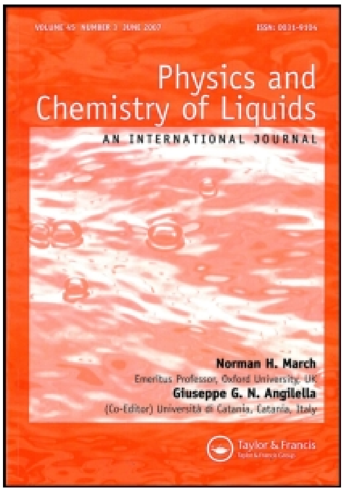

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Excess molar volumes, viscosity deviations and speeds of sound for some alkoxyethanols and amines in cyclohexanone at 298.15 K

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Excess molar volumes, viscosity deviations and speeds of sound for some alkoxyethanols and amines in cyclohexanone at 298.15 K

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Densities, viscosities and ultrasonic speeds of sound were measured for the binary mixtures of cyclohexanone + 2-methoxy ethanol, + 2-ethoxy ethanol, + 2-butoxy ethanol, + diethylamine and + isopropylamine over the entire range of composition at 298.15 K. From the experimental density, viscosity and ultrasonic speed data, excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$) and deviation in isentropic compressibility ($\Delta\kappa_S$) have been calculated. The excess or deviation properties were fitted to Redlich–Kister polynomial equation. From excess molar volumes (V_m^E), partial molar volumes ($\overline{V}_{m,1}^0$ and $\overline{V}_{m,2}^0$) and excess partial molar volumes ($\overline{V}_{m,1}^{0,E}$ and $\overline{V}_{m,2}^{0,E}$) at infinite dilution were calculated. Various acoustic parameters have also been calculated from the density and ultrasonic speed data. McAllister's three-body and Heric–Brewer model have been used to correlate viscosities of the binary mixtures. The various properties were discussed in terms of molecular and structural changes.

Keywords: density; viscosity; ultrasonic speeds; excess molar volumes; viscosity deviations

1. Introduction

In recent years, there has been considerable interest in theoretical and experimental investigations of the excess or deviation of thermodynamic properties of binary mixtures. In principle, the nature of interactions between the molecules can be established from the study of the characteristic departure from ideal behaviour of some physical properties such as volume, compressibility and viscosity. It is well known that cyclohexanone (CY) has numerous applications [1] both in pure and applied chemistry. Alkoxyethanols have wide use as monomers in the production of polymers and emulsion formulations. They are also of considerable interest for studying the hetero-proximity effects of the etheric oxygen on the –O–H bond, and hence its influence on the associated nature of the species in these molecules. Diethylamine (DEA) and isopropylamine (IPA) are also important in characterising the associated nature of the liquids in mixtures, because of the presence of both a proton donor and a proton acceptor and they form water insoluble compounds of medical importance [2]. Therefore in continuation of our systematic study [3–6] of the physicochemical properties of non-aqueous binary liquid mixtures, the present study attempts to unravel the nature of molecular interactions in the binary mixtures of CY with alkoxyethanols (2-methoxy (ME), 2-ethoxy (EE), 2-butoxy ethanol (BE)) and amines

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(DEA and IPA) by measuring their densities, viscosities and ultrasonic speeds of sound over the entire range of composition at 298.15 K and atmospheric pressure.

The calculated excess or deviation functions from the experimental data along with other derived parameters such as partial molar volumes ($\overline{V}^{0}_{\mathrm{m},1}$ and $\overline{V}^{0}_{\mathrm{m},2}$) and excess partial molar volumes ($\overline{V}^{0,\mathrm{E}}_{\mathrm{m},1}$ and $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},2}$) at infinite dilution, intermolecular free length (L_f), specific acoustic impedance (Z), etc. have been interpreted in terms of molecular interactions and structural effects. The work provides a test of various empirical equations to correlate viscosity and acoustic data of binary mixtures in terms of pure component properties.

2. Experimental

All the chemicals used were of analytical reagent grade (S.D. Fine Chemicals, India). CY was purified by distillation [7] and stored over activated 4 Å molecular sieves to reduce water content. All the alkoxyethanols were purified as described in the literature [8] and the amines were used without further purification. Physical properties of pure liquids at 298.15 K as measured are listed in Table 1 and are in good agreement with the literature values [8–12].

All the binary solutions were prepared afresh before use by mixing known volumes of pure liquids in airtight-stopper glass bottles, and each solution thus prepared was distributed into three recipients to perform all the measurements with the aim of determining possible dispersion of the results obtained. Care was taken to avoid evaporation and contamination during mixing. The reproducibility in mole fraction was within ±0.0002.

Densities (ρ) were measured with an Ostwald–Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ±0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried and weighed in an electronic balance with a precision of ±0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The total uncertainty of density was $\pm 3 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$. The viscosity was measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [13–15]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ±0.01 K. After attainment of thermal

Table 1. Physical properties of pure components at 298.15 K.

	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		
Pure liquids	Expt.	Lit.	Expt.	Lit.	u (m s^{-1})
CY	0.9422	0.9425 [9]	1.963	1.963 [9]	1417.4
ME	0.9603	0.9602 [10]	1.540	1.5414 [10]	1340.2
EE	0.9250	0.9256 [11]	1.850	1.850 [11]	1302.8
BE	0.8965	0.8966 [8]	2.792	2.795 [8]	1303.2
DEA	0.6984	0.6984 [12]	0.265	0.265 [12]	1130.6
IPA	0.6815	0.6815 [12]	0.278	0.278 [12]	1075.6

equilibrium, efflux times of flow were recorded with a stopwatch correct to ±0.1 s. At least three repetitions of each data reproducible to ±0.1 s were taken to average the flow times. The uncertainty of the viscosity was within ±0.03% of the reported values. Ultrasonic speeds of sound (u) were measured with an accuracy of 0.3% by using a single crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi, M-81) working at 2 MHz. It was calibrated with doubly distilled water, purified methanol and benzene at 298.15 K. During the measurements, temperature was maintained within 298.15 ± 0.01 K by circulating thermostated water around the jacketed cell (2 MHz) containing the experimental solutions with the aid of a circulating pump. The estimated uncertainty of ultrasonic speeds of sound was found to be around $\pm 0.2\,\mathrm{ms}^{-1}$. The details of the methods and measurement techniques have been described in other works [16–18].

3. Results and discussion

Densities (ρ), viscosities (η), excess molar volumes (V_m^E) and viscosity deviations ($\Delta\eta$) for the binary mixtures studied at 298.15 K are listed in Table 2.

