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# STUDY OF INTERMOLECULAR INTERACTIONS IN BINARY MIXTURES OF CYCLOHEXANE WITH 1-ALKANOLS AT 308 K

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Densities,  $\rho$ , viscosities,  $\eta$ , and ultrasonic speeds,  $u$ , of pure cyclohexane, cyclohexanol, 1-octanol, 1-decanol and those of their binary mixtures with cyclohexane, as a common component, were measured at 308 K over the entire composition range. These experimental data were used to calculate the values of isentropic compressibility,  $K_s$ , intermolecular free length,  $L_f$ , acoustic impedance,  $Z$ , relative association,  $R_A$ , molar sound speed,  $R_m$ , molecular association,  $M_A$ , excess volume,  $V^E$  and deviations in isentropic compressibility,  $\Delta K_s$ , viscosity,  $\Delta\eta$ , and ultrasonic speed,  $\Delta u$ , at all mole fractions of cyclohexane. These parameters, especially excess functions, are found to be quite sensitive towards the intermolecular interactions in liquid mixtures. Theoretical values of viscosities and ultrasonic speeds of the binary mixtures were calculated using different empirical relations and theories. The relative merits of these relations and theories were discussed.

*Keywords:* Ultrasonic speed; Viscosity; Alkanols; Excess properties; Intermolecular interactions

## 1. INTRODUCTION

In the technological, biological and industrial applications binary mixtures are frequently used as they provide a wide choice of solvents with appropriate compositions and properties, and such solvents also influence the rate of a reaction differently from those of pure solvents. Therefore, the study of intermolecular interactions in the binary liquid mixtures is of considerable importance. Although this field has been widely exploited, the basic processes are still relatively poorly understood at a detailed molecular level. In continuation of our series of investigations on intermolecular interaction in non-aqueous binary liquid mixtures [1–3], we report here the results of density,  $\rho$ , viscosity,  $\eta$ , and ultrasonic speed,  $u$ , in cyclohexane + cyclohexanol, cyclohexane + 1-octanol and cyclohexane + 1-decanol binary mixtures at 308 K over the whole composition range. Cyclohexane is aprotic, unassociated and has a globular structure [4], whereas cyclohexanol, 1-octanol and 1-decanol are protic and self associated through hydrogen bond [5]. The degree of association in alkanols containing cyclic alkyl group is very low due to steric factors [6]. A survey of the literature revealed

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that no work has been done on these binary mixtures from the point of view of their ultrasonic and viscometric behaviours.

The densities, viscosities and ultrasonic speeds of pure cyclohexane, cyclohexanol, 1-octanol, 1-decanol and those of their binary mixtures with cyclohexane, as common component, were measured at 308 K. From these data, various derived parameters such as isentropic compressibility,  $K_s$ , intermolecular free length,  $L_f$ , acoustic impedance,  $Z$ , relative association,  $R_A$ , molar sound speed,  $R_m$ , molecular association,  $M_A$ , excess volume,  $V^E$ , and deviations in isentropic compressibility,  $\Delta K_s$ , viscosity,  $\Delta\eta$ , and ultrasonic speed,  $\Delta u$ , were computed. The variations in these parameters with composition of the binary mixtures reveal the qualitative nature and extent of intermolecular interactions between the component molecules. This study will also provide a test of various empirical equations to correlate the viscosity data of binary mixtures with various interaction parameters. The viscosities were used to test the semi-empirical relations of Grunberg and Nissan [7], Katti and Chaudhri [8] and Heric [9]. Moreover, the ultrasonic speeds for all the binary mixtures were theoretically evaluated as a function of composition using free length theory (FLT) [10], Nomoto's empirical relation [11] and Van Dael and Vangeel ideal mixing relation [12]. The suitability of these theories and relations for the present liquid mixtures was checked.

## 2. EXPERIMENTAL

Cyclohexane, cyclohexanol (s.d. fine chemicals, India) purity >99%, 1-octanol and 1-decanol (E. Merck) purity >99% were used after further purification and drying by the standard procedures [13]. The mixtures were prepared by mixing known masses of pure liquids in air tight narrow mouthed stoppered bottles taking due precautions to minimise the evaporation losses. All the mass measurements were performed on an Afcoset ER-120-A electronic balance accurate to  $\pm 0.05$  mg. The probable error in mole fraction was estimated to be less than  $1.5 \times 10^{-4}$ . All the solutions were prepared in a dry box.

The densities of pure components and mixtures were measured by using a single stem pycnometer (made of pyrex glass) of bulb capacity  $8 \times 10^{-6}$  m<sup>3</sup> having a graduated stem with  $5 \times 10^{-8}$  m<sup>3</sup> divisions. The marks on the stem were calibrated using known densities of triple-distilled water. The ultrasonic speeds were measured using a single crystal variable path interferometer at 3 MHz by the method of Pradhan *et al.* [14]. The imprecision in ultrasonic speed was of the order of  $\pm 0.5$  ms<sup>-1</sup>. Viscosities were determined using Ubbelohde viscometer [15] calibrated with triple-distilled water. The viscometer containing the test liquids was allowed to stand for about 20 min in a thermostatic water bath in order to minimise thermal fluctuation. The overall experimental uncertainty was estimated to be  $\pm 1.5 \times 10^{-3}$ . The temperature of the test liquid was maintained to an accuracy of  $\pm 0.02$  K in an electronically controlled thermostatic water bath.

