Density, Viscosity, and Speed of Sound of (1-Octanol + 2-Methoxyethanol), (1-Octanol + *N*,*N*-Dimethylacetamide), and (1-Octanol + Acetophenone) at Temperatures of (298.15, 308.15, and 318.15) K

Arijit Bhattacharjee and Mahendra Nath Roy*

Department of Chemistry, North Bengal University, Darjeeling 734013, India

Densities and viscosities of the binary mixtures of 1-octanol + 2-methoxyethanol (2ME), + *N*,*N*-dimethylacetamide (DMAc), and + acetophenone (APH) were measured over the entire range of composition at $T = (298.15, 308.15, \text{ and } 318.15)$ K. Ultrasonic speeds of these binary mixtures have also been measured at 298.15 K. From the experimental data, values of excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and excess isentropic compressibility (κ_S^E) have been calculated. These results were fitted to the Redlich−Kister polynomial equation. Partial molar volumes of 2ME/DMAc/APH in 1-octanol at infinite dilution and at different temperatures have also been evaluated. The results were discussed in terms of molecular interactions prevailing in the mixtures. The measured viscosities were correlated with McAllister's three-body interaction model.

Introduction

The mixing of different solvents gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of solvent mixtures correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute−solute, solute−solvent, and solvent−solvent species. 1-Octanol occurs naturally in the form of esters in some essential oils. The primary use of 1-octanol is in the manufacturing of various esters (both synthetic and naturally occurring), such as octyl acetate, which are used in perfumery and flavors. Other uses include experimental medical applications utilizing 1-octanol to control essential tremor and other types of involuntary neurological tremors. 2-Methoxyethanol (2ME) finds a wide range of applications of technological importance, namely, as solvents and solubilizing agents in organic synthesis, reaction kinetics, and electrochemical studies.[1] *N*,*N*-Dimethylacetamide (DMAc) is useful as a medium for strong bases such as sodium hydroxide. DMAc is commonly used as a solvent for fibers or in the adhesive industry. It is also employed in the production of pharmaceuticals and plasticizers as a reaction medium. Acetophenone (APH), a typical ketone, has been used in perfumery and as a hypnotic under the name "hypnone". It is also used as a solvent for cellulose ethers.

Hence, we report in this paper the experimental values of densities ρ and viscosities η for the binary mixtures of 1-octanol (1) with 2ME (2), DMAc (2), and APH (2) over the entire range of compositions at $T = (298.15, 308.15, \text{ and } 318.15)$ K and $p = 0.1$ MPa. Also, the experimental values of ultrasonic speeds of sound u have been reported at $T = 298.15$ K and at the same pressure.

From the measured ρ data, excess molar volumes, V^E, have been calculated at each temperature. Partial molar volumes, $\bar{V}^0_{\phi,2}$, of 2ME/DMAc/APH in 1-octanol have also been calculated. The derived functions, V^E and $V_{\phi,2}$, have been used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures. We have chosen thermodynamic methods for this study, as these methods are important because changes in properties of the system caused by variations of temperature and composition can be studied without any reference to assumptions, models, or hypotheses.[2]

Experimental Section

Materials. 1-Octanol and DMAc were Fluka chemicals. The purity of the chemical was stated to be more than 99 % on a molar basis. So the reagents were used as such without any purification.

2-ME and APH were purified in similar ways as described previously.[3]

The purity of each compound was ascertained by the constancy of the density and also from viscosities, and their values were in good agreement with values found in the literature,[1,3–12] as reported in Table 1.

Apparatus and Procedures. All binary mixtures were prepared gravimetrically in airtight bottles. The mass measurements were performed on a digital electronic balance (model: Mettler, AG 285, Switzerland) with an uncertainty of ± 0.0001 g. The binary mixtures were prepared just before use. The uncertainty in mole fraction was estimated to be < ± 0.0001. Caution was taken to prevent the evaporation of the solutions after preparation. The required properties of the mixture were determined on the same day. Density measurements of binary mixtures were performed at atmospheric pressure at $T = (298.15, 308.15, \text{ and } 318.15)$ K by means of a vibrating-tube densimeter (model: DMA 4500, Anton Paar) which was calibrated with distilled water and air. The uncertainty in the density measurement was $\pm\ 0.0005\ \text{g}\cdot\text{cm}^{-3}$. The temperature was automatically kept constant within ± 0.01 K. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water.