The excess molar volumes (V_m^E) was calculated using Equation (1)

$$V_m^E = \sum_{i=1}^{2} x_i M_i (1/\rho - 1/\rho_i), \tag{1}$$

where ρ, M_i, x_i and ρ_i are the mixture density, molecular weight, mole fraction, density of i-th component in the mixture, respectively. The total uncertainty of excess molar volumes (V_m^E) is $\pm 0.005\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. Figure 1 shows that while the excess molar volumes (V_m^E) for all the alkoxyethanol systems are positive, they are negative for the mixtures containing amines over the entire range of composition at the experimental temperature. The negative values of excess molar volume (V_m^E) suggest specific interactions [3,4,19] between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces [3,4,19] between them. Several effects may contribute to the value of V_m^E and three different effects may be considered as being important: (a) disruption of liquid order on mixing and unfavourable interactions between unlike molecules producing a positive contribution to V_m^E, (b) differences in molecular volumes and free volumes [20] between liquid components and (c) the possible association due to hydrogen bond interactions between the unlike molecules. The actual volume change would, therefore, depend on the relative strength of these opposing effects. In the present study, the very large negative V_m^E values for the amines are attributed to the presence of strong intermolecular hydrogen bond interactions between the amine molecules and the CY molecules. It has also been found that DEA has less negative values of V_m^E, compared to those of IPA. This is probably due to decreased proton donating ability of DEA, thereby decreasing hydrogen bond interaction (–C=O$\cdots$H–N–) between CY and DEA molecules. Thus, unlike molecular interactions decrease as one shifts from primary to secondary amines [21,22]. The alkoxyethanols undergo less self-association in contrast to the high tendency of amines to undergo self-association through intermolecular hydrogen bonding. But, the presence of etheric oxygen in alkoxyethanols facilitates the formation of intramolecular hydrogen bonding between the etheric oxygen and hydrogen of –OH group of the same molecule. Infrared, microwave and calorimetric studies [23,24] have proved the presence of mostly 10-membered dimers and linear associates in R–O–C_2H_5OH (where R = –CH_3, –C_2H_5, –C_4H_9 etc,) and the positive values of V_m^E for the mixtures of alkoxyethanols under investigation may be

Table 2. Experimental values of density (ρ), viscosity (η), excess molar volume (V_m^E) and viscosity deviations ($\Delta\eta$) for the binary mixtures under investigation at 298.15 K.

Mole fraction of CY (x_1)	$\rho \times 10^{-3}$ ($kg\,m^{-3}$)	η (mPa s)	$V_m^E \times 10^6$ ($m^3\,mol^{-1}$)	$\Delta\eta$ (mPa s)
CY (1) + ME (2)				
0.0793	0.9581	1.432	0.031	−0.142
0.1624	0.9559	1.369	0.062	−0.240
0.2494	0.9538	1.330	0.094	−0.316
0.3408	0.9517	1.325	0.121	−0.360
0.4367	0.9496	1.330	0.147	−0.395
0.5377	0.9477	1.354	0.164	−0.414
0.6440	0.9458	1.402	0.180	−0.411
0.7562	0.9440	1.504	0.182	−0.356
0.8746	0.9428	1.665	0.131	−0.245
CY (1) + EE (2)				
0.0926	0.9265	1.684	0.016	−0.177
0.1867	0.9275	1.587	0.100	−0.284
0.2824	0.9285	1.529	0.170	−0.353
0.3797	0.9297	1.494	0.229	−0.399
0.4787	0.9307	1.469	0.310	−0.435
0.5793	0.9319	1.472	0.360	−0.444
0.6818	0.9342	1.506	0.300	−0.421
0.7860	0.9369	1.564	0.200	−0.375
0.8920	0.9395	1.691	0.110	−0.260
CY (1) + BE (2)				
0.1180	0.8993	2.522	0.224	−0.172
0.2314	0.9007	2.280	0.640	−0.320
0.3404	0.9024	2.108	1.000	−0.402
0.4453	0.9048	1.972	1.246	−0.451
0.5463	0.9083	1.873	1.350	−0.466
0.6436	0.9128	1.795	1.323	−0.464
0.7375	0.9188	1.763	1.120	−0.418
0.8281	0.9259	1.766	0.800	−0.340
0.9155	0.9338	1.822	0.411	−0.211
CY (1) + DEA (2)				
0.0760	0.7183	0.296	−0.200	−0.098
0.1570	0.7395	0.338	−0.425	−0.194
0.2421	0.7616	0.415	−0.605	−0.261
0.3319	0.7847	0.502	−0.756	−0.327
0.4270	0.8088	0.639	−0.853	−0.351
0.5278	0.8337	0.790	−0.872	−0.371
0.6349	0.8601	0.970	−0.873	−0.373
0.7488	0.8864	1.224	−0.669	−0.313
0.8702	0.9140	1.540	−0.410	−0.203
CY (1) + IPA (2)				
0.0627	0.7123	0.410	−1.400	0.026
0.1309	0.7452	0.604	−2.838	0.105
0.2051	0.7772	0.844	−3.950	0.220
0.2865	0.8084	1.135	−4.770	0.374
0.3759	0.8390	1.498	−5.340	0.586
0.4746	0.8662	1.904	−5.377	0.826
0.5842	0.8888	2.083	−4.757	0.820
0.7067	0.9078	2.162	−3.548	0.693
0.8442	0.9244	2.051	−1.851	0.350

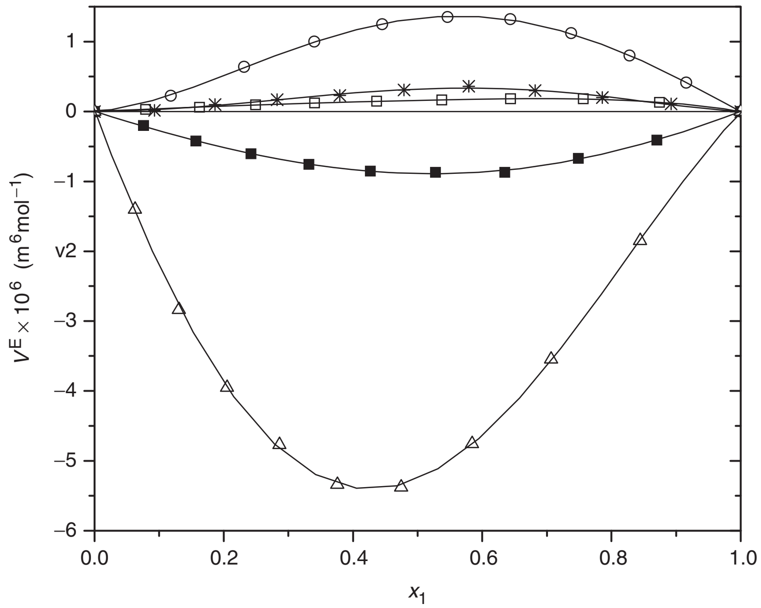

Figure 1. Plot of excess molar volume (V_m^E) against mole fraction (x_1) of CY with ME (□), EE (∗), BE (○), DEA (■) and IPA (Δ) at 298.15 K.

attributed to the presence of weak hydrogen bond interaction or dipole–dipole interactions due to these intramolecular associations of the alkoxyethanols. This justified that intramolecular H-bonds are more relevant than the intermolecular H-bonds for the binary mixtures of the alkoxyethanols. It has also been observed that the increase in chain length of alkoxyethanol molecules increases the V_m^E values.

