\,s^{-1})$	−3.4330	1.5980	0.7198	0.0735	−4.0890	0.0014
η^E $(10^{-3}\,kg\,m^{-1}\,s^{-1})$	−1.5525	−0.8021	−2.1649	0.6968	3.6859	0.0006
G^{*E} $(kJ\,mol^{-1})$	−2.2659	−0.7331	−2.1276	0.4124	4.4095	0.0009
$[R^E]$ $(m^3(kg\,m^{-1}\,s^{-1})^{1/8})$	−4.3413	−2.3601	−3.8009	0.5837	8.2773	0.0019
			DMSO + 1-Hexanol			
K_s^E $(10^{-11}\,m^2\,N^{-1})$	3.4932	−3.5840	18.4198	−16.1326	−27.3021	0.0026
L_f^E $(10^{-12}\,m)$	3.6461	−2.0886	8.8058	−7.4870	−11.8959	0.0010
u^E $(m\,s^{-1})$	−124.71	101.78	−250.81	181.91	307.83	0.0075
Z^E $(10^5\,kg\,m^{-2}\,s^{-1})$	−3.3088	1.1363	−3.0002	2.8670	2.7785	0.0045
η^E $(10^{-3}\,kg\,m^{-1}\,s^{-1})$	−2.5608	−1.9053	−3.2336	2.1687	5.0832	0.0012
G^{*E} $(kJ\,mol^{-1})$	−1.5859	−1.1130	−3.3879	2.5676	6.3872	0.0005
$[R^E]$ $(m^3(kg\,m^{-1}\,s^{-1})^{1/8})$	−9.2173	−3.1358	−6.4007	4.1105	13.2212	0.0015
			DMSO + 1-Octanol			
K_s^E $(10^{-11}\,m^2\,N^{-1})$	11.5431	15.6263	12.4487	−26.1214	−14.4300	0.0057
L_f^E $(10^{-12}\,m)$	6.6562	5.8426	4.7985	−11.4433	−4.8547	0.0020
u^E $(m\,s^{-1})$	−190.39	92.4367	−46.1191	28.5633	−145.11	0.0224
Z^E $(10^5\,kg\,m^{-2}\,s^{-1})$	−3.8859	−2.2804	−0.7142	5.0903	0.7949	0.0065
η^E $(10^{-3}\,kg\,m^{-1}\,s^{-1})$	−5.7738	−1.9188	0.2787	−4.1418	−5.8436	0.0012
G^{*E} $(kJ\,mol^{-1})$	−1.7736	−0.7651	−0.1064	1.1523	−0.5273	0.0018
$[R^E]$ $(m^3(kg\,m^{-1}\,s^{-1})^{1/8})$	−19.8105	15.5184	13.3797	−32.3592	−34.5214	0.0082

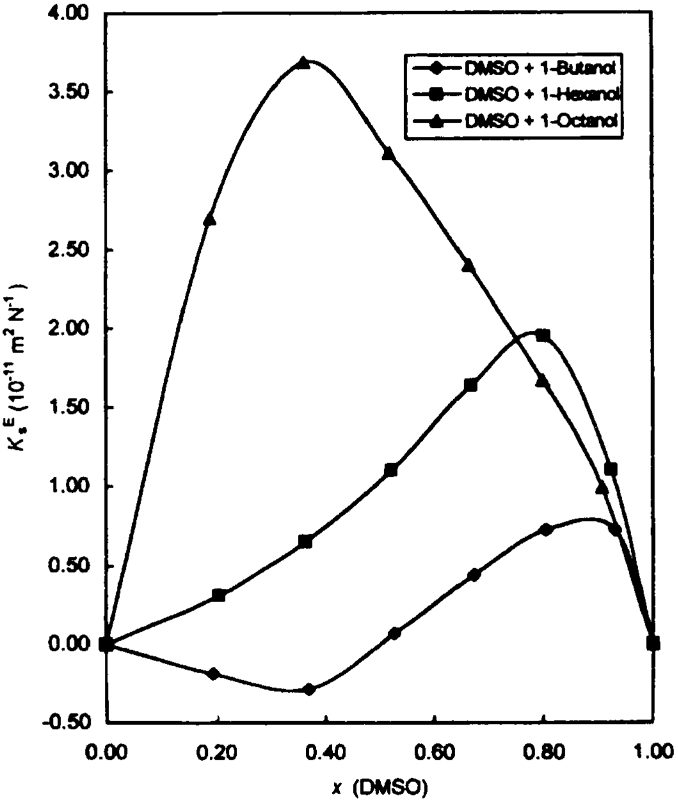

FIGURE 1 Variation of K_s^E against x (DMSO) of binary mixtures at 303.15 K.