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* Corresponding author. E-mail: mahendraroy2002@yahoo.co.in. Tel.: +91-353-2776381. Fax: + 91-353-2699001.

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Table 1. Experimental Results for Pure Components

		$\rho \cdot 10^{-3}$/kg·m^{-3}		$\eta \cdot 10^{3}$/kg·m^{-1}·s^{-1}		u/m·s^{-1}		$\alpha \cdot 10^{-3}$/K^{-1}	C_p°
solvent	T/K	expt.	lit.	expt.	lit.	expt.	lit.	expt.	J·mol^{-1}·K^{-1}
1-octanol	298.15	0.8215	0.8211[4]	7.365	7.363[4]	1349.1	1347.3[5]	0.852[a]	308.39[6]
	308.15	0.814	0.8142[4]	5.251	5.256[4]				
	318.15	0.8077	0.8078[4]	3.865	3.868[4]				
2ME	298.15	0.9595	0.9597[1]	1.543	1.543[1]	1339.3	1339.3[1]	0.867[a]	172.43[7]
	308.15	0.9521	0.9525[1]	1.256	1.257[1]				
	318.15	0.9458	0.9462[1]	1.047	1.051[1]				
DMAc	298.15	0.9372	0.9366[8]	0.937	0.937[9]	1458.2	1458[10]	1.067[a]	178.0[9]
	308.15	0.9258	0.9262[11]	0.841					
	318.15	0.9171	0.9172[11]	0.763					
APH	298.15	1.0231	1.0231[3]	1.653	1.653[3]	1296.2	1296.4[3]	0.860[a]	198.4[12]
	308.15	1.0149	1.0148[3]	1.411	1.412[3]				
	318.15	1.0072	1.0075[3]	1.115	1.117[3]				

[a] Derived from our measured densities.

The viscosity was measured by means of a suspended Ubbelohde type viscometer, which was calibrated at 298.15 K with triple-distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was within ± 0.003 mPa·s of the reported value.

The speeds of sound were determined by a multifrequency ultrasonic interferometer (model: Mittal Enterprise, New Delhi) working at 5 MHz. The apparatus has been tested with water, methanol, and benzene at 298.15 K. The details of the methods and techniques have been described earlier.[13] The uncertainty of ultrasonic speed measurements is $\pm\ 0.2\ \mathrm{m \cdot s^{-1}}$.

Results and Discussion

The experimental densities, ρ, viscosities, η, and speed of sound, u, for the binary mixtures studied at $T = (298.15, 308.15,$ and $318.15)$ K are reported in Table 2. Furthermore, excess molar volumes, V^{E}, and viscosity deviations, $\Delta\eta$, at $T = (298.15,$ $308.15,$ and $318.15)$ K, and the excess isentropic compressibilities, κ_S^{E}, investigated at $T = 298.15$ K are also reported in Table 3.

The plots of V^{E} and $\Delta\eta$ over the entire range of composition at $T = (298.15, 308.15,$ and $318.15)$ K against mole fractions of 1-octanol, x_1, are represented in Figures 1 and 2, respectively, and the same for κ_S^{E} against the mole fraction of 1-octanol, x_1, at 298.15 K is depicted in Figure 3.

Excess Molar Volume. The excess molar volumes, V^{E}, for the mixtures were calculated using the following equation,

$$V^{\mathrm{E}} = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{1}$$

where ρ is the density of the mixture and M_i, x_i, and ρ_i are the molecular weight, mole fraction, and viscosity of the ith component in the mixture, respectively. The estimated uncertainty for excess molar volume, V^{E}, is $\pm\ 0.005 \cdot 10^{6}\ \mathrm{m^3 \cdot mol^{-1}}$.