The excess molar volumes (V_m^E) were fitted by the Redlich–Kister polynomial Equation (2) [25],

$$V_m^E = x_1 x_2 \sum_{i=0}^{j} a_i (1 - 2x_2)^i, \tag{2}$$

where x_1 and x_2 are the mole fractions of the components 1 and 2, and a_i represents the multiple-regression coefficients listed in Table 3 along with their standard deviations (σ). The standard deviations were calculated using the relation:

$$\sigma = \left[\sum_{i=1}^{n} (V_{m,\text{Calcd}}^E - V_{m,\text{Expt}}^E)^2 / (n - j) \right]^{1/2}, \tag{3}$$

where n is the number of experimental data points and j is the number of a_i coefficients. The partial molar volumes, $\overline{V}_{m,1}^0$ of component 1 and $\overline{V}_{m,2}^0$ of component 2, in these mixtures over the entire composition range at 298.15 K were calculated by using the relations:

$$\overline{V}_{m,1}^0 = V_m^E + V_{m,1}^* + x_2 \left(\partial V_m^E / \partial x_1 \right)_{T,P}, \tag{4}$$

$$\overline{V}_{m,2}^0 = V_m^E + V_{m,2}^* - x_1 \left(\partial V_m^E / \partial x_1 \right)_{T,P}, \tag{5}$$

Table 3. Redlich–Kister coefficients and corresponding standard deviations (σ) for excess molar volumes ($V_{\mathrm{m}}^{\mathrm{E}}$) of the binary mixtures at 298.15 K.

$V_{\mathrm{m}}^{\mathrm{E}} \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$)	a_0	a_1	a_2	a_3	σ
CY (1) + ME (2)	0.631	0.363	0.496	0.586	0.01
CY (1) + EE (2)	1.287	0.758	−0.986	−0.567	0.02
CY (1) + BE (2)	5.332	2.069	−2.458	–	0.01
CY (1) + DEA (2)	−3.560	−0.348	0.367	–	0.02
CY (1) + IPA (2)	−21.049	7.625	3.962	–	0.04

where $V_{\mathrm{m},1}^{*}$ and $V_{\mathrm{m},2}^{*}$ are the molar volumes of the pure components 1 and 2, respectively. The derivative, $(\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial x_1)_{T,P}$ in Equations (4) and (5) was obtained by differentiating Equation (2) with respect to x_1 leading to the following equations for $\overline{V}_{\mathrm{m},1}$ and $\overline{V}_{\mathrm{m},2}$:

$$\overline{V}_{\mathrm{m},1} = V_{\mathrm{m},1}^{*} + x_2^2 \sum_{i=0}^{j} a_i(1-2x_1)^i - 2x_1x_2^2 \sum_{i=1}^{j} a_i(1-2x_1)^{i-1} \tag{6}$$

$$\overline{V}_{\mathrm{m},2} = V_{\mathrm{m},2}^{*} + x_1^2 \sum_{i=0}^{j} a_i(1-2x_1)^i + 2x_1^2x_2 \sum_{i=1}^{j} a_i(1-2x_1)^{i-1}. \tag{7}$$

The values of partial molar volumes, $\overline{V}_{\mathrm{m},1}^{0}$ and $\overline{V}_{\mathrm{m},2}^{0}$ at infinite dilution obtained from Equations (4) to (7) allow the calculation of the excess partial molar volumes $\overline{V}_{\mathrm{m},1}^{0,\mathrm{E}}$ and $\overline{V}_{\mathrm{m},2}^{0,\mathrm{E}}$ at infinite dilution by using the following relations:

$$\overline{V}_{\mathrm{m},1}^{0,\mathrm{E}} = \overline{V}_{\mathrm{m},1}^{0} - V_{\mathrm{m},1}^{*} \tag{8}$$

$$\overline{V}_{\mathrm{m},2}^{0,\mathrm{E}} = \overline{V}_{\mathrm{m},2}^{0} - V_{\mathrm{m},2}^{*}. \tag{9}$$

According to Lewis and Randall [26], the partial molar volumes at infinite dilution can also be calculated by using another approach.

$$V_{\phi,1} = (V_{\mathrm{m}} - n_2 V_{\mathrm{m},2}^{*})/n_1 \tag{10}$$

$$V_{\phi,2} = (V_{\mathrm{m}} - n_1 V_{\mathrm{m},2}^{*})/n_2, \tag{11}$$

where $V_{\phi,1}$ and $V_{\phi,2}$ are the apparent molar volumes of component 1 in component 2 and that of the component 2 in component 1, respectively; n_1 and n_1 are the number of moles of the components 1 and 2, respectively.

The molar volume of the mixture, V_{m} can be written as

$$V_{\mathrm{m}} = V_{\mathrm{m}}^{\mathrm{E}} + x_1 V_{\mathrm{m},1}^{*} + x_2 V_{\mathrm{m},2}^{*}. \tag{12}$$

Combinations of Equations (10) and (12) and Equations (11) and (12) give

$$V_{\phi,1} = V_{\mathrm{m},1}^{*} + (V_{\mathrm{m}}^{\mathrm{E}}/x_1) \tag{13}$$

$$V_{\phi,2} = V_{\mathrm{m},2}^{*} + \left(V_{\mathrm{m}}^{\mathrm{E}}/x_2\right). \tag{14}$$

Table 4. The values $\overline{V}^{0}_{\mathrm{m},1}$, $\overline{V}^{0}_{\phi,1}$, $V^{*}_{\mathrm{m},1}$, $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},1}$, $\overline{V}^{0,\mathrm{E}}_{\phi,1}$, $\overline{V}^{0}_{\mathrm{m},2}$, $\overline{V}^{0}_{\phi,2}$, $V^{*}_{\mathrm{m},2}$, $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},2}$ and $\overline{V}^{0,\mathrm{E}}_{\phi,2}$ for all the five binary mixtures at 298.15 K.[a]

CY (1) +	$\overline{V}^{0}_{\mathrm{m},1}$	$\overline{V}^{0}_{\phi,1}$	$\overline{V}^{*}_{\mathrm{m},1}$	$\overline{V}^{0,\mathrm{E}}_{\mathrm{m},1}$	$\overline{V}^{0,E}_{\phi,1}$	$\overline{V}^{0}_{\mathrm{m},2}$	$\overline{V}^{0}_{\phi,2}$	$\overline{V}^{*}_{m,2}$	$\overline{V}^{0,E}_{m,2}$	$\overline{V}^{0,E}_{\phi,2}$
ME (2)	99.100	99.361	98.922	0.178	0.439	81.322	80.269	79.246	2.076	1.023
EE (2)	99.032	99.481	98.922	0.110	0.559	97.919	98.708	97.427	0.492	1.281
BE (2)	99.727	102.183	98.922	0.805	3.261	136.767	137.521	131.824	4.943	5.679
DEA (2)	96.077	95.800	98.922	−2.845	−3.122	101.184	101.080	104.725	−3.541	−3.645
IPA (2)	74.210	74.408	98.922	−24.712	−24.514	77.273	70.561	86.735	−9.462	−16.174

Note: [a]All quantities have the unit: $10^6\,\mathrm{m}^3\,\mathrm{mol}^{-1}$.