accommodation of component molecules into each other's structure. The first effect leads to an increase in excess functions, while the second effect tends to decrease the excess functions. The observed positive values of K_s^E for DMSO + 1-hexanol and DMSO + 1-octanol and also the positive values of L_f^E for DMSO + 1-butanol, + 1-hexanol, and + 1-octanol systems over the whole composition range suggest that the rupture of hydrogen bonded chains of the alkanols and the loosening of the dipolar interactions between the DMSO molecules exceeds the interactions (hydrogen bond and dipole–dipole) between unlike molecules. K_s^E values for DMSO + 1-butanol system change from negative to positive with increase in mole fraction of DMSO. This is attributed to the decrease in the strength of interaction between

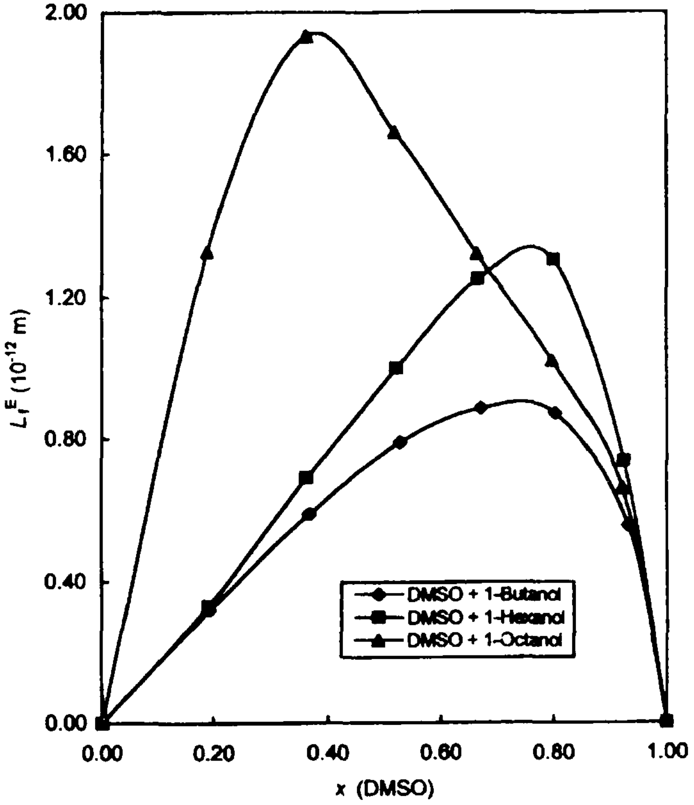

FIGURE 2 Variation of L_f^E against x (DMSO) of binary mixtures at 303.15 K.

unlike molecules, as suggested by Fort and Moore [15]. The curves in Figures 1 and 2 show that the values of K_s^E and L_f^E become increasingly positive and the maxima of these curves shift from DMSO-rich region to the alkanol-rich region as the carbon chain length increases from 1-butanol to 1-octanol. This is due to the fact that increasing the chain length of the alkanols (hence, decreasing the strength of hydrogen bond [5]) facilitates the disruption of associated structures in alkanols on the addition of DMSO. It is therefore expected that K_s^E and L_f^E should increase in the order: 1-octanol > 1-hexanol > 1-butanol, and consequently the positions of the maxima in the curves (Figs. 1 and 2) should shift from the DMSO-rich region (1-butanol) to the alkanol-rich region (1-octanol).