## 3. RESULTS AND DISCUSSION

The experimental values of density,  $\rho$ , viscosity,  $\eta$ , and ultrasonic speed,  $u$ , of pure liquids and their binary mixtures as a function of mole fraction  $x$  of cyclohexane at

TABLE I Experimental values of density,  $\rho$ , ultrasonic speed,  $u$ , and viscosity,  $\eta$ , for the binary mixtures at 308 K

$x$ (Cyclohexane)	$\rho$ ( $\text{kg m}^{-3}$ )	$u$ ( $\text{ms}^{-1}$ )	$\eta$ ( $10^{-3} \text{ N m}^{-2} \text{ s}$ )
<i>Cyclohexane + cyclohexanol</i>			
0.0000	937.9	1448.3	27.9502
0.1168	918.2	1405.1	10.6847
0.2322	898.6	1367.0	7.1432
0.3358	880.5	1336.4	4.9367
0.4443	860.9	1308.8	3.5099
0.5452	842.7	1283.7	2.4532
0.6483	824.1	1260.8	1.7158
0.7411	808.0	1243.1	1.3257
0.8311	792.6	1229.3	1.0493
0.9180	778.0	1218.0	0.8891
1.0000	764.4	1211.1	0.7836
<i>Cyclohexane + 1-octanol</i>			
0.0000	817.7	1319.7	5.2280
0.1494	810.0	1296.8	4.1342
0.2768	803.7	1279.2	3.3477
0.3962	797.8	1263.0	2.6585
0.5076	792.1	1249.4	2.0902
0.6146	786.4	1236.0	1.6402
0.7054	781.2	1227.0	1.3601
0.7911	776.4	1219.0	1.1321
0.8587	772.5	1213.7	0.9600
0.9354	767.9	1208.3	0.8280
1.0000	764.4	1211.1	0.7836
<i>Cyclohexane + 1-decanol</i>			
0.0000	819.8	1350.0	7.6462
0.0801	816.6	1339.5	6.9118
0.2421	810.0	1317.5	5.3970
0.3455	805.3	1303.0	4.4681
0.4703	799.1	1285.2	3.3964
0.5762	793.2	1268.0	2.5789
0.6347	789.7	1257.0	2.1405
0.7203	784.5	1243.5	1.7020
0.8752	773.5	1222.5	1.0612
0.9408	768.7	1215.6	0.8600
1.0000	764.4	1211.1	0.7836

308 K are given in Table I. The derived parameters such as  $K_s$ ,  $L_f$ ,  $Z$ ,  $R_A$ ,  $R_m$  and  $M_A$  were calculated using the following relations [1–3]:

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

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

$$Z = u \rho \tag{3}$$

$$R_A = (\rho/\rho_o)(u_o/u)^{1/3} \tag{4}$$

$$R_m = u^{1/3} V \tag{5}$$

$$M_A = [(u^2/u_{im}^2) - 1] \tag{6}$$

TABLE II Calculated values of isentropic compressibility,  $K_s$ , intermolecular free length,  $L_f$ , specific acoustic impedance,  $Z$ , relative association,  $R_A$ , molar sound speed,  $R_m$ , and molecular association,  $M_A$ , for the binary mixtures at 308 K

$x$ (Cyclohexane)	$K_s$ ( $10^{-10} \text{ m}^2 \text{ N}^{-1}$ )	$L_f$ ( $10^{-11} \text{ m}$ )	$Z$ ( $10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ )	$R_A$	$R_m$ [ $10^{-3} \text{ m}^3 \text{ mol}^{-1}$ ( $\text{ms}^{-1}$ ) $^{1/3}$ ]	$M_A$
<i>Cyclohexane + cyclohexanol</i>						
0.0000	5.0831	4.7205	1.3584	1.0000	1.2136	0.0000
0.1168	5.5163	4.9176	1.2902	0.9889	1.2037	-0.0003
0.2322	5.9552	5.1094	1.2284	0.9767	1.1953	-0.0017
0.3358	6.3591	5.2799	1.1767	0.9643	1.1894	-0.0036
0.4443	6.7811	5.4522	1.1267	0.9494	1.1854	-0.0040
0.5452	7.2011	5.6186	1.0818	0.9354	1.1818	-0.0076
0.6483	7.6336	5.7848	1.0390	0.9202	1.1790	-0.0108
0.7411	8.0090	5.9253	1.0044	0.9065	1.1766	-0.0121
0.8311	8.3489	6.0498	0.9743	0.8925	1.1750	-0.0103
0.9180	8.6641	6.1629	0.9476	0.8788	1.1738	-0.0074
1.0000	8.9191	6.2529	0.9258	0.8651	1.1736	0.0000
<i>Cyclohexane + 1-octanol</i>						
0.0000	7.0219	5.5482	1.0791	1.0000	1.7469	0.0000
0.1494	7.3412	5.6730	1.0504	0.9964	1.6606	0.0290
0.2768	7.6038	5.7735	1.0281	0.9931	1.5868	0.0440
0.3962	7.8578	5.8691	1.0076	0.9901	1.5172	0.0488
0.5076	8.0876	5.9543	0.9896	0.9865	1.4528	0.0479
0.6146	8.3238	6.0407	0.9720	0.9830	1.3908	0.0397
0.7054	8.5025	6.1052	0.9585	0.9788	1.3393	0.0319
0.7911	8.6678	6.1642	0.9464	0.9749	1.2904	0.0215
0.8587	8.7878	6.2067	0.9376	0.9715	1.2520	0.0123
0.9354	8.9196	6.2531	0.9279	0.9671	1.2086	0.0002
1.0000	8.9191	6.2529	0.9258	0.9620	1.1736	0.0000
<i>Cyclohexane + 1-decanol</i>						
0.0000	6.6931	5.4167	1.1067	1.0000	2.1333	0.0000
0.0801	6.8250	5.4699	1.0938	0.9987	2.0560	0.0490
0.2421	7.1124	5.5838	1.0672	0.9961	1.8989	0.1177
0.3455	7.3140	5.6624	1.0493	0.9940	1.7991	0.1414
0.4703	7.5763	5.7631	1.0270	0.9909	1.6789	0.1509
0.5762	7.8411	5.8629	1.0058	0.9880	1.5768	0.1403
0.6347	8.0143	5.9273	0.9927	0.9865	1.5200	0.1262
0.7203	8.2436	6.0115	0.9755	0.9835	1.4377	0.1036
0.8752	8.6505	6.1581	0.9456	0.9752	1.2913	0.0501
0.9408	8.8036	6.2123	0.9344	0.9710	1.2293	0.0240
1.0000	8.9191	6.2529	0.9258	0.9668	1.1736	0.0000