Equations (13) and (14) allow easy calculation of apparent molar volumes from experimental $V^{\mathrm{E}}_{\mathrm{m}}$ values and the corresponding mole fractions. The linear regressions of $V_{\phi,1}$ *versus* x_1 and $V_{\phi,2}$ *versus* x_1 give the values of the limiting apparent molar volumes, $\overline{V}^{0}_{\phi,1}$ and $\overline{V}^{0}_{\phi,2}$ at infinite dilution. These quantities are also known as the partial molar volumes at infinite dilution, represented as $\overline{V}^{0}_{\mathrm{m},1}$ and $\overline{V}^{0}_{\mathrm{m},2}$ earlier. $\overline{V}^{0,\mathrm{E}}_{\phi,1}$ and $\overline{V}^{0,\mathrm{E}}_{\phi,2}$ were also calculated by equations similar to Equations (8) and (9). The values $\overline{V}^{0}_{\mathrm{m},1}$, $\overline{V}^{0}_{\phi,1}$, $V^{*}_{\mathrm{m},1}$, $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},1}$, $\overline{V}^{0,\mathrm{E}}_{\phi,1}$, $\overline{V}^{0}_{\mathrm{m},2}$, $\overline{V}^{0}_{\phi,2}$, $V^{*}_{\mathrm{m},2}$, $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},2}$ and $\overline{V}^{0,\mathrm{E}}_{\phi,2}$ for all the five binary mixtures at 298.15 K are listed in Table 4. A perusal of Table 4 indicates that the values of $\overline{V}^{0}_{\mathrm{m},1}$ and $\overline{V}^{0}_{\phi,1}$; $\overline{V}^{0}_{\mathrm{m},2}$ and $\overline{V}^{0}_{\phi,2}$ are nearly of same magnitude except for the IPA in CY. The values of $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},1}$, $\overline{V}^{0,\mathrm{E}}_{\mathrm{m},2}$, $\overline{V}^{0,\mathrm{E}}_{\phi,1}$ and $\overline{V}^{0,\mathrm{E}}_{\phi,2}$ are positive over the entire composition range for all the alkoxyethanol systems, but negative for the amine systems. This suggests that while alkoxyethanol systems are characterised by volume expansion, the amine systems are characterised by volume contraction on mixing with CY.

Viscosity deviations ($\Delta\eta$) were calculated using the following equations:

$$\Delta\eta = \eta - \Sigma^{2}_{i=1}(x_i\eta_i), \tag{15}$$

where η is the absolute viscosity of the mixture and η_i is the absolute viscosity of the *i*-th pure component in the mixture. The estimated uncertainty of viscosity deviations ($\Delta\eta$) is ±0.004 mPa s.

Table 2 shows that $\Delta\eta$ values are negative for all the mixtures, except for the mixture containing IPA, over the entire composition range at the experimental temperature. The negative $\Delta\eta$ values indicate the presence of weak interactions between the unlike molecules in the mixture. The decrease of mixture viscosities indicates the weakening of the self-association of alkoxyethanols in presence of CY. According to Fort and Moore [27], viscosity deviations are negative in mixtures of components having unequal size and in which dispersion forces are present. As expected, the values of $\Delta\eta$ become more negative as the chain length of the alkoxyethanol molecules increases and one shifts from primary amine to secondary amine [21,22]. This suggests that the strength of interaction in the mixtures is in the order: CY + BE < CY + EE < CY + ME < CY + DEA < CY + IPA. Thus, Figure 2 showing the variation of $\Delta\eta$ *versus* x_1 of CY at 298.15 K complements with the variation of $V^{\mathrm{E}}_{\mathrm{m}}$ in describing the behaviours of the binary mixtures in Figure 1.

In an attempt to explore the nature of molecular interactions, various acoustic parameters such as isentropic compressibility (κ_{S}), deviation in isentropic compressibility ($\Delta\kappa_{\mathrm{S}}$), intermolecular free length (L_{f}), specific acoustic impedance (Z), Vander Waal's constant (b), molecular radius (r), geometrical volume (B), molar surface area (Y), available

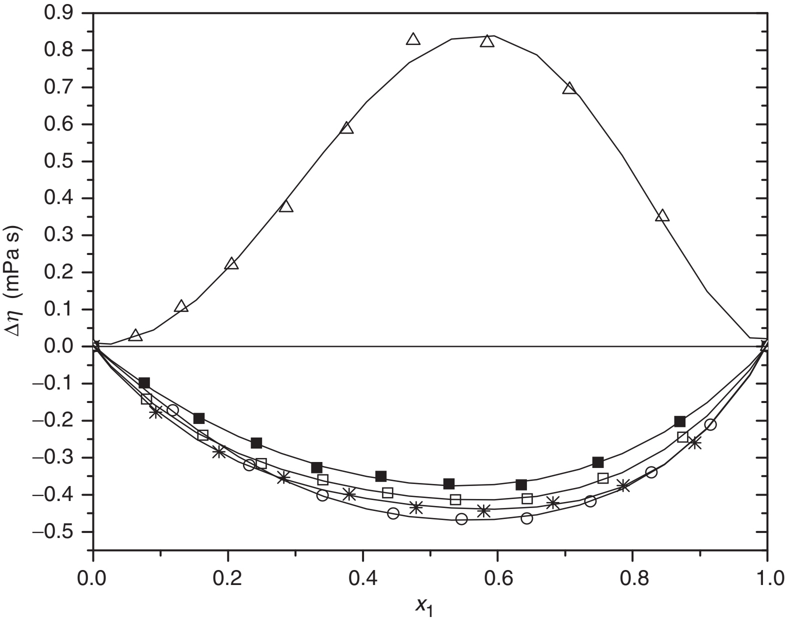

Figure 2. Plot of viscosity deviation ($\Delta\eta$) against mole fraction (x_1) of CY with ME (□), EE (∗), BE (○), DEA (■) and IPA (Δ) at 298.15 K.