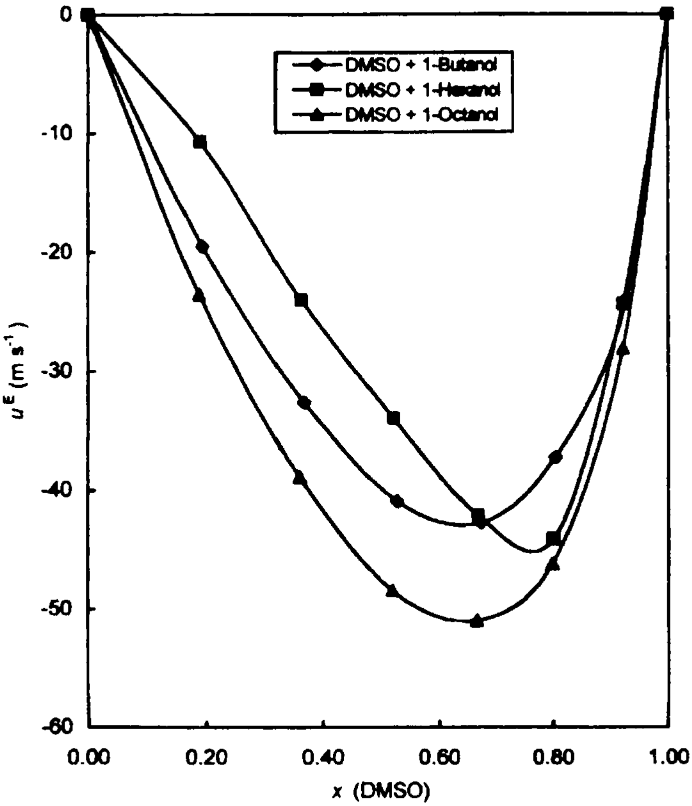

FIGURE 3 Variation of u^E against x (DMSO) of the binary mixtures at 303.15 K.

The variation of excess velocity, u^E and excess specific acoustic impedance, Z^E with mole fraction, x of DMSO are represented in Figures 3 and 4. respectively. The behaviour of u^E curves are similar to that of Z^E curves both exhibit negative deviation throughout the mole fraction range; and in general, the deviation becomes more negative as the length of carbon chain of alkanols increases. Negative deviations in Z^E values show weak interaction between the component molecules and, as expected, this interaction decreases with increase in carbon chain length from 1-butanol to 1-octanol. Similar behaviour in Z^E with composition was also reported for DMSO + toluene [3] and DMSO + isobutylmethyl ketone [17] binary mixtures. The observed negative deviations of Z^E curves (Fig. 4), where $Z = u\rho$, and an opposite

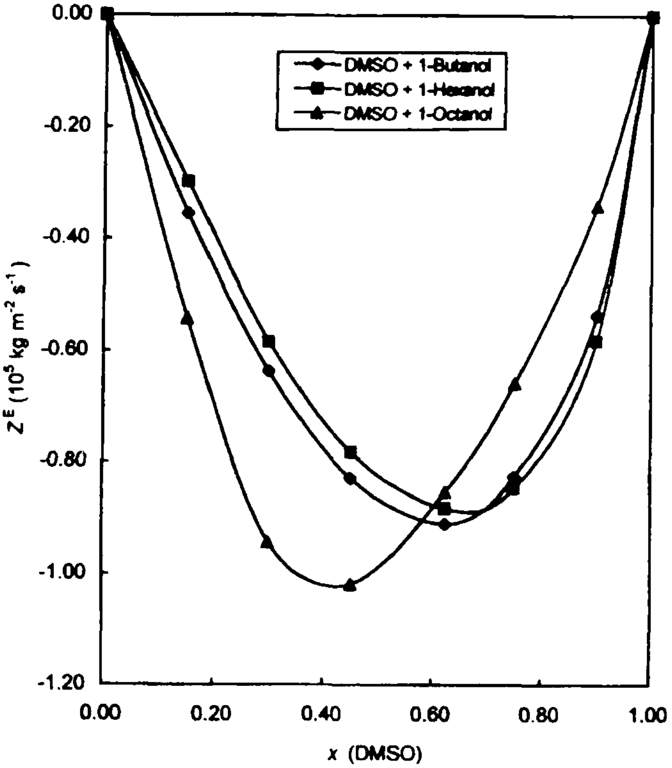

FIGURE 4 Variation of Z^E against x (DMSO) of binary mixtures at 303.15 K.

behaviour in K_s^E curves (Fig. 1), where $K_s = 1/u^2\rho$, over the entire composition range of the systems investigated reinforce our view that the structure-breaking effect and weak interactions between unlike molecules predominates in all the DMSO + 1-alkanol (1-butanol, 1-hexanol, and 1-octanol) systems.