where  $\rho_o$ ,  $\rho$  and  $u_o$ ,  $u$  are the densities and ultrasonic speeds of solvent and solution, respectively,  $K$  is a temperature-dependent constant [10],  $V$  is the molar volume of the mixture and  $u_{im}$  is the ultrasonic speed of ideal mixture, obtained by the method given by Van Dael and Vangeel [12]. The variations of  $K_s$ ,  $L_f$ ,  $Z$ ,  $R_A$ ,  $R_m$  and  $M_A$  with  $x$  are presented in Table II.

It is obvious from Table II that  $K_s$  and  $L_f$  increase, while  $Z$ ,  $R_A$  and  $R_m$  decrease with increasing mole fraction  $x$  of cyclohexane for all the three systems under study. The increase in  $K_s$  and  $L_f$  while opposite trends in  $Z$ ,  $R_A$  and  $R_m$  with  $x$  reveal the presence of weak interactions between the component molecules of the mixtures. A qualitative explanation may be proposed. The addition of a diluent (cyclohexane) to the polar self-associated molecules of alkanols (cyclohexanol, 1-octanol and 1-decanol) may cause a progressive breaking up of the hydrogen bonds in alkanols if the diluent is

unable to form any complexes with the alkanol molecules [16]. The observed decrease in  $R_A$  supports the above view. Similar increase in  $K_s$  and  $L_f$  is also observed in *n*-butanol + cyclohexanol [16] binary mixtures wherein weak interaction between component molecules has been reported. The decrease in  $Z$  and  $R_m$  with increasing amount of cyclohexane in all the systems under study is in good agreement with the requirements given in Eqs. (3) and (4), as  $\rho$ ,  $u$  and  $V$  decrease with  $x$  (Table I).  $M_A$  is a measure of non-ideality of the system as a result of association/dissociation between the component molecules. The results (Table II) indicate that  $M_A$  is positive for the mixtures with 1-octanol and 1-decanol, which may be due to the existence of weak interaction between the component molecules [2]. An increasingly negative value of  $M_A$  for the mixtures with cyclohexanol suggests the presence of an appreciable interaction between cyclohexane and cyclohexanol molecules. Similar behaviours of  $M_A$  were also observed for DMA + hexanol/octanol [2] and pyrrolidin-2-one + alkanols (C<sub>1</sub>–C<sub>5</sub>) [17] binary mixtures.

The deviations in excess functions from ideality provide a relatively better tool to assess the strength of interaction between the component molecules of the binary mixtures.  $V^E$ ,  $\Delta K_s$ ,  $\Delta\eta$  and  $\Delta u$  were evaluated from the experimental data using the following relevant expressions:

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

$$\Delta K_s = K_s - [(1-x)K_{s1} + xK_{s2}] \quad (8)$$

$$\Delta\eta = \eta - [(1-x)\eta_1 + x\eta_2] \quad (9)$$

$$\Delta u = u - [(1-x)u_1 + xu_2] \quad (10)$$

where subscript 1 refers to cyclohexanol/1-octanol/1-decanol, subscript 2 refers to cyclohexane and absence of subscript refers to the mixtures. The variations of  $V^E$ ,  $\Delta K_s$ ,  $\Delta\eta$  and  $\Delta u$  with  $x$  were fitted to the Redlich–Kister [18] type polynomial equation by the method of least-squares, as given below:

$$Y^E = x(1-x) \sum_{i=1}^5 A_i (1-2x)^{i-1} \quad (11)$$

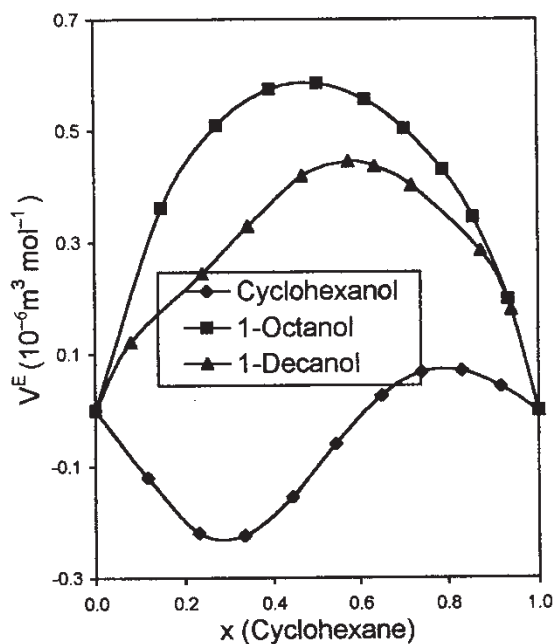
The  $A_i$  coefficients of Eq. (11) along with the standard deviations ( $Y^E$ ) are given in Table III. The variations of the above mentioned properties with  $x$  are presented graphically in Figs. 1–4.

Figures 1 and 2 show that  $V^E$  and  $\Delta K_s$  are positive for cyclohexane + 1-octanol and + 1-decanol binary mixtures over the whole composition range. For cyclohexane + cyclohexanol binary mixtures  $V^E$  and  $\Delta K_s$  show negative deviations in cyclohexanol-rich region and tend to change to positive values at higher mole fractions ( $x \gtrsim 0.60$ ) of cyclohexane.

The magnitude of  $V^E$  is the result of contributions from several effects [19]. The disruption of alkanol aggregates on the addition of cyclohexane due to the breaking up of hydrogen bonds in alkanols makes  $V^E$  positive. Positive  $V^E$  values are also attributed to the weak interaction between the component molecules. Apart from this, molecules of the components having nearly equal molar volumes do not fit well into each others' structures, thereby, resulting in positive  $V^E$  values. On the other

TABLE III Coefficients  $A_i$  of Eq. (11) along with standard deviations ( $\sigma$ ) for the binary mixtures at 308 K

Functions	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$\sigma(Y^E)$
<i>Cyclohexane + cyclohexanol</i>						
$V^E(10^{-6} \text{ m}^3 \text{ mol}^{-1})$	-0.4123	-1.9275	-0.1521	1.3854	0.5695	0.0077
$\Delta K_s(10^{-10} \text{ m}^2 \text{ N}^{-1})$	-0.0485	-0.5492	-0.5483	-0.0372	-0.2475	0.0031
$\Delta\eta(10^{-3} \text{ N m}^{-1} \text{ s}^{-1})$	-44.7095	-30.9609	-41.1395	-66.8300	-40.4080	0.0439
$\Delta u(10^2 \text{ m s}^{-1})$	-1.4142	0.0835	-0.3127	0.0233	0.1022	0.0044
<i>Cyclohexane + 1-octanol</i>						
$V^E(10^{-6} \text{ m}^3 \text{ mol}^{-1})$	2.3446	0.1544	0.6150	-0.2543	0.7412	0.0061
$\Delta K_s(10^{-10} \text{ m}^2 \text{ N}^{-1})$	1.1597	-0.6066	-0.6285	-0.3602	2.4558	0.0037
$\Delta\eta(10^{-3} \text{ N m}^{-1} \text{ s}^{-1})$	-3.5485	0.5844	1.6221	-0.8564	-3.0695	0.0038
$\Delta u(10^2 \text{ m s}^{-1})$	-0.6461	0.3121	0.4684	0.1922	-1.6273	0.0030
<i>Cyclohexane + 1-decanol</i>						
$V^E(10^{-6} \text{ m}^3 \text{ mol}^{-1})$	1.7259	-0.7198	-0.7144	-0.0080	2.3396	0.0111
$\Delta K_s(10^{-10} \text{ m}^2 \text{ N}^{-1})$	0.5870	-0.7574	1.2475	-0.1786	-0.7294	0.0057
$\Delta\eta(10^{-3} \text{ N m}^{-1} \text{ s}^{-1})$	-4.3434	2.2131	1.8184	-0.3766	-2.145	0.0185
$\Delta u(\text{m s}^{-1})$	-0.0033	0.4232	-0.9069	0.0325	0.7084	0.0043

FIGURE 1 Plot of excess volume  $V^E$  against mole fraction  $x$  of cyclohexane for the binary systems at 308 K.

hand, negative  $V^E$  arises from several contributions, which may involve specific interactions like strong hydrogen-bonding, dipole-dipole and charge-transfer interactions between unlike molecules in the mixture. Negative  $V^E$  values are also observed for the systems in which favourable interstitial accommodation of component molecules into each others' structures due to difference in their molar volumes takes place. The large positive  $V^E$  values (Fig. 1) for cyclohexane + 1-octanol/1-decanol mixtures are attributed to the breaking up of three-dimensional hydrogen-bonded