volume (V_a), molar speed of sound (R), relative association (R_A) and molecular association (M_A) of the binary mixtures have been calculated using the following equations:

$$\kappa_S = 1/u^2\rho \tag{16}$$

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{j} x_i \kappa_{S,i} \tag{17}$$

$$L_f = K\kappa_S^{1/2} \tag{18}$$

$$Z = u\rho \tag{19}$$

$$b = (M/\rho) - (RT/\rho^2u^2)\left\{[1 + (Mu^2/3RT)]^{1/2} - 1\right\} \tag{20}$$

$$r = (3b/16\pi N)^{1/3} \tag{21}$$

$$B = \frac{4}{3}\pi r^3 N \tag{22}$$

$$Y = [36\pi NB^2]^{1/3} \tag{23}$$

$$V_a = V(1 - u/u_\infty) \tag{24}$$

$$V_0 = V - V_a \tag{25}$$

$$R = \overline{M}u^{1/3}/\rho \tag{26}$$

$$R_{\mathrm{A}} = (\rho_{\mathrm{mix}}/\rho)(u/u_{\mathrm{mix}})^{1/3} \tag{27}$$

$$M_{\mathrm{A}} = \left[\left(u_{\mathrm{mix}}\Big/\sum_{i=1}^{2} x_i u_i\right)^2 - 1\right], \tag{28}$$

where K is a temperature dependent constant [27], T is the absolute temperature, $\overline{M}$ is the average molecular weight, V_0 is the volume at absolute zero and u_∞ is taken as 1600 ms^{-1}.

Table 5 contains ultrasonic speeds of sound (u), isentropic compressibility (κ_{S}) and deviation in isentropic compressibility ($\Delta\kappa_{\mathrm{S}}$) for the studied binary mixtures at 298.15 K. It shows that $\Delta\kappa_{\mathrm{S}}$ values increase in the order: CY + IPA < CY + DEA < CY + ME < CY + EE < CY + BE and this trend (depicted in Figure 3) is justified by the presence of weak interaction or structure disruptive effects between the mixing liquids for alkoxyethanol systems and by the presence of strong hydrogen bond interactions between the mixing liquids for the amine systems. As stated earlier, alkoxyethanols in their pure state associate predominantly to form 10-membered dimeric rings and these structures can thus resist the structure disruptions in the presence of CY. This effect increases with the number of carbon atoms in the alkoxyethanols. Sastry and Patel [8] have also reported similar result observation while studying binary mixtures of some alkoxyethanols and some monoalkanols in methyl methacrylate at 298.15 and 308.15 K.

Other acoustic parameters, except $\Delta\kappa_{\mathrm{S}}$, are listed in Table 6 for the pure components and in Table 7 for the mixtures as a function of x_1 of CY, respectively. A perusal of Table 7 shows that the value of the specific acoustic impedance (Z) and intermolecular free length (L_{f}) for the mixtures behave in an opposite manner; while the specific acoustic impedance (Z) values increases as the intermolecular free length (L_{f}) values decreases for the studied systems. But, while both the molecular association (M_{A}) and relative association (R_{A}) values decrease for the alkoxyethanol systems, they increase for the amine systems with the mole fraction (x_1) of CY, respectively. The relative association (R_{A}) measures the ability of molecules to build associates or supramolecular structure by intermolecular interactions. The increase in chain length is expected to lower self-association, hence R_{A} values decreases almost linearly from ME to BE as CY is added to these binaries. This implies the dominance of dissociative interactions between the unlike molecules in the alkoxyethanols systems. However, the interactive pattern is different for the amines systems [8,22,28]. Similarly, the molecular association (M_{A}) measures the degree of molecular association by intermolecular interactions and the non-linear variation of M_{A} values for the amine systems implies the formation of strong cross-association between the unlike molecules through hydrogen bonding in amine binaries.

Deviations in intermolecular free length (ΔL_{f}) and specific acoustic impedance (ΔZ) for the binary mixtures were calculated using the following equations:

$$\Delta L_{\mathrm{f}} = L_{\mathrm{f}} - \sum_{i=1}^{2} x_i L_{\mathrm{f},i} \tag{29}$$

$$\Delta Z = Z - \sum_{i=1}^{2} x_i Z_i, \tag{30}$$

Table 5. Experimental values of ultrasonic speed (u), isentropic compressibility (κ_S) and deviation in isentropic compressibility ($\Delta\kappa_S$) for binary mixtures of alkoxyethanols at 298.15 K.

x_1	u (m s^{-1})	$\kappa_S \times 10^{10}$ (Pa^{-1})	$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})	x_1	u (m s^{-1})	$\kappa_S \times 10^{10}$ (Pa^{-1})	$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})
CY (1) + ME (2)							
0.0793	1350.1	5.726	−0.030	0.6440	1411.6	5.306	−0.160
0.1624	1359.5	5.660	−0.053	0.7562	1415.4	5.288	−0.120
0.2494	1371.7	5.572	−0.097	0.8746	1416.1	5.289	−0.058
0.3408	1383.8	5.487	−0.135	–	–	–	–
0.4367	1394.4	5.416	−0.156	–	–	–	–
0.5377	1406.4	5.335	−0.186	–	–	–	–
CY (1) + EE (2)							
0.0926	1307.4	6.314	0.046	0.6818	1353.4	5.844	0.215
0.1867	1313.2	6.252	0.086	0.7860	1371.8	5.672	0.157
0.2824	1319.0	6.19	0.128	0.8920	1392.8	5.487	0.087
0.3797	1323.9	6.137	0.180	–	–	–	–
0.4787	1330.7	6.068	0.219	–	–	–	–
0.5793	1340.3	5.973	0.233	–	–	–	–
CY (1) + BE (2)							
0.1180	1306.3	6.516	0.100	0.7375	1354.2	5.935	0.315
0.2314	1312.6	6.444	0.173	0.8281	1372.7	5.732	0.228
0.3404	1317.2	6.387	0.256	0.9155	1393.5	5.515	0.123
0.4453	1323.0	6.314	0.318	–	–	–	–
0.5463	1329.5	6.229	0.363	–	–	–	–
0.6436	1339.7	6.104	0.363	–	–	–	–
CY (1) + DEA (2)							
0.0760	1163.8	10.279	−0.472	0.6349	1351.6	6.364	−1.080
0.1570	1197.6	9.428	−0.844	0.7488	1371.9	5.994	−0.776
0.2421	1232.1	8.649	−1.119	0.8702	1391.2	5.653	−0.398
0.3319	1266.3	7.947	−1.290	–	–	–	–
0.4270	1299.8	7.318	−1.360	–	–	–	–
0.5278	1332.4	6.756	−1.321	–	–	–	–
CY (1) + IPA (2)							
0.0627	1125.0	11.093	−1.079	0.5842	1298.6	6.672	−1.667
0.1309	1159.8	9.976	−1.695	0.7067	1337.8	6.155	−1.284
0.2051	1187.7	9.121	−2.004	0.8442	1378.6	5.692	−0.736
0.2865	1212.4	8.416	−2.111	–	–	–	–
0.3759	1235.0	7.815	−2.055	–	–	–	–
0.4746	1264.1	7.225	−1.920	–	–	–	–

where $L_{f,i}$ and Z_i are the intermolecular free length and specific acoustic impedance of i-th component in the mixture, respectively. Deviations in intermolecular free length (ΔL_f) and specific acoustic impedance (ΔZ) for the binaries are listed in Table 7.