Excess molar volumes, which are a measure of the deviations of the actual property from the property if the system behaves ideally, give information on molecular interactions between the component molecules of the mixture and are influenced by effects such as differences in shape and size of the component molecules, reorientation of the component molecules in the mixture, and intermolecular interactions.[14,15]

The curves in Figure 1 reveal that the values of V^{E} are positive over the entire mole fraction of 1-octanol for all three systems investigated and follows the sequence: APH > DMAc > 2ME. Such behavior is the result of contributions from several contraction and expansion processes that proceed simultaneously when APH/DMAc/2ME octanol "molecules" are formed. The following effects are considered: (i) the disruption of liquid order upon mixing and unfavorable interactions, that is, the dominance of dispersion forces[16,17] between unlike molecules produce positive contributions to V^{E}; (ii) a possible decrease in association through hydrogen-bond formation between the mixing components; and (iii) the interstitial accommodation of the smaller molecules into the voids created by large molecules due to the difference in molar volumes. The observed positive V^{E} values suggest that the combined effects of i and ii exceeds the iii effect due to the packing of smaller molecules of 2ME (molar volume $= 79.312\ \mathrm{cm^3 \cdot mol^{-1}}$), DMAc (molar volume $= 92.958$ $\mathrm{cm^3 \cdot mol^{-1}}$), and APH (molar volume $= 117.437\ \mathrm{cm^3 \cdot mol^{-1}}$) into the voids created by larger molecules of larger molecules of 1-octanol (molar volume $= 158.527\ \mathrm{cm^3 \cdot mol^{-1}}$) at 298.15 K.

It has been reported[18,19] that liquids of different molecular sizes mix into each other's structure and, thereby, decrease the volume of the mixture. Thus, a decrease in positive V^{E} values as we move from APH to 2ME clearly suggests increasingly better packing (on account of the increasing difference in molar volume of 1-octanol and APH, DMAc, and 2ME) of the component molecules in the mixture and justifies the observed trend.

Alcohols themselves are strongly self-associated with the degree of association depending on such variables as molecular size, position of the OH group, and temperature. Because of the electron-donating inductive effect of the alkyl group, the strength of bonding in alcohols is expected to decrease with an increase in the molecular size, implying that higher alcohols have a smaller proton-donating capacity and consequently attributing this to the diminished presence of hydrogen-bond effects, thereby yielding positive V^{E} values.

As the temperature increases, V^{E} values increase for all of the mixtures over the entire mole fraction range and, thereby, suggest a decrease in the strength of interactions between the component molecules.

Furthermore, the extent of interactions between the component molecules in a mixture is well-reflected in the parameters like apparent molar volume and partial molar volume.[20,21] The apparent molar volumes $V_{\phi,2}$ of 2ME, DMAc, and APH in 1-octanol were calculated by using[20]

$$V_{\phi,2} = V_2^{*} + \left(\frac{V^{\mathrm{E}}}{x_2}\right) \tag{2}$$

Table 2. Values of Density, ρ, Viscosity, η, and Speed of Sound, u, for the Binary Liquid Mixtures under Investigation

