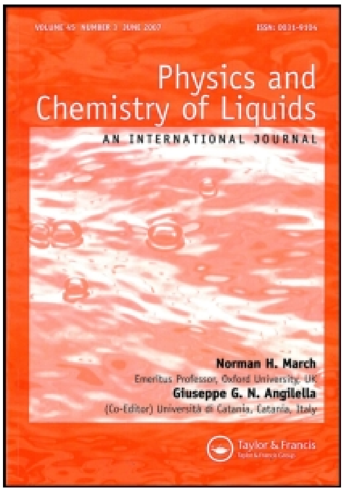

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Effect of toluene in the dipolar interaction of some aliphatic alcohols

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Sound velocity, density and viscosity values have been measured at 303 K in the three binary systems of toluene + methanol, ethanol, 1-propanol. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been estimated using the standard relations. The results are interpreted in terms of molecular interaction between the components of the mixtures. Observed excess value in all the mixture indicates that the molecular symmetry existing in the system is highly disturbed by the non-polar toluene molecules and dipole–dipole type interactions exist in the systems.

Keywords: Ultrasonic velocity; Acoustic parameters; Dipolar interactions

1. Introduction

Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variations of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [1–3] as well as strongly interacting components [4–6]. Though, a number of investigations were carried out in liquid mixtures having alcohol as one of the components a systematic study of aliphatic alcohol C_1–C_3 with toluene was not at all attempted. Furthermore, mixtures with alcohol as one component, are indispensable for the industrial rectification column to avoid the formation of azeotropes. The present work deals with the measurement of ultrasonic velocity and computation of related parameters in the system of toluene + methanol, ethanol, 1-propanol at 303 K.

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2. Experimental details

The mixtures of various concentrations in mole fraction were prepared by taking purified AR grade samples at 303 K. The ultrasonic velocities in liquid mixtures have been measured using an ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of $\pm 0.1\,\mathrm{m\,s^{-1}}$. The density and viscosity are measured using a pycknometer and an Ostwald's viscometer, respectively, with an accuracy of 3 parts in 10^5 for density and $0.001\,\mathrm{N\,s\,m^{-2}}$ for viscosity.

Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following standard expressions [7]:

$$\beta = (U^2\rho)^{-1} \tag{1}$$

$$L_\mathrm{f} = K_\mathrm{T}\beta^{1/2} \tag{2}$$

$$V_\mathrm{f} = \left[\frac{M_\mathrm{eff}U}{\eta k}\right]^{3/2} \tag{3}$$

$$\pi_\mathrm{i} = bRT\left[\frac{k\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_\mathrm{eff}^{7/6}}\right] \tag{4}$$

$$A^\mathrm{E} = A_\mathrm{exp} - A_\mathrm{id} \tag{5}$$

and

$$A_\mathrm{id} = \sum x_\mathrm{i}A_\mathrm{i} \tag{6}$$

where, K_T is the temperature-dependent constant having a value 199.53×10^{-8} in MKS system, k is a constant equal to 4.28×10^9 in MKS system, independent of temperature for all liquids, $M_\mathrm{eff} = \sum x_\mathrm{i}m_\mathrm{i}$ where, x is the mole fraction and m is the molecular weight of ith component and A^E stands for excess property of any given parameter, A_exp is the experimental value and A_id is the ideal value.

3. Results

The measured values of density, viscosity and ultrasonic velocity for the non-polar toluene mixed with polar alcohols are given in table 1.

Density and sound velocity are observed to be of increasing nature with increasing mole fraction of toluene in all the systems. The coefficients of viscosity initially increases up to 0.3 mole fraction of toluene and then decreases for methanol system but for the other two systems, a continuous decrease with increasing mole fraction of toluene is noticed. As commented by Edward Peters [8], an elevated boiling point (111°C for toluene) or a higher density is a clear indication of the extent of interaction; thus toluene has maximum intramolecular interaction than methanol. Such high intra interactions are reflected in the extent of intermolecular cases also as is noticed in the present case. The existence of such high intra interactions of toluene and the associative nature of methanol may be attributed to the increasing nature of sound velocity. As the addition

Table 1. Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303 K.

	ρ ($\mathrm{kg\,m^{-3}}$)			$\eta \times 10^3$ ($\mathrm{N\,s\,m^{-2}}$)			U ($\mathrm{m\,s^{-1}}$)		
Mole fraction of A	B	C	D	B	C	D	B	C	D
0.0000	776.0	780.5	795.6	0.501	0.983	1.634	1103.0	1130.0	1193.0
0.1006	781.5	791.6	810.3	0.549	0.821	1.367	1126.4	1145.3	1197.5
0.2012	804.0	804.2	820.2	0.599	0.786	1.171	1157.0	1177.6	1210.0
0.3009	815.6	812.6	827.6	0.585	0.724	1.025	1171.6	1189.6	1217.6
0.3981	821.6	817.0	833.3	0.578	0.686	0.902	1191.0	1204.0	1222.0
0.5016	827.5	825.3	836.4	0.573	0.643	0.785	1208.7	1216.7	1228.5
0.6052	837.2	830.2	840.0	0.566	0.613	0.699	1225.6	1228.3	1236.3
0.7001	846.4	836.8	846.4	0.562	0.602	0.645	1238.5	1240.4	1244.8
0.8095	849.3	843.9	852.2	0.559	0.569	0.598	1251.3	1253.3	1255.0
0.9011	855.3	848.6	855.3	0.537	0.551	0.546	1265.4	1269.7	1269.3
1.0000	857.8	857.8	857.8	0.526	0.526	0.526	1287.2	1287.2	1287.2

A: toluene, B: methanol, C: ethanol, D: 1-propanol.