Figure 4 shows that ΔL_f values are positive for the mixtures of EE and BE, while for the remaining mixtures ΔL_f values are negative and ΔZ (depicted in Figure 5 as a function of x_1) behaves in an opposite manner to ΔL_f. Positive and negative deviations in these functions from rectilinear dependence on composition of the mixtures indicate the extent of association or dissociation between the mixing components [22]. Thus, the graded trend obtained from the values of these parameters support our earlier results.

Several semi-empirical models have been proposed to estimate kinematic viscosities ($\nu = \eta\rho^{-1}$) of the binary liquid mixtures in terms of pure-component data. Here we have

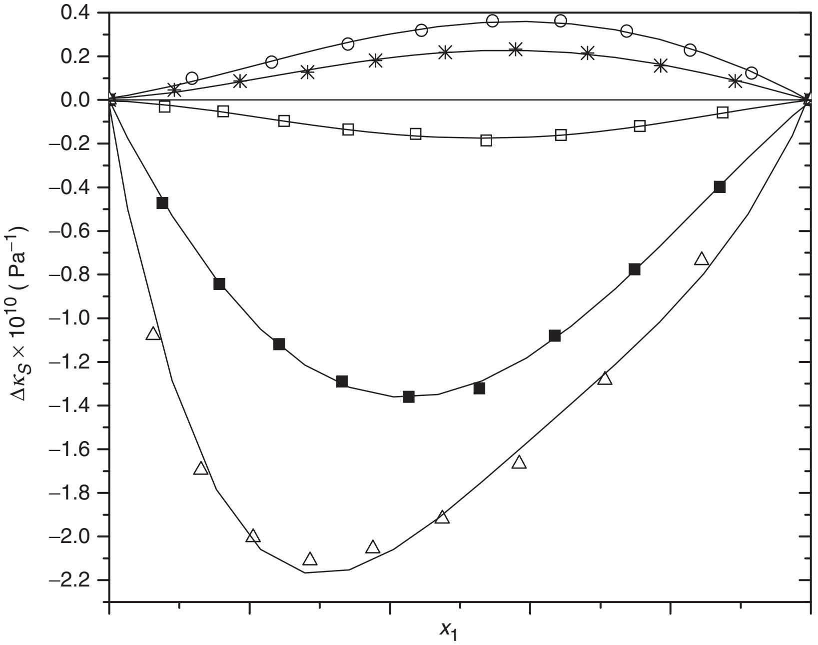

Figure 3. Plot of deviation in isentropic compressibility ($\Delta\kappa_S$) against mole fraction (x_1) of CY with ME (□), EE (∗), BE (○), DEA (■) and IPA (Δ) at 298.15 K.

Table 6. Derived values of Vander Waal's constant (*b*), molecular radius (*r*), geometrical volume (*B*), molar speed of sound (*R*), available volume (V_a), intermolecular free length (L_f), molar volume at absolute zero (V_0), molar surface area (*Y*) and specific acoustic impedance (*Z*) of the pure components at 298.15 K.

Liquids	$b \times 10^6$ (m^3)	r (nm)	$B \times 10^6$ ($m^3\,mol^{-1}$)	$R \times 10^3$ ($m^3\,mol^{-1}(m\,s^{-1})^{1/3}$)	$V_a \times 10^6$ ($m^3\,mol^{-1}$)	L_f (Å)	$V_0 \times 10^6$ ($(m^3\,mol^{-1})^{-1}$)	Y (Å^2)	$Z \times 10^6$ ($kg\,m^{-2}\,s^{-1}$)
CY	98.61	0.214	24.65	1170.1	11.89	0.4727	92.28	34.59	1.3355
ME	74.35	0.195	18.59	873.7	12.87	0.4952	66.38	28.65	1.2870
EE	91.67	0.209	22.92	1064.1	18.10	0.5191	79.33	32.95	1.2051
BE	124.83	0.231	31.21	1439.8	24.45	0.5271	107.37	40.48	1.1684
DEA	97.27	0.213	24.32	1091.0	30.72	0.6884	74.00	34.27	0.7896
IPA	79.82	0.199	19.96	888.5	28.42	0.7325	58.30	30.04	0.7330

used McAllister's three-body interaction model [30] based on Eyring's theory of reaction rates [31] and Heric–Brewer model [32] to correlate kinematic viscosities of the binary mixtures. McAllister's three-body model:

$$\begin{aligned}\ln \nu = {} & x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln \nu_{12} + 3x_2^3 x_1 \ln \nu_{21} - \ln[x_1 + x_2 M_2/M_1] \\ & + 3x_1^2 x_2 \ln[2/3 + M_2/3M_1] + 3x_2^2 x_1 \ln[1/3 + 2M_2/3M_1] \\ & + x_2^3 \ln[M_2/M_1]. \end{aligned} \tag{31}$$

Table 7. Ultrasonic speed (u), available volume (V_a), relative association (R_A), specific acoustic impedance (Z), molar speed of sound (R), molecular association (M_A), intermolecular free length (L_f), deviation in intermolecular free length (ΔL_f) and deviation in specific acoustic impedance (ΔZ) for the binary mixtures at 298.15 K.