x_1	$\rho \cdot 10^{-3}$ / $\mathrm{kg \cdot m^{-3}}$	$\eta \cdot 10^{3}$ / $\mathrm{kg \cdot m^{-1} \cdot s^{-1}}$	u / $\mathrm{m \cdot s^{-1}}$	x_1	$\rho \cdot 10^{-3}$ / $\mathrm{kg \cdot m^{-3}}$	$\eta \cdot 10^{3}$ / $\mathrm{kg \cdot m^{-1} \cdot s^{-1}}$	u / $\mathrm{m \cdot s^{-1}}$
1-Octanol + 2ME (298.15 K)							
0.0000	0.9595	1.543	1339.3	0.4671	0.8699	2.774	1315.4
0.0610	0.9430	1.677	1334.3	0.5769	0.8570	3.432	1320.0
0.1275	0.9271	1.822	1329.3	0.7004	0.8446	4.238	1326.5
0.2003	0.9121	1.983	1323.0	0.8402	0.8328	5.412	1335.8
0.2804	0.8974	2.145	1318.0	1.0000	0.8215	7.365	1349.1
0.3688	0.8834	2.408	1314.6				
1-Octanol + 2ME (308.15 K)							
0.0000	0.9521	1.256		0.4671	0.8629	2.190	
0.0610	0.9356	1.368		0.5769	0.8500	2.670	
0.1275	0.9200	1.454		0.7004	0.8376	3.190	
0.2003	0.9049	1.582		0.8402	0.8256	4.012	
0.2804	0.8905	1.749		1.0000	0.8140	5.251	
0.3688	0.8764	1.948					
1-Octanol + 2ME (318.15 K)							
0.0000	0.9458	1.047		0.4671	0.8570	1.781	
0.0610	0.9295	1.141		0.5769	0.8440	2.062	
0.1275	0.9138	1.209		0.7004	0.8315	2.466	
0.2003	0.8988	1.304		0.8402	0.8194	3.064	
0.2804	0.8844	1.426		1.0000	0.8077	3.865	
0.3688	0.8705	1.571					
1-Octanol + DMAc (298.15 K)							
0.0000	0.9372	0.937	1458.2	0.5009	0.8623	2.399	1353.4
0.0692	0.9235	1.072	1433.5	0.6095	0.8514	3.111	1348.5
0.1433	0.9104	1.246	1412.4	0.7280	0.8409	4.009	1346.4
0.2228	0.8977	1.418	1390.3	0.8576	0.8309	5.318	1348.0
0.3084	0.8855	1.702	1372.5	1.0000	0.8215	7.365	1349.2
0.4008	0.8737	2.023	1360.0				
1-Octanol + DMAc (308.15 K)							
0.0000	0.9258	0.841		0.5009	0.8539	1.893	
0.0692	0.9127	0.942		0.6095	0.8434	2.406	
0.1433	0.9002	1.063		0.7280	0.8331	2.988	
0.2228	0.8881	1.194		0.8576	0.8234	3.849	
0.3084	0.8763	1.376		1.0000	0.8140	5.251	
0.4008	0.8648	1.614					
1-Octanol + DMAc (318.15 K)							
0.0000	0.9171	0.763		0.5009	0.8470	1.585	
0.0692	0.9044	0.851		0.6095	0.8367	1.935	
0.1433	0.8922	0.947		0.7280	0.8266	2.350	
0.2228	0.8804	1.046		0.8576	0.8169	2.965	
0.3084	0.8689	1.185		1.0000	0.8077	3.865	
0.4008	0.8578	1.361					
1-Octanol + APH (298.15 K)							
0.0000	1.0231	1.653	1296.2	0.5805	0.8898	2.997	1281.8
0.0930	0.9977	1.713	1278.5	0.6828	0.8713	3.650	1295.4
0.1874	0.9737	1.831	1266.5	0.7868	0.8538	4.475	1311.1
0.2834	0.9512	1.994	1263.3	0.8925	0.8371	5.625	1327.8
0.3808	0.9297	2.205	1264.7	1.0000	0.8215	7.365	1349.2
0.4799	0.9093	2.519	1271.8				
1-Octanol + APH (308.15 K)							
0.0000	1.0149	1.411		0.5805	0.8825	2.400	
0.0930	0.9897	1.528		0.6828	0.8641	2.799	
0.1874	0.9661	1.669		0.7868	0.8466	3.249	
0.2834	0.9436	1.785		0.8925	0.8299	3.931	
0.3808	0.9222	1.949		1.0000	0.8140	5.251	
0.4799	0.9020	2.167					
1-Octanol + APH (318.15 K)							
0.0000	1.0072	1.115		0.5805	0.8760	1.807	
0.0930	0.9824	1.208		0.6828	0.8577	2.095	
0.1874	0.9589	1.327		0.7868	0.8402	2.432	
0.2834	0.9366	1.424		0.8925	0.8236	2.926	
0.3808	0.9155	1.535		1.0000	0.8077	3.865	
0.4799	0.8953	1.671					

where V_2^* is the molar volume of 2ME/DMAc/APH. The partial molar volumes, $\bar{V}^0_{\phi,2}$ of 2ME, DMAc, and APH in 1-octanol at infinite dilution were obtained by the method described earlier.[21,22] The deviations in $V_{\phi,2}$ at infinite dilution, ΔV, were calculated by using[22]

$$\Delta V = \bar{V}^0_{\phi,2} - V_2^* \qquad (3)$$

The values of $\bar{V}^0_{\phi,2}$, V_2^*, and ΔV are listed in Table 4. It is clear from Table 4 that the values of ΔV are positive (i.e., the partial molar volumes, $\bar{V}^0_{\phi,2}$, of 2ME/DMAc/APH in 1-octanol at infinite dilution are greater than their corresponding molar volumes in the pure state, V_2^*), suggesting that on mixing there is an expansion in the volume of the mixture, which may be due to the presence of weak interactions between the component