The excess viscosity, η^E, values are negative over the entire range of mole fraction of DMSO (Fig. 5) for all three systems investigated. According to Fort and Moore [18], negative values of excess viscosity are observed for the systems of different molecular size in which the dispersion forces are dominant. The negative deviations in η^E reported for DMSO + acetonitrile, + methanol [18], and + isopropanol [19] systems were also explained by considering the differences in molecular size of the component liquids. The excess free energies of activation of

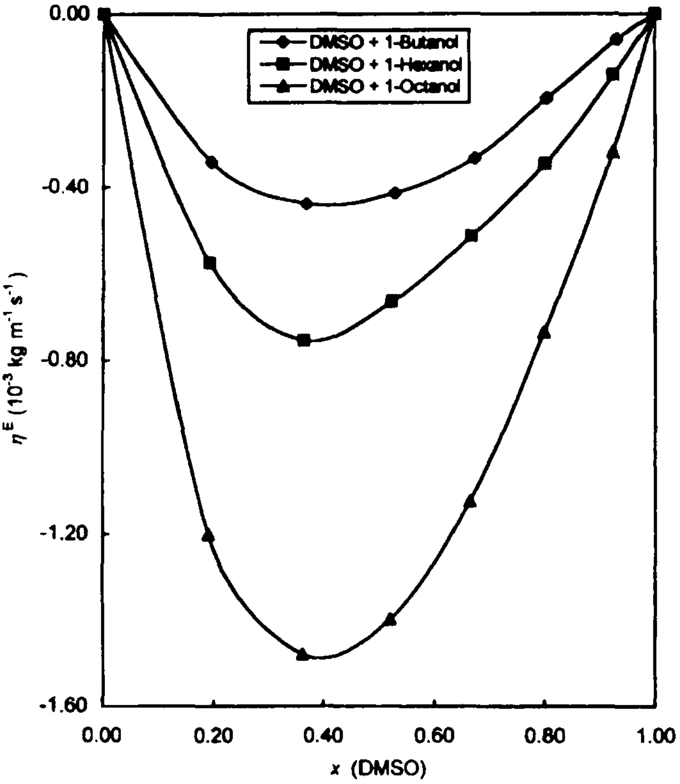

FIGURE 5 Variation of η^E against x (DMSO) of binary mixtures at 303.15 K.

viscous flow, G^{*E}, like η^E, are negative throughout the mole fraction range (Fig. 6). Some authors [20, 21] pointed out that excess free energy of activation may be considered a reliable parameter to study the presence of intermolecular interactions in liquid mixtures. Negative G^{*E} values indicate that dispersion forces are prevailing in the mixtures, as suggested by Garcia *et al.* [22]. Thus, the observed variation of G^{*E} with x supports the behaviour of η^E, suggesting that dispersion forces are operative between unlike molecules of the binary mixtures under study.

It is interesting to consider the rheochore excess function, $[R^E]$, which is very sensitive to intermolecular interactions. Figure 7 shows the variation of $[R^E]$ with x. These curves indicate that the values of

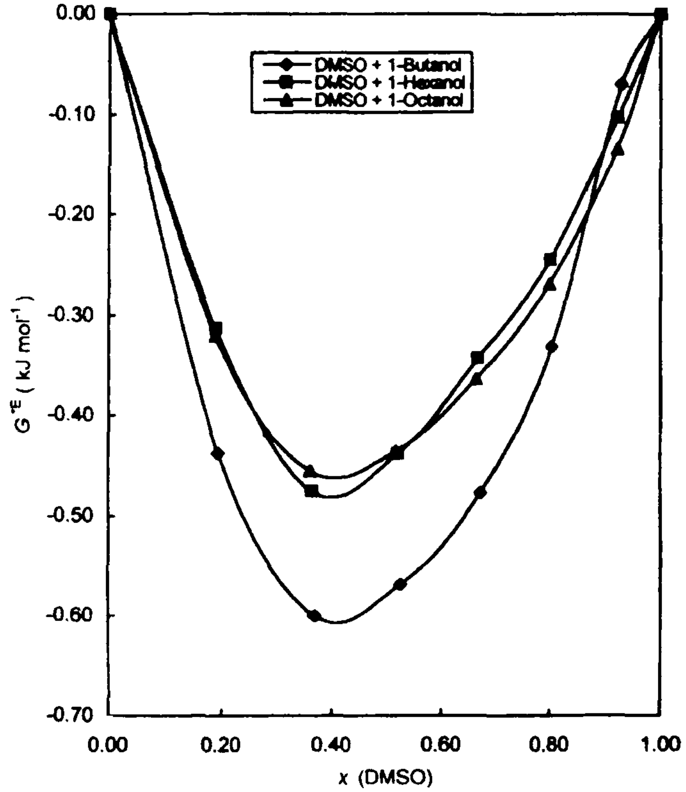

FIGURE 6 Variation of G^{*E} against x (DMSO) of binary mixtures at 303.15 K.