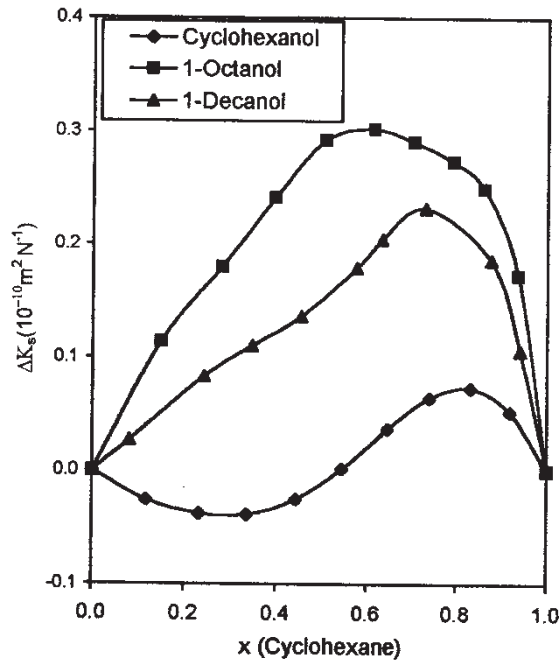


FIGURE 2 Plot of deviations in isentropic compressibility  $\Delta K$  against mole fraction  $x$  of cyclohexane for the binary systems at 308 K.

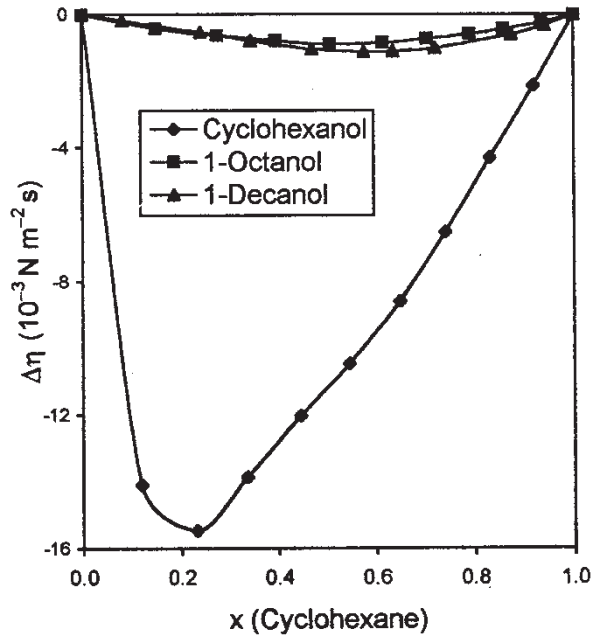


FIGURE 3 Plot of deviations in viscosity  $\Delta\eta$  against mole fraction  $x$  of cyclohexane for the binary systems at 308 K.



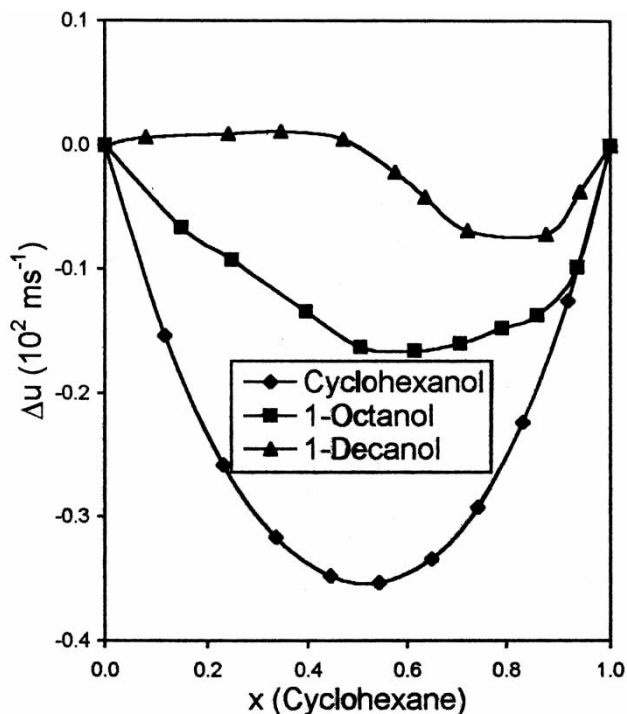


FIGURE 4 Plot of deviations in ultrasonic speed  $\Delta u$  against mole fraction  $x$  of cyclohexane for the binary systems at 308 K.

network of 1-octanol/1-decanol due to the addition of cyclohexane (a structure breaker liquid) [20], which is not compensated by the interaction between unlike molecules. Although there is considerable difference between the molar volumes of cyclohexane and 1-octanol/1-decanol, packing of the component molecules into each others' structures seems to have little effect in overcoming the dissociative effect of alkanols. However, it should be noted that at all mole fractions, observed  $V^E$  has greater positive values for 1-octanol than for 1-decanol. This may be due to the larger molar volume of 1-decanol ( $= 1.9 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ ) than that of 1-octanol ( $= 1.59 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ ) at 308 K, thereby, allowing relatively better packing of smaller cyclohexane ( $= 1.10 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ ) molecules into the voids of 1-decanol molecules than in the voids of 1-octanol molecules. Similar trends in  $V^E$  were also observed in binary mixtures of cyclohexane + isomers of butanol [21] and acetonitrile + 1-octanol/1-decanol [22] binary mixtures.  $V^E$  exhibits an inversion in sign in the mixtures of cyclohexane with cyclohexanol.  $V^E$  values are negative up to  $x \sim 0.60$ , probably due to dipole-induced-dipole interactions between the component molecules. Beyond  $x \sim 0.60$ , as the amount of cyclohexane increases in the mixture the effect due to breaking up of hydrogen bonds in cyclohexanol is more as compared to the interaction between unlike molecules, thereby making a positive contribution to  $V^E$ . Similar trends in  $V^E$  were observed for *p*-chlorotoluene + 1-pentanol/hexanol systems [23].