Table 3. Values of Excess Molar Volume, V^E, Viscosity Deviation, $\Delta\eta$, and Excess Isentropic Compressibility, κ_S^E, for the Binary Liquid Mixtures under Investigation

x_1	$V^E\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$	$\Delta\eta\cdot 10^3/\mathrm{kg\cdot m^{-1}\cdot s^{-1}}$	$\kappa_S^E/\mathrm{TPa^{-1}}$	x_1	$V^E\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$	$\Delta\eta\cdot 10^3/\mathrm{kg\cdot m^{-1}\cdot s^{-1}}$	$\kappa_S^E/\mathrm{TPa^{-1}}$
1-Octanol + 2ME (298.15 K)							
0.0610	0.041	−0.221	0.036	0.4671	0.113	−1.488	0.248
0.1275	0.068	−0.463	0.078	0.5769	0.106	−1.470	0.221
0.2003	0.087	−0.726	0.139	0.7004	0.083	−1.383	0.177
0.2804	0.104	−1.030	0.194	0.8402	0.049	−1.023	0.107
0.3688	0.109	−1.282	0.240				
1-Octanol + 2ME (308.15 K)							
0.0610	0.056	−0.132		0.4671	0.163	−0.932	
0.1275	0.086	−0.311		0.5769	0.152	−0.891	
0.2003	0.112	−0.474		0.7004	0.117	−0.864	
0.2804	0.122	−0.627		0.8402	0.073	−0.601	
0.3688	0.154	−0.781					
1-Octanol + 2ME (318.15 K)							
0.0610	0.059	−0.078		0.4671	0.236	−0.611	
0.1275	0.113	−0.197		0.5769	0.229	−0.582	
0.2003	0.147	−0.307		0.7004	0.189	−0.555	
0.2804	0.192	−0.411		0.8402	0.123	−0.351	
0.3688	0.217	−0.515					
1-Octanol + DMAc (298.15 K)							
0.0692	0.052	−0.310	0.046	0.5009	0.173	−1.758	0.216
0.1433	0.082	−0.612	0.086	0.6095	0.162	−1.744	0.189
0.2228	0.112	−0.951	0.156	0.7280	0.146	−1.607	0.144
0.3084	0.137	−1.218	0.211	0.8576	0.097	−1.131	0.068
0.4008	0.162	−1.491	0.234				
1-Octanol + DMAc (308.15 K)							
0.0692	0.064	−0.204		0.5009	0.213	−1.157	
0.1433	0.095	−0.410		0.6095	0.198	−1.123	
0.2228	0.132	−0.630		0.7280	0.170	−1.063	
0.3084	0.171	−0.825		0.8576	0.102	−0.774	
0.4008	0.204	−0.995					
1-Octanol + DMAc (318.15 K)							
0.0692	0.072	−0.127		0.5009	0.270	−0.732	
0.1433	0.130	−0.260		0.6095	0.261	−0.719	
0.2228	0.185	−0.408		0.7280	0.230	−0.671	
0.3084	0.220	−0.535		0.8576	0.150	−0.458	
0.4008	0.253	−0.645					
1-Octanol + APH (298.15 K)							
0.0930	0.071	−0.471	0.207	0.5805	0.195	−1.972	0.449
0.1874	0.119	−0.893	0.375	0.6828	0.178	−1.903	0.369
0.2834	0.152	−1.278	0.463	0.7868	0.145	−1.672	0.266
0.3808	0.175	−1.623	0.507	0.8925	0.086	−1.126	0.156
0.4799	0.187	−1.875	0.493				
1-Octanol + APH (308.15 K)							
0.0930	0.088	−0.240		0.5805	0.235	−1.240	
0.1874	0.137	−0.462		0.6828	0.213	−1.234	
0.2834	0.181	−0.714		0.7868	0.167	−1.183	
0.3808	0.213	−0.924		0.8925	0.105	−0.907	
0.4799	0.224	−1.087					
1-Octanol + APH (318.15 K)							
0.0930	0.113	−0.163		0.5805	0.314	−0.904	
0.1874	0.192	−0.303		0.6828	0.301	−0.898	
0.2834	0.242	−0.470		0.7868	0.249	−0.847	
0.3808	0.276	−0.627		0.8925	0.171	−0.643	
0.4799	0.298	−0.764					