$[R^E]$ are negative over the entire range of mole fraction and tend to become more negative as the carbon chain length of alkanol increases from 1-butanol to 1-octanol. As suggested earlier, addition of DMSO to 1-alkanols disrupts the hydrogen bonded structure of higher alkanol (1-octanol) more easily than that of lower alkanol (1-butanol), releasing more free dipoles. Consequently, the intermolecular hydrogen bonding and/or dipole–dipole interactions are not sufficient to override the negative contributions (due to disruption of associated structures of liquids) to $[R^E]$ which is more pronounced in case of DMSO + 1-octanol mixtures. Such trend in the behaviour of $[R^E]$ with x has also been reported for N,N-dimethylformamide + 1,2-ethanediol binary mixtures [14].

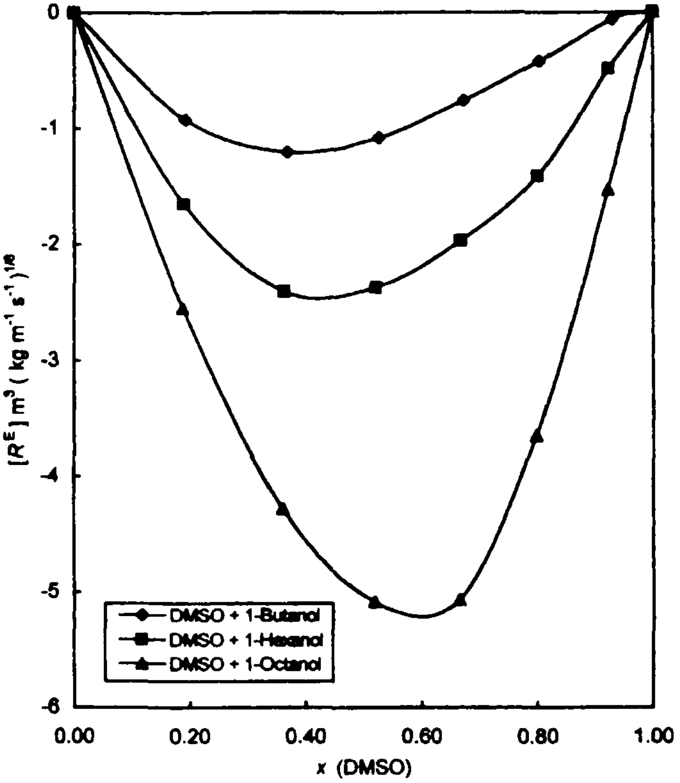

FIGURE 7 Variation of $[R^E]$ against x (DMSO) of binary mixtures at 303.15 K.

In order to establish the dependence of u on the composition of the binary mixtures, a polynomial equation of the type

$$\ln u = \sum_{i=1}^{5} \ln u_i x^{i-1} \tag{3}$$

was used to fit the experimental data. The coefficients $\ln u_i$, evaluated by means of the least squares method, along with the standard deviations $\sigma(\ln u)$ at 303.15 K for each binary mixture are presented in Table III. The goodness of this fit equation is ascertained by the magnitude of standard deviations given in the table. The dependence of η on the composition of the binary mixtures under study was

TABLE III Coefficients $\ln u_i$ and $\ln \eta_i$ of Equations 3 and 4 along with standard deviations $\sigma(\ln u)$ and $\sigma(\ln \eta)$ of binary mixtures at 303.15 K