Table 2. Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 303 K.

	$\beta \times 10^{10}$ ($\mathrm{Pa^{-1}}$)			$L_\mathrm{f} \times 10^{11}$ (m)			$V_\mathrm{f} \times 10^7$ ($\mathrm{m^3\,mol^{-1}}$)			$\pi_\mathrm{i} \times 10^{-8}$ (Pa)		
Mole fraction of A	B	C	D	B	C	D	B	C	D	B	C	D
0.0000	10.592	10.033	8.831	6.493	6.370	5.976	0.669	0.435	0.328	10.38	9.49	8.80
0.1006	10.085	9.630	8.606	6.336	6.191	5.850	0.783	0.672	0.466	8.81	7.73	7.65
0.2012	9.291	8.966	8.327	6.080	5.972	5.753	0.888	0.851	0.643	7.81	6.82	6.70
0.3009	8.932	8.696	8.150	5.960	5.880	5.691	1.137	1.101	0.852	6.66	5.97	5.95
0.3981	8.580	8.443	8.036	5.841	5.794	5.651	1.398	1.359	1.107	5.81	5.32	5.32
0.5016	8.271	8.185	7.922	5.734	5.703	5.610	1.699	1.815	1.467	5.10	4.75	4.72
0.6052	7.951	7.983	7.788	5.621	5.632	5.562	2.035	2.027	1.876	4.54	4.30	4.24
0.7001	7.702	7.767	7.624	5.531	5.552	5.503	2.357	2.314	2.269	4.13	3.97	3.89
0.8095	7.519	7.543	7.450	5.465	5.474	5.439	2.740	2.787	2.736	3.72	3.62	3.57
0.9011	7.311	7.309	7.256	5.388	5.434	5.367	3.263	3.563	3.358	3.37	3.35	3.28
1.0000	7.034	7.034	7.034	5.334	5.334	5.334	3.823	3.823	3.823	3.07	3.07	3.07

A: toluene, B: methanol, C: ethanol, D: 1-propanol.

of methanol to toluene leads to high degree of intermolecular interaction, the inertial nature of toluene is reflected initially in the trend of viscosity. However, the methyl group attached with cyclic rings freely interacts with the methyl or hydroxyl group of methanol [9], beyond 0.3 mole fraction of toluene, again viscosity decreases. For other two systems, on increasing the mole fraction of toluene, the system is having more and more ring-structured molecules and depleted of linear molecules that leads to reduce the existing particle–particle friction and thus viscosity shows continuously decreasing trend. All these trends clearly indicates the presence of intra and inter molecular interactions [10,11].

The perusal of calculated parameters of adiabatic compressibility, intermolecular free length, free volume and internal pressure for the present binary systems in table 2 reveals that β and L_f behave similar in nature whereas, V_f and π_i shows opposite trend to each other.

As toluene molecules are basic in nature due to the presence of π electrons [6,12], there are some possibilities of interactions between the alcohol and toluene. Such interactions bring the components close to each other and hence β and L_f is of decreasing magnitude.

The extent of free volume offers the knowledge of type of interaction. In the present case, an increasing trend of V_f with decreasing trend of π_i is found with increasing mole fraction of toluene. As cited already, toluene is more well-structured than alcohol and further if a given mole fraction of alcohol is replaced by same mole fraction of toluene as in the present case, only less number of toluene molecules will be existed due to its higher molecular weight. Thus, on increasing the mole fraction of toluene, total number of components in the system is reduced. This leads to the observed increase in V_f even though specific intermolecular interactions are present. Moreover, the methyl group of toluene and the methyl or hydroxyl group of ethanol can mutually form dipoles and this dipolar interaction also supports the existence of more space between the components. This is always attributed with a reduction of internal pressure as noticed.

It is to be noted that the V_f and π_i trend with respect to benzene mole fraction in ethanol system is similar to other two systems. But at lower mole fraction, free volume of ethanol systems are higher than 1-propanol systems whereas at higher mole fraction it exhibits maximum. However, in the case of π_i values, methanol systems always exhibit maximum values. The presence of a single methyl group comparatively maintain the nature of methanol and thus V_f variations by the added toluene is less at some selected mole fraction of benzene. All the variations observed in V_f and π_i parameters clearly reveals that as the number of methyl group increases, the dipole inducement is restricted.

The predictions offered by the respective excess parameters give excellent confirmations to the obtained suggestions [13,14]. The presented excess parameters in figures 1 and 2 for these binary systems reveal that, β^E and L_f^E are negative and show a specific trend.