molecules, as mentioned above. However, as the temperature increases, ΔV becomes more positive, thereby indicating the weakening of the interactions between the component molecules of the mixture.

Viscosity Deviation. The deviation in viscosities, $\Delta\eta$, was computed using the relationship

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i\eta_i) \qquad (4)$$

where η is the dynamic viscosity of the mixture and x_i and η_i are the mole fraction and viscosity of the ith component in the mixture, respectively. The estimated uncertainty for viscosity deviation, $\Delta\eta$, is ± 0.004 mPa·s.

The graphical variation of $\Delta\eta$ as a function of the mole fraction of 1-octanol at 298.15 is shown in Figure 2, which along with the values in Table 3, indicates negative viscosity deviation, for all studied binary mixtures over the entire composition range and at all experimental temperatures. The negative values imply the presence of dispersion forces between the mixing components in the mixtures.

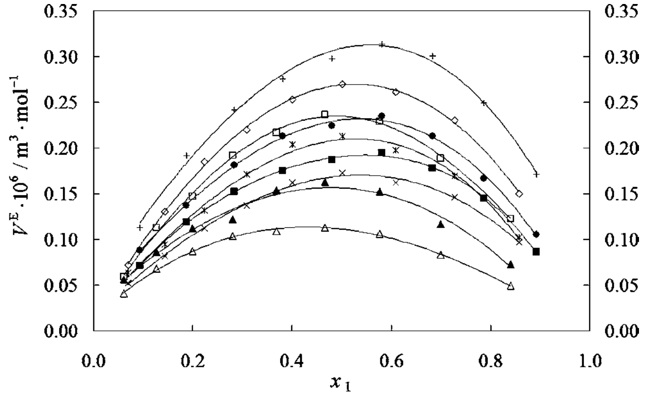

Figure 1. Excess molar volume (V^E) measured over the entire range of composition for binary mixtures of 1-octanol (1) with 2ME at △, 298.15 K; ▲, 308.15 K; □, 318.15 K; DMAc at ×, 298.15 K; ∗, 308.15 K; ◇, 318.15 K; APH at ■, 298.15 K; ●, 308.15 K; +, 318.15 K obtained from Redlich−Kister equation.

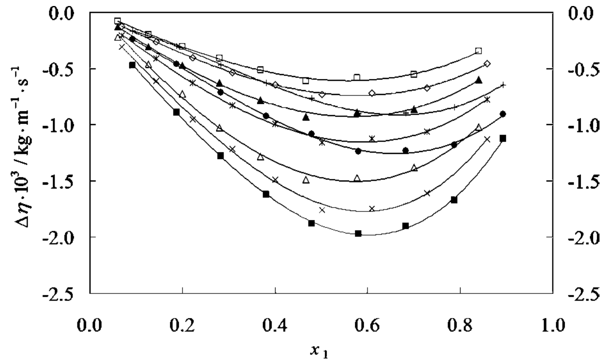

Figure 2. Viscosity deviations ($\Delta\eta$) measured over the entire range of composition for binary mixtures of 1-octanol (1) with 2ME at △, 298.15 K; ▲, 308.15 K; □, 318.15 K; DMAc at ×, 298.15 K; ∗, 308.15 K; ◇, 318.15 K; APH at ■, 298.15 K; ●, 308.15 K; +, 318.15 K obtained from Redlich−Kister equation.