		DMSO + 1-Butanol			
$\ln u_1$	$\ln u_2$	$\ln u_3$	$\ln u_4$	$\ln u_5$	$\sigma(\ln u) \times 10^5$
7.1164	0.0956	0.2140	−0.3607	0.2469	3.203
$\ln \eta_1$	$\ln \eta_2$	$\ln \eta_3$	$\ln \eta_4$	$\ln \eta_5$	$\sigma(\ln \eta) \times 10^5$
0.7516	−1.5038	2.0160	−0.9486	0.2219	2.934
		DMSO + 1-Hexanol			
$\ln u_1$	$\ln u_2$	$\ln u_3$	$\ln u_4$	$\ln u_5$	$\sigma(\ln u) \times 10^5$
7.1564	0.0987	0.1188	−0.3416	0.2746	7.778
$\ln \eta_1$	$\ln \eta_2$	$\ln \eta_3$	$\ln \eta_4$	$\ln \eta_5$	$\sigma(\ln \eta) \times 10^5$
1.3389	−2.0525	2.7369	−2.6259	1.1356	0.672
		DMSO + 1-Octanol			
$\ln u_1$	$\ln u_2$	$\ln u_3$	$\ln u_4$	$\ln u_5$	$\sigma(\ln u) \times 10^5$
7.1924	−0.0390	0.3958	−0.6115	0.3690	6.576
$\ln \eta_1$	$\ln \eta_2$	$\ln \eta_3$	$\ln \eta_4$	$\ln \eta_5$	$\sigma(\ln \eta) \times 10^5$
1.8732	−2.6750	2.9264	−2.7576	1.1605	0.194

checked by using a similar polynomial equation

$$\ln \eta = \sum_{i=1}^{5} \ln \eta_i x^{i-1} \tag{4}$$

The results of this fit equation are also included in the Table III along with the standard deviations $\sigma(\ln \eta)$ at 303.15 K for each binary mixture. The standard deviations given in the table suggest the usefulness of Equation 4. The significance of data fitting using similar polynomials in reproducing the experimental values of η and ρ has also been reported for binary mixtures [14].

The theoretical values of ultrasonic velocity in the systems: DMSO + 1-butanol, + 1-hexanol, and + 1-octanol were evaluated using the following empirical equations:

Nomoto equation [23]:

$$u = [(xR_1 + (1 - x)R_2)/(xV_1 + (1 - x)V_2)]^3 \tag{5}$$

Van Dael [24]:

$$1/u^2 = [(1/u_1^2 M_1) + (1/u_2^2 M_2)][xM_1 + (1 - x)M_2] \tag{6}$$

where R_1, R_2 and V_1, V_2 are the Rao's constants [25] and molar volumes of DMSO and 1-alkanol, respectively. The calculated and

TABLE IV Theoretical values of ultrasonic velocity calculated from Nomoto relation and Van Dael equation along with the experimental ultrasonic velocity and percentage error for the binary systems at 303.15 K

x (DMSO)	*u* (ms^{-1})			*% error*	
	Expt	*NOM*	*VD*	*NOM*	*VD*
		DMSO + 1-Butanol			
0.0000	1232.0	1232.0	1232.0	0.00	0.00
0.1941	1262.8	1270.4	1269.8	0.60	0.55
0.3691	1296.2	1309.0	1307.8	0.99	0.90
0.5276	1328.1	1347.8	1346.3	1.48	1.37
0.6718	1363.2	1386.6	1385.1	1.72	1.61
0.8037	1402.1	1425.7	1424.4	1.68	1.59
0.9297	1448.8	1466.5	1465.8	1.22	1.18
1.0000	1490.9	1490.9	1490.9	0.00	0.00
		DMSO + 1-Hexanol			
0.0000	1282.0	1282.0	1282.0	0.00	0.00
0.1907	1311.1	1305.5	1315.9	0.42	0.37
0.3639	1332.5	1331.2	1348.8	0.10	1.23
0.5220	1356.5	1359.4	1380.8	0.21	1.79
0.6669	1379.2	1390.4	1411.9	0.82	2.37
0.8002	1405.1	1424.8	1442.2	1.40	2.64
0.9231	1450.5	1463.0	1471.6	0.86	1.46
1.0000	1490.9	1490.9	1490.9	0.00	0.00
		DMSO + 1-Octanol			
0.0000	1329.0	1329.0	1329.0	0.00	0.00
0.1888	1334.2	1343.8	1341.7	0.72	0.56
0.3612	1348.6	1360.7	1359.4	0.90	0.80
0.5190	1366.5	1380.4	1381.2	1.02	1.08
0.6642	1385.6	1403.5	1406.7	1.29	1.53
0.7982	1412.1	1431.1	1435.6	1.34	1.67
0.9223	1450.2	1464.4	1467.8	0.98	1.21
1.0000	1490.9	1490.9	1490.9	0.00	0.00

experimental ultrasonic velocities along with the percentage error in the calculated values are listed in Table IV. The results indicate that, for almost all three systems investigated, the Nomoto equation predicts the data well than the Van Dael equation. This is in accordance with the results reported by Mehta *et al.* [26] for pyrrolidin-2-one + alkanols (C_1-C_5) binary mixtures.

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