Like  $V^E$ , the behaviour of  $\Delta K_s$  (Fig. 2) shows positive trends for cyclohexane + 1-octanol/1-decanol (with greater positive values for 1-decanol than 1-octanol) over the whole composition range. Again, the trends in  $\Delta K_s$  change from small negative

(up to  $x \sim 0.54$ ) to small positive ( $x \gtrsim 0.54$ ) values for cyclohexane + cyclohexanol binary mixtures. Thus, we conclude that the behaviour of  $V^E$  with  $x$  is well reflected in the behaviour of  $\Delta K_s$  for all the binary mixtures investigated. Similar behaviour was also reported by Ali *et al.* [24] for DMSO + 1-hexanol/1-octanol and by Fort and Moore [25] for benzene + cyclohexane binary systems. The relative values of  $V^E$  and  $\Delta K_s$  (Figs. 1 and 2) show that the strength of interaction between the component molecules follows the order: cyclohexanol > 1-decanol > 1-octanol.

The negative trends in  $\Delta\eta$  for all the three binary systems under investigation (Fig. 3), over the whole composition range, suggest that the viscosities of associates formed between unlike molecules are relatively less than those of pure components. However, according to Fort and Moore [25] negative  $\Delta\eta$  value are ascribed to an increase in the dispersion forces in the mixtures. There is a sharp fall in the viscosity of cyclohexane + cyclohexanol mixtures as compared to pure cyclohexanol, thus large negative deviations in  $\Delta\eta$  are resulted in the system.

It is clear from Fig. 4 that the values of  $\Delta u$  are negative for the mixtures cyclohexane + cyclohexanol/1-octanol over the whole mole fraction range, while they change sign from small positive (upto  $x \sim 0.50$ ) to small negative ( $x \gtrsim 0.50$ ) for the mixtures cyclohexane + 1-decanol. Negative or very small positive deviations from linear dependence on composition in  $\Delta u$  suggest weak interaction between unlike molecules in the present binaries. Thus, the trends in  $\Delta u$  with  $x$  reinforce our earlier view that the effect of breaking up of hydrogen-bonded structure in alkanols seems to dominate over that of the weak interaction between component molecules in the mixtures investigated. Similar behaviour in  $\Delta u$  has also been reported for benzene + cyclohexane [26] and dimethylsulphoxide + toluene [27] binary mixtures.

Various equations exist in the literature to estimate the dynamic viscosity  $\eta$ . Grunberg and Nissan [7] suggested the expression:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (12)$$

where  $d$  is a parameter proportional to interchange energy, which reflects the non-ideality of the system. This parameter has usually been considered as a valid measure for detecting the presence of interactions between the components. Katti and Chaudhri [8] derived the following equation:

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{\text{vis}}/RT \quad (13)$$

where  $W_{\text{vis}}$  is an interaction term. The Heric's equation [9] is of the form

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 + \ln(x_1 M_1 + x_2 M_2) + \Delta_{12} \quad (14)$$

where  $\Delta_{12}(=\alpha_{12}x_1x_2)$  is a function representing molecular interaction and  $\alpha_{12}=\alpha_{21}$  is the interaction parameter. Heric expressed  $\alpha_{12}$  or  $\alpha_{21}$  as a linear function of composition. Table IV gives the values of interaction parameters calculated from the above equations together with the standard percentage deviations, while Table V presents the theoretically evaluated viscosity data using Eqs. (12)–(14). From the different equations for calculating viscosities of mixtures, we conclude that for cyclohexane + 1-octanol and cyclohexane + 1-decanol systems Katti and Chaudhri (Eq. (13)) produces

TABLE IV Values of the interaction parameters of Eqs. (12)–(14) together with standard percentage deviations for the binary mixtures at 308 K

<i>Cyclohexane</i>	<i>Eq. (12)</i>		<i>Eq. (13)</i>		<i>Eq. (14)</i>	
	<i>d</i>	$\sigma(\%)$	$W_{vis}/RT$	$\sigma(\%)$	$\Delta_{12}$	$\sigma(\%)$
+ Cyclohexanol	−2.5764	12.5597	−2.5789	12.6034	−2.5604	12.5633
+ 1-Octanol	−0.0608	5.2610	0.0289	5.1729	0.0367	5.1783
+ 1-Decanol	0.6824	5.7157	0.8568	5.5081	0.8850	5.5135

TABLE V Theoretically evaluated viscosity data from Eqs. (12)–(14) for the binary mixtures at 308 K