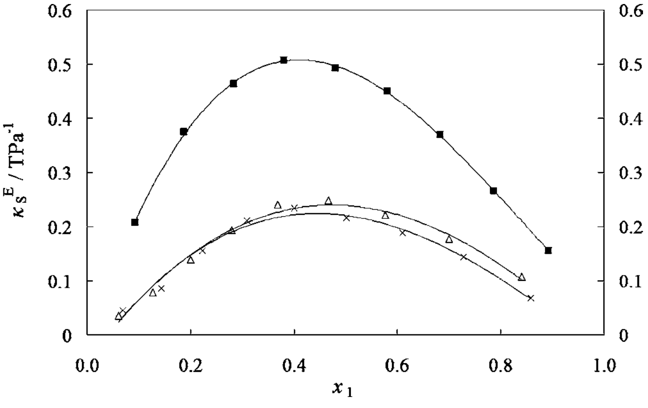

Figure 3. Excess isentropic compressibility (κ_S^E) for binary mixtures of 1-octanol (1) with △, 2ME; ×, DMAc; ■, APH at T = 298.15 K obtained from Redlich−Kister equation.

It is also evident from Table 3 that $\Delta\eta$ values of the mixtures decrease as the experimental temperatures increase, thereby suggesting an increase in the fluidity of the mixtures.[23]

Excess Isentropic Compressibility. The isentropic compressibilities, κ_S, are calculated from the experimental densities, ρ, and speeds of sound, u, using the following equations

$$\kappa_S = \frac{1}{u^2\rho} \tag{5}$$

Table 4. Values of $\bar{V}^{o}_{\phi,2}$, V_2^*, and ΔV for the Binary Liquid Mixtures at Different Temperatures

	$\bar{V}^{o}_{\phi,2}$	V_2^*	ΔV
T/K	10^{-5} m^3·mol^{-1}		
	1-Octanol + 2ME		
298.15	8.59	7.93	0.66
308.15	8.71	7.99	0.72
318.15	8.81	8.05	0.76
	1-Octanol + DMAc		
298.15	9.96	9.29	0.67
308.15	10.09	9.41	0.68
318.15	10.22	9.49	0.73
	1-Octanol + APH		
298.15	13.05	11.74	1.31
308.15	13.21	11.84	1.37
318.15	13.39	11.93	1.46

The excess isentropic compressibilities were calculated from

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{6}$$

where the isentropic compressibility of the ideal solution, κ_S^{id}, was computed using the relation[24–26]

$$\kappa_S^{id} = \sum \phi_i \left\{ \frac{\kappa_{S,i}^o + TV_i^o(\alpha_i^o)^2}{C_{p,i}^o} \right\} - \left\{ \frac{T(\sum x_i V_i^o)(\sum \phi_i \alpha_i^o)^2}{\sum x_i C_{p,i}^o} \right\} \tag{7}$$

where T is the temperature; x_i is the mole fraction of the pure component in the mixture; $C_{p,i}^o$, V_i^o, and α_i^o are the isobaric heat capacity, molar volume, and isobaric thermal expansion coefficient of pure component i, respectively. ϕ_i is the ideal volume fraction of pure component i in the mixture. The values of α_i^o and $C_{p,i}^o$ used for these calculations are listed in Table 1.

The isobaric thermal expansion coefficients, α, have been calculated from the density fitting equation:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{8}$$

Table 3 shows that κ_S^E values are positive for the three binary systems over the entire range of compositions at 298.15 K. The graphical variation of κ_S^E as a function of 1-octanol mole fraction, x_1, for the binary mixtures at 298.15 K is presented in Figure 3. The behavior of excess molar volumes seems to be consistent with a obtained values of κ_S^E. Positive values of κ_S^E mean that the mixture is more compressible than the corresponding ideal mixture, suggesting presence of weak interactions between the component molecules, as mentioned above.

Redlich−Kister Polynomial Equation. The excess (V^E and κ_S^E) and derived ($\Delta\eta$) properties were fitted to the Redlich−Kister polynomial equation[27]

$$Y^E = x_1 x_2 \sum_{i=1}^{k} a_i (x_1 - x_2)^i \tag{9}$$

where Y^E refers to excess and derived properties; x_1 and x_2 are the mole fraction of 1-octanol and the other component, respectively. The coefficients a_i were obtained by fitting eq 9 to experimental results using a least-squares regression method.