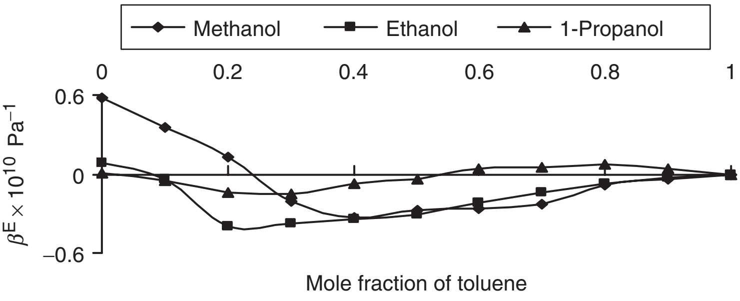

Figure 1. Mole fraction *vs*. excess adiabatic compressibilities at 303 K.

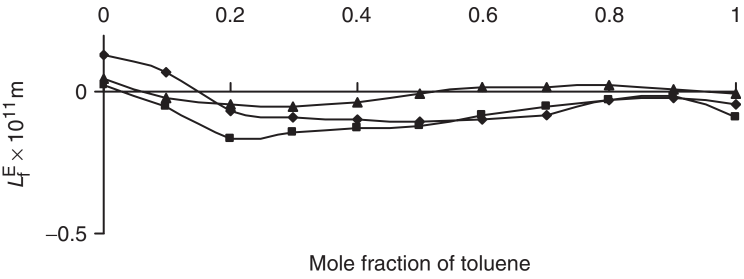

Figure 2. Mole fraction *vs*. excess intermolecular free lengths at 303 K.

In the case of methanol system, β^E shifts from positive to negative at 0.2 mole fraction of toluene whereas, for ethanol system, a dip exist at the same 0.2 mole fraction of toluene. The negative value of these parameters clearly confirms the presence of strong intermolecular interaction [15].

However, the estimated excess values in propanol system indicates that β^E, initially negative, becomes positive beyond 0.6 mole fraction of toluene, i.e., the exiting strong interaction in the system become weak at 0.6 mole fraction of toluene. This suggests that the methyl or hydroxyl group of alcohol is fully saturated by the excessive toluene molecules and so, the chances of inducement of dipoles are remote in this system. As the experimental free length is lower than that expected, components are held more close, which is possible only by the existing strong type interactions. These are reflected by the observed negative L_f^E values.

The trend shown by V_f^E and π_i^E in methanol mixtures (figures 3 and 4) are interesting that they are fully negative and follow a specific trend. A dip seems to occur at 0.5 mole fraction of toluene and clearly shows that the existing interactions are strong and are dipole–dipole type [16].

The values of V_f^E and π_i^E in ethanol system are also negative but randomly fluctuating. Such random variations clearly convey that both dipole–dipole and induced dipole–dipole interactions are existing in ethanol system.

In the case of 1-propanol system, specific variation shown by V_f^E and π_i^E, in which they exhibit negative values and shows a dip formation at 0.4 mole fraction for V_f^E and at 0.5 mole fraction for π_i^Econfirms the earlier prediction. As there are no fluctuations in these parameters, the chances of induced dipole–dipole interaction are overruled and the strong dipolar type interactions alone are confirmed.

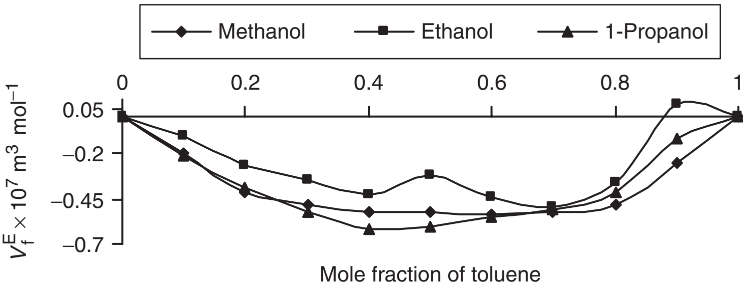

Figure 3. Mole fraction *vs.* excess free volumes at 303 K.

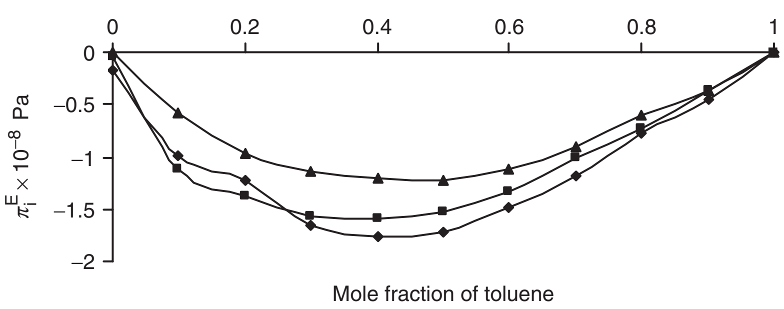

Figure 4. Mole fraction *vs.* excess internal pressures at 303 K.

4. Conclusion

Existence of specific interaction of strong magnitude is noticed in all the systems. Dipole–dipole type of interactions are existing in all the systems and, the induced dipole–dipole interactions are additionally existing in ethanol system.

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