<i>x</i> ( <i>Cyclohexane</i> )	<i>Eq. (12)</i>	<i>Eq. (13)</i>	<i>Eq. (14)</i>
<i>Cyclohexane + cyclohexanol</i>			
0.1168	14.1177	14.1293	14.1188
0.2322	7.6998	7.7113	7.7006
0.3358	4.7382	4.7453	4.7386
0.4443	3.0233	3.0254	3.0235
0.5452	2.1024	2.1021	2.1023
0.6483	1.5306	1.5291	1.5306
0.7411	1.2058	1.2045	1.2057
0.8311	0.9981	0.9971	0.9980
0.9180	0.8653	0.8648	0.8653
<i>Cyclohexane + 1-octanol</i>			
0.1494	3.9067	3.9109	3.9124
0.2768	3.0544	3.0591	3.0597
0.3962	2.4293	2.4330	2.4326
0.5076	1.9648	1.9671	1.9662
0.6146	1.6050	1.6057	1.6048
0.7054	1.3533	1.3528	1.3525
0.7911	1.1533	1.1524	1.1521
0.8587	1.0171	1.0161	1.0161
0.9354	0.8825	0.8817	0.8819
<i>Cyclohexane + 1-decanol</i>			
0.0801	6.6993	6.7140	6.7166
0.2421	4.9921	5.0138	5.0151
0.3455	4.0613	4.0778	4.0780
0.4703	3.1042	3.1120	3.1111
0.5762	2.4308	2.4319	2.4309
0.6347	2.1096	2.1081	2.1071
0.7203	1.7005	1.6971	1.6959
0.8752	1.1220	1.1183	1.1183
0.9408	0.9314	0.9293	0.9294

best results, since it gives smallest deviations, whereas, for cyclohexane + cyclohexanol binary mixtures all the relations predict exceptionally high deviations.

Theoretical evaluation of ultrasonic speed in binary liquid mixtures using different theories and empirical relations and its comparisons with experimental values reveals the extent of molecular interactions in the liquid mixtures. Therefore, the ultrasonic speed was evaluated using free length theory (FLT) [10]:

$$u_{FLT} = K/(L_f \rho^{1/2}) \quad (15)$$

Nomoto's empirical relation [11]:

$$u_{\text{NOM}} = [(xR_1 + (1 - x)R_2)/(xV_1 + (1 - x)V_2)] \tag{16}$$

and Van Dael and Vangeel's ideal mixing relation [12]:

$$1/u_{\text{VD}}^2 = [(1/u_1^2M_1) + (1/u_2^2M_2)][(1 - x)M_1 + xM_2] \tag{17}$$

where  $K$  is Jacobson's constant [10],  $R_1$ ,  $R_2$ ,  $V_1$ ,  $V_2$  and  $M_1$ ,  $M_2$  are the Rao's constants [28], molar volumes and molar masses of 1-alkanols and cyclohexane, respectively. The calculated ultrasonic speeds along with the experimental speeds and percentage error in the calculated values from those of the experimental values are listed in Table VI.

TABLE VI Theoretically evaluated ultrasonic speed from FLT, NOM and VDV along with experimental values and percentage error for the binary mixtures at 308 K

$x$ (Cyclohexane)	$u$ (m s <sup>-1</sup> )				% Error		
	<i>Expt.</i>	<i>FLT</i>	<i>NOM</i>	<i>VDV</i>	<i>FLT</i>	<i>NOM</i>	<i>VDV</i>
<i>Cyclohexane + cyclohexanol</i>							
0.0000	1448.3	1448.3	1448.3	1448.3	0.00	0.00	0.00
0.1168	1405.1	1385.0	1418.5	1405.3	1.43	0.95	0.01
0.2322	1367.0	1339.6	1389.5	1368.2	2.01	1.65	0.09
0.3358	1336.4	1304.7	1364.1	1338.8	2.37	2.07	0.18
0.4443	1308.8	1271.6	1337.9	1311.4	2.85	2.22	0.20
0.5452	1283.7	1247.9	1314.0	1288.6	2.79	2.36	0.38
0.6483	1260.8	1228.9	1289.9	1267.7	2.53	2.31	0.55
0.7411	1243.1	1219.5	1268.7	1250.7	1.90	2.06	0.61
0.8311	1229.3	1213.8	1248.4	1235.7	1.26	1.55	0.52
0.9180	1218.0	1211.3	1229.1	1222.5	0.55	0.91	0.37
1.0000	1211.1	1211.1	1211.1	1211.1	0.00	0.00	0.00
<i>Cyclohexane + 1-octanol</i>							
0.0000	1319.7	1319.7	1319.7	1319.7	0.00	0.00	0.00
0.1494	1296.8	1287.6	1307.6	1278.4	0.71	0.84	1.42
0.2768	1279.2	1267.1	1296.5	1252.0	0.94	1.35	2.13
0.3962	1263.0	1251.8	1285.1	1233.3	0.89	1.75	2.35
0.5076	1249.4	1239.4	1273.8	1220.5	0.80	1.95	2.31
0.6146	1236.0	1229.2	1262.0	1212.1	0.55	2.10	1.93
0.7054	1227.0	1220.7	1251.3	1207.9	0.52	1.98	1.56
0.7911	1219.0	1215.6	1240.5	1206.1	0.28	1.76	1.06
0.8587	1213.7	1212.5	1231.5	1206.3	0.10	1.47	0.61
0.9354	1208.3	1209.7	1220.7	1208.2	0.12	1.03	0.01
1.0000	1211.1	1211.1	1211.1	1211.1	0.00	0.00	0.00
<i>Cyclohexane + 1-decanol</i>							
0.0000	1350.0	1350.0	1350.0	1350.0	0.00	0.00	0.00
0.0801	1339.5	1333.8	1343.2	1307.8	0.43	0.28	2.36
0.2421	1317.5	1306.0	1327.9	1246.2	0.87	0.79	5.41
0.3455	1303.0	1288.7	1317.0	1219.6	1.09	1.07	6.40
0.4703	1285.2	1269.0	1302.2	1198.0	1.26	1.32	6.79
0.5762	1268.0	1252.6	1288.1	1187.5	1.22	1.58	6.35
0.6347	1257.0	1244.0	1279.6	1184.5	1.04	1.80	5.77
0.7203	1243.5	1234.0	1266.2	1183.7	0.77	1.82	4.81
0.8752	1222.5	1215.9	1238.1	1193.0	0.54	1.28	2.42
0.9408	1215.6	1212.0	1224.4	1201.2	0.30	0.73	1.18
1.0000	1211.1	1211.1	1211.1	1211.1	0.00	0.00	0.00