x_1	$V_a \times 10^6$ ($m^3 mol^{-1}$)	R_A	$Z \times 10^{-6}$ ($kg m^{-2} s^{-1}$)	$R \times 10^3$ ($m^3 mol^{-1} (m s^{-1})^{1/3}$)	M_A	L_f (Å)	ΔL_f (Å)	$\Delta Z \times 10^{-6}$ ($kg m^{-2} s^{-1}$)
CY (1) + ME (2)								
0.0793	12.63	1.033	1.2936	908.87	−0.4935	0.4922	−0.0013	0.0027
0.1624	12.42	1.029	1.2996	928.61	−0.5006	0.4893	−0.0023	0.0047
0.2494	12.06	1.023	1.3083	950.68	−0.5078	0.4855	−0.0041	0.0092
0.3408	11.70	1.018	1.3169	974.65	−0.5150	0.4818	−0.0058	0.0134
0.4367	11.42	1.013	1.3242	1000.49	−0.5223	0.4787	−0.0068	0.0160
0.5377	11.05	1.008	1.3328	1029.24	−0.5296	0.4751	−0.0081	0.0198
0.6440	11.08	1.005	1.3351	1059.29	−0.5370	0.4738	−0.0070	0.0168
0.7562	11.20	1.002	1.3362	1092.42	−0.5444	0.4730	−0.0053	0.0125
0.8746	11.55	1.001	1.3351	1128.79	−0.5515	0.4730	−0.0025	0.0056
CY (1) + EE (2)								
0.0926	17.92	1.010	1.2114	1053.85	−0.5023	0.5168	0.0020	−0.0058
0.1867	17.69	1.010	1.2179	1063.66	−0.5094	0.5143	0.0039	−0.0115
0.2824	17.45	1.009	1.2247	1073.76	−0.5164	0.5117	0.0057	−0.0172
0.3797	17.26	1.009	1.2308	1083.92	−0.5232	0.5095	0.0080	−0.0238
0.4787	16.96	1.009	1.2384	1094.92	−0.5301	0.5067	0.0097	−0.0291
0.5793	16.48	1.008	1.2491	1107.04	−0.5367	0.5027	0.0104	−0.0316
0.6818	15.75	1.007	1.2644	1120.49	−0.5423	0.4972	0.0097	−0.0296
0.7860	14.66	1.005	1.2852	1135.80	−0.5476	0.4898	0.0072	−0.0223
0.8920	13.40	1.003	1.3085	1152.25	−0.5529	0.4818	0.0040	−0.0129
CY (1) + BE (2)								
0.1180	23.55	0.981	1.1748	1338.89	−0.5335	0.5250	0.0043	−0.0133
0.2314	22.50	0.981	1.1823	1311.41	−0.5411	0.5221	0.0076	−0.0247
0.3404	21.64	0.982	1.1886	1285.63	−0.5479	0.5198	0.0112	−0.0366
0.4453	20.73	0.983	1.1971	1262.24	−0.5535	0.5168	0.0139	−0.0457
0.5463	19.79	0.985	1.2076	1240.86	−0.5576	0.5133	0.0159	−0.0521
0.6436	18.62	0.987	1.2229	1222.18	−0.5604	0.5082	0.0160	−0.0530
0.7375	17.17	0.990	1.2442	1206.15	−0.5615	0.5011	0.0141	−0.0474
0.8281	15.51	0.993	1.2710	1192.46	−0.5612	0.4924	0.0103	−0.0358
0.9155	13.76	0.997	1.3013	1180.44	−0.5600	0.4830	0.0057	−0.0201
CY (1) + DEA (2)								
0.0760	835.99	0.814	0.8360	832.74	−0.6115	0.6594	−0.0125	0.0046
0.1570	885.66	0.830	0.8857	858.71	−0.6043	0.6315	−0.0230	0.0103
0.2421	938.36	0.847	0.9384	886.89	−0.5972	0.6049	−0.0313	0.0166
0.3319	993.69	0.865	0.9937	917.41	−0.5902	0.5798	−0.0370	0.0229
0.4270	1051.28	0.884	1.0513	950.59	−0.5834	0.5564	−0.0399	0.0286
0.5278	1110.86	0.903	1.1108	986.92	−0.5770	0.5346	−0.0399	0.0331
0.6349	1162.5	0.927	1.1625	1023.91	−0.5707	0.5189	−0.0326	0.0263
0.7488	1216.07	0.951	1.2161	1065.93	−0.5659	0.5036	−0.0234	0.0177
0.8702	1271.6	0.976	1.2716	1113.49	−0.5614	0.4890	−0.0117	0.0069
CY (1) + IPA (2)								
0.0627	783.78	0.822	0.7838	664.15	−0.5785	0.7004	−0.0158	0.0129
0.1309	848.78	0.851	0.8488	691.04	−0.5576	0.6615	−0.0370	0.0369
0.2051	909.56	0.879	0.9096	719.75	−0.5398	0.6304	−0.0488	0.0529
0.2865	973.03	0.906	0.9730	753.07	−0.5255	0.6010	−0.0571	0.0674
0.3759	1042.41	0.930	1.0424	792.90	−0.5145	0.5715	−0.0633	0.0829
0.4746	1118.09	0.948	1.1181	841.94	−0.5103	0.5414	−0.0678	0.0991
0.5842	1191.67	0.961	1.1917	901.10	−0.5142	0.5146	−0.0662	0.1066
0.7067	1223.67	0.980	1.2237	963.90	−0.5250	0.5064	−0.0425	0.0649
0.8442	1265.54	0.992	1.2655	1048.76	−0.5409	0.4941	−0.0191	0.0239

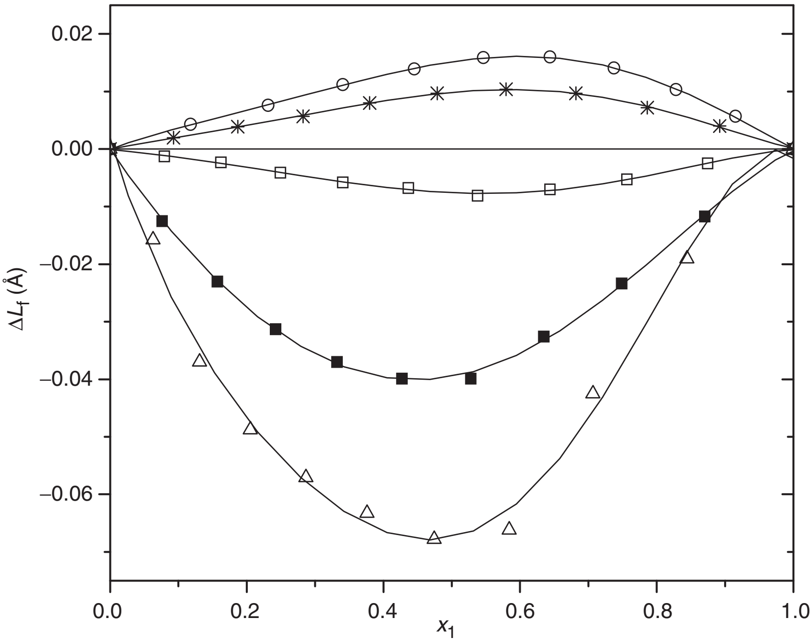

Figure 4. Plots of deviations in intermolecular free length (ΔL_f) against mole fraction (x_1) of CY with ME (□), EE (∗), BE (○), DEA (■) and IPA (Δ) at 298.15 K.