Table 5. Redlich−Kister Coefficients, a_k, and Standard Deviations, σ, for the Binary Mixtures at Different Temperatures

	T/K	a_0	a_1	a_2	a_3	a_4	σ
				1-Octanol + 2ME			
$V^E \cdot 10^6$/m$^3\cdot$mol^{-1}	298.15	0.934	−0.040				0.003
	308.15	0.626	−0.127				0.007
	318.15	0.448	−0.103	−0.030	−0.124	0.183	0.001
$\Delta\eta \cdot 10^3$/kg$\cdot$m$^{-1}\cdot$s^{-1}	298.15	1.070	0.117	0.161			0.002
	308.15	0.833	0.044				0.006
	318.15	0.673	0.081	0.121			0.004
κ_S^E/TPa^{-1}	298.15	0.970	−0.393	−0.292	1.481	−0.229	0.002
				1-Octanol + DMAc			
$V^E \cdot 10^6$/m$^3\cdot$mol^{-1}	298.15	0.934	−0.040				0.004
	308.15	0.626	−0.127				0.007
	318.15	0.448	−0.103	−0.030	−0.124	0.183	0.001
$\Delta\eta \cdot 10^3$/kg$\cdot$m$^{-1}\cdot$s^{-1}	298.15	1.070	0.117	0.161			0.002
	308.15	0.833	0.044				0.006
	318.15	0.673	0.081	0.121			0.004
κ_S^E/TPa^{-1}	298.15	0.901	−0.387	−0.418	−0.505		0.007
				1-Octanol + APH			
$V^E \cdot 10^6$/m$^3\cdot$mol^{-1}	298.15	0.934	−0.040				0.004
	308.15	0.626	−0.127				0.007
	318.15	0.448	−0.103	−0.030	−0.124	0.183	0.001
$\Delta\eta \cdot 10^3$/kg$\cdot$m$^{-1}\cdot$s^{-1}	298.15	1.070	0.117	0.161			0.002
	308.15	0.833	0.044				0.006
	318.15	0.673	0.081	0.121			0.004
κ_S^E/TPa^{-1}	298.15	1.953	−0.804	0.148	0.381		0.004

Table 6. Parameters of McAllister Model and Standard Deviations for Kinematic Viscosities at Various Temperatures

	McAllister (three-body model)		
T/K	υ_{12}	υ_{21}	σ (%)
	1-Octanol + 2ME		
298.15	2.745	2.006	0.007
308.15	0.958	1.641	0.006
318.15	0.709	1.412	0.005
	1-Octanol + DMAc		
298.15	2.278	1.557	0.005
308.15	2.187	1.250	0.003
318.15	1.624	1.226	0.002
	1-Octanol + APH		
298.15	3.245	1.764	0.002
308.15	2.094	1.817	0.002
318.15	1.606	1.392	0.002

In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The calculated values of a_i along with the tabulated standard deviations (σ) are listed in Table 5.

The McAllister three-body interaction model[28] is widely used to correlate the kinematic viscosities ($\upsilon = \eta/\rho$) of the binary mixtures with mole fraction. The three-body model is defined as

$$\ln \upsilon = {x_1}^3 \ln \upsilon_1 + {x_2}^3 \ln \upsilon_2 + 3{x_1}^2 x_2 \ln \upsilon_{12} + 3{x_2}^3 x_1 \ln \upsilon_{21} - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 3{x_1}^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3{x_2}^2 x_1 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + {x_2}^3 \ln\left[\frac{M_2}{M_1}\right] \quad (10)$$

where υ, υ_1, and υ_2 are kinematic viscosities of the mixture, the pure 1-octanol and the corresponding second component, respectively. υ_{12} and υ_{21} are model parameters; M_i and x_i are the molecular weight and mole fraction of the ith pure component in the mixture. Table 6 records the parameters calculated using eq 10 along with the standard deviations. It is seen that the values of the model parameters are positive and adequate for all of the binary mixtures.

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