The results indicate that for cyclohexane + 1-octanol and cyclohexane + 1-decanol mixtures FLT predicts the experimental data well, showing smallest deviations, while Van Dael and Vangeel's relation gives maximum deviation. For cyclohexane + cyclohexanol mixtures Van Dael and Vangeel's relation, with minimum deviations, is reasonable in producing the experimental ultrasonic speeds while FLT gives largest deviations.

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### References

- [1] A. Ali, S. Hyder and A.K. Nain (1999). *J. Mol. Liq.*, **79**, 89.
- [2] A. Ali, S. Hyder and A.K. Nain (1997). *Acoustics Lett.*, **21**, 77.
- [3] A. Ali, S. Hyder and A.K. Nain (2000). *Acoustics Lett.*, **23**, 183.
- [4] R. Mehra, A. Gupta and R. Israni (2001). *Indian J. Chem.*, **40A**, 505.
- [5] Y. Marcus (1977). *Introduction to Liquid State Chemistry*. Wiley-Interscience, New York.
- [6] G.A. Krestov (1991). *Thermodynamics of Solvation*. Ellis Horwood, England.
- [7] L. Grunberg and A.H. Nissan (1949). *Nature*, **164**, 799.
- [8] P.K. Katti and M.M. Chaudhri (1964). *J. Chem. Eng. Data*, **9**, 442.
- [9] E.L. Heric (1966). *J. Chem. Eng. Data*, **11**, 66.
- [10] B. Jacobson (1951). *Acta Chem. Scand.*, **5**, 1214; (1952). **6**, 1485; (1952). *J. Chem. Phys.*, **20**, 927.
- [11] O. Nomoto (1958). *J. Phys. Soc. Jpn.*, **13**, 1528.
- [12] W. van Dael and E. Vangeel (1969). *Proc. Ist Internal Conf. On Calorimetry Thermodyn.* Warsa.
- [13] A. Wiesberger, F.S. Prokauer, J.A. Reddick and E.E. Toops (1955). *Techniques of Organic Chemistry, Organic Solvents*, Vol. VII. Interscience Publications, New York.
- [14] S. Pradhan, B.K. Maheshwari and R.L. Yadav (1985). *Indian J. Pure Appl. Phys.*, **26**, 426.
- [15] R.H. Stokes and R. Mills (1965). *Viscosity of Electrolytes and Related Properties*. Pergamon Press, New York.
- [16] S.S. Bhatti (1983). *Indian J. Pure Appl. Phys.*, **21**, 506.
- [17] S.K. Mehta, R.K. Chauha and R.K. Dewan (1996). *J. Chem. Soc., Faraday Trans.*, **92**, 1167.
- [18] O. Redlich and A.T. Kister (1948). *Ind. Eng. Chem.*, **40**, 345.
- [19] A.J. Treszczanowcz, O. Kiyohara and G.C. Benson (1981). *J. Chem. Thermodyn.*, **13**, 253.
- [20] D. Patterson (1994). *J. Solution Chem.*, **23**, 105.
- [21] U. Bhardwaj and K.C. Singh (1998). *Indian J. Chem.*, **37A**, 316.
- [22] P.S. Nikam, L.N. Shirsat and M. Hasan (2000). *J. Indian Chem. Soc.*, **77**, 244.
- [23] K.S. Kumar and P.R. Naidu (1993). *J. Chem. Eng. Data*, **38**, 156.
- [24] A. Ali, K. Tiwari, A.K. Nain and V. Chakravorthy (2000). *Phys. Chem. Liq.*, **38**, 459.
- [25] R.J. Fort and W.R. Moore (1965). *Trans Faraday Soc.*, **61**, 2102.
- [26] D. Veerkhadraiah (1997). *J. Pure. Appl. Ultrason.*, **19**, 57.
- [27] K. Tiwari, C. Patra and V. Chakravorty (1995). *Acoustics Letters*, **19**, 53.
- [28] M.R. Rao. (1940). *Indian. J. Phys.*, **14**, 109.