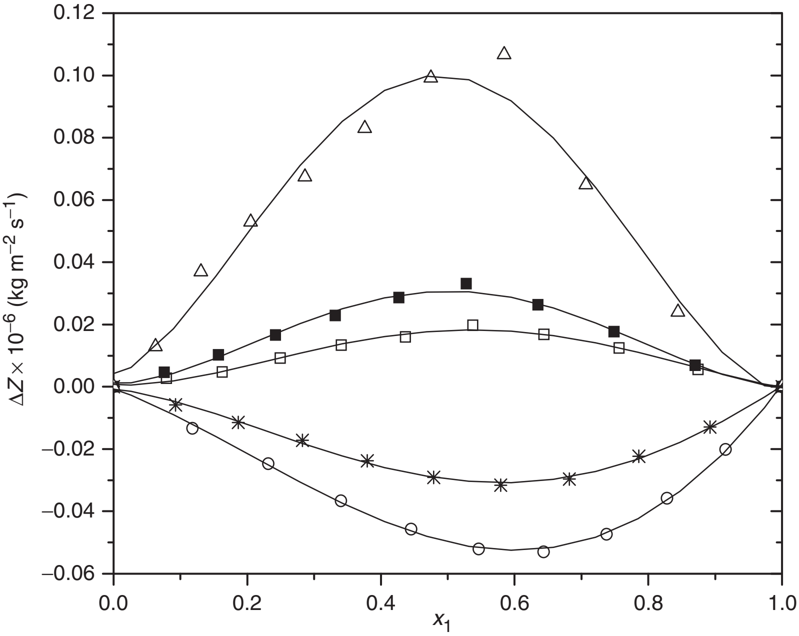

Figure 5. Plots of deviations in specific acoustic impedance (ΔZ) against mole fraction (x_1) of CY with ME (□), EE (∗), BE (○), DEA (■) and IPA (Δ) at 298.15 K.

Table 8. Values of McAllister and Heric–Brewer parameters for the binary mixtures at 298.15 K.

	McAllister's three-body model			Heric–Brewer model			
CY (1) +	ν_{12}	ν_{21}	σ	$a \times 10^2$ ($cm^2\,s^{-1}$)	$b \times 10^2$ ($cm^2\,s^{-1}$)	$c \times 10^2$ ($cm^2\,s^{-1}$)	σ
ME (2)	1.2506	1.1211	0.007	−2.1805	−1.7996	−2.2533	0.008
EE (2)	1.1852	1.3208	0.003	−1.9611	−0.9259	−2.0559	0.005
BE (2)	1.4787	2.2482	0.004	−2.2777	−0.6965	−2.0608	0.003
DEA (2)	1.1577	0.4455	0.005	−1.7733	−1.8397	−1.9865	0.007
IPA (2)	2.1886	2.2568	0.002	2.2196	−1.8546	−10.3250	0.010

Table 9. Redlich–Kister coefficients and their standard deviations (σ) for deviation properties of the binary mixtures at 298.15 K.

Excess or deviation property	a_0	a_1	a_2	a_3	σ
CY (1) + ME (2)					
$\Delta\eta$ (mPa s)	−1.635	−0.269	−0.700	–	0.01
$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})	−0.557	−0.234	0.435	0.250	0.01
ΔL_f (Å)	−0.030	−0.006	0.018	–	0.01
$\Delta Z \times 10^{-6}$ ($kg\,m^{-2}\,s^{-1}$)	0.073	0.030	−0.056	−0.037	0.00
CY (1) + EE (2)					
$\Delta\eta$ (mPa s)	−1.727	−0.357	−0.969	–	0.01
$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})	0.966	0.465	−0.572	−0.405	0.01
ΔL_f (Å)	0.039	0.021	−0.013	−0.018	0.00
$\Delta Z \times 10^{-6}$ ($kg\,m^{-2}\,s^{-1}$)	−0.120	−0.075	0.061	0.108	0.00
CY (1) + BE (2)					
$\Delta\eta$ (mPa s)	−1.861	−0.299	−0.480	−0.489	0.01
$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})	1.075	0.745	−0.418	−0.638	0.01
ΔL_f (Å)	0.060	0.027	–	–	0.01
$\Delta Z \times 10^{-6}$ ($kg\,m^{-2}\,s^{-1}$)	−0.198	−0.117	0.014	0.056	0.01
CY (1) + DEA (2)					
$\Delta\eta$ (mPa s)	−1.493	−0.242	−0.245	–	0.01
$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})	−5.288	1.967	0.617	–	0.02
ΔL_f (Å)	−0.158	0.047	0.038	–	0.01
$\Delta Z \times 10^{-6}$ ($kg\,m^{-2}\,s^{-1}$)	0.126	0.014	−0.164	−0.040	0.00
CY (1) + IPA (2)					
$\Delta\eta$ (mPa s)	3.275	1.886	−4.171	−1.365	0.03
$\Delta\kappa_S \times 10^{10}$ (Pa^{-1})	−7.468	4.162	−3.733	3.404	0.01
ΔL_f (Å)	−0.270	0.051	0.110	0.140	0.01
$\Delta Z \times 10^{-6}$ ($kg\,m^{-2}\,s^{-1}$)	0.405	0.074	−0.370	−0.366	0.01

Heric–Brewer model:

$$\nu = x_1\nu_1 + x_2\nu_2 + x_1x_2\left\{a + b(x_1 - x_2) + c(x_1 - x_2)^2\right\}, \tag{32}$$

where ν, ν_1 and ν_2 are kinematic viscosities of the mixture, the pure components 1 and 2, respectively. ν_{12}, ν_{21}, a, b and c are model parameters and x_i and M_i are the mole fraction and molecular weight of the i-th pure component in the mixture, respectively. The calculated coefficients are listed in Table 8, where the standard deviation (σ) values for McAllister's three-body model and Heric–Brewer model were in the range of 0.002–0.007 and 0.003–0.010, respectively; the smaller σ values for McAllister's three-body model indicated that it is a better one than Heric–Brewer model to describe the viscosities of the studied binary mixtures. Similar to V_m^E values $\Delta\eta$, $\Delta\kappa_S$, ΔL_f and ΔZ are also fitted to the Redlich–Kister polynomial Equation (2) to obtain the multiple-regression coefficients, a_i as listed in Table 9 along with their corresponding standard deviations (σ) calculated by Equation (3). In the present study, the small σ values in the range 0.00–0.04 for V_m^E, $\Delta\eta$, $\Delta\kappa_S$, ΔL_f and ΔZ indicated that the system under study are quite systematic and function of the binary compositions.

4. Conclusion

In summary, the study revealed that amine systems are characterised by the presence of strong hydrogen bond interaction between the mixing liquids and the strength of interaction follows the order: primary amine > secondary amine; also steric and other effects play a pivotal role in this regard. On the contrary, alkoxyethanols systems are characterised by the presence of weak intermolecular interaction probably due to the formation of intramolecular associates *via* the interaction of the etheric oxygen and hydrogen of –OH group in the same alkoxyethanol molecule.

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