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## Ultrasonic Analysis of Intermolecular Interaction in the Mixtures of Benzene with Methanol, Ethanol, 1-propanol

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### ABSTRACT

Sound velocity, density and viscosity values have been measured at 303 K in the three binary systems of benzene + 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 mixtures indicate that the molecular symmetry existing in the alcohol is highly disturbed by the nonpolar benzene molecules and induced dipole-dipole type interactions are predominantly exist in higher members.

**Key words:** Ultrasonic velocity, acoustic parameters, dipolar interactions, molecular symmetry

### INTRODUCTION

The ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules (Hornowski *et al.*, 2008). The variations of ultrasonic velocity (Hornowski *et al.*, 2010) and related parameters (Palaniappan, 2001) throw much light upon the structural changes associated with the liquid mixtures having strongly interacting components (Srivastava *et al.*, 2010; Thirumaran and Thenmozhi, 2010) as well as weakly interacting components (Arul and Palaniappan, 2005). Though, a number of investigations were carried out in liquid mixtures having alcohol as one of the components a systematic study of aliphatic alcohols C<sub>1</sub>-C<sub>3</sub> with benzene was not at all attempted. Alcohols are high polar and can associate with any other group having some degree of polar attractions. Though benzene is of negligible polarity, due to higher dipole moment of alcohol, temporary dipoles or induced dipoles can be formed by the inductive effects in the benzene environment which leads to pronounced interactions in the mixture. Further, mixtures with alcohols as one component are indispensable for the industrial rectification column to avoid the formation of azeotropes (Palaniappan and Mahendran, 2010). Owing to these considerations we undertake the present study of molecular association behavior of benzene with these three aliphatic alcohols. The present study deals with the measurement of ultrasonic velocity and computation of related parameters in the system of benzene+methanol, ethanol and 1-propanol at 303 K.

### MATERIALS AND METHODS

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 a fixed frequency variable path ultrasonic interferometer (Mittal type) working at 2 MHz frequency with an accuracy of  $\pm 0.1 \text{ m sec}^{-1}$ . The density and viscosity are measured using a pycnometer and an Ostwald's viscometer, respectively with an accuracy of 3 parts in  $10^5$  for density and  $0.001 \text{ Nsec m}^{-2}$  for viscosity. The temperature of the systems is maintained at 303 K using a thermostat with an accuracy of  $\pm 0.1 \text{ K}$ .

Acoustical parameters such as adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), free volume ( $V_f$ ) and internal pressure ( $p_i$ ) and their excess parameters have been calculated from the measured data using the following standard expressions (Thirumaran and Thenmozhi, 2010):

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

$$L_f = K_T \beta^{1/2} \quad (2)$$

$$V_f = \left[ \frac{M_{\text{eff}} U}{\eta k} \right]^{1/2} \quad (3)$$

$$\pi_i = bRT \left[ \frac{k\eta}{U} \right]^{1/2} \left[ \frac{\rho^{3/2}}{M_{\text{eff}}^{1/2}} \right] \quad (4)$$

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (5)$$

and:

$$A_{\text{id}} = \sum x_i A_i \quad (6)$$

where,  $K_T$  is the temperature dependent constant having a value  $199.53 \times 10^{-8}$  n MKS system,  $k$  is a constant equal to  $4.28 \times 10^9$  in MKS system, independent of temperature for all liquids:

$$M_{\text{eff}} = \sum x_i m_i$$

where,  $x$  is the mole fraction and  $m$  is the molecular weight of  $i$ th component and  $A^E$  stands for excess property of any given parameter,  $A_{\text{exp}}$  is the experimental value and  $A_{\text{id}}$  is the ideal value.

## RESULTS

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

Density and sound velocity are observed to be of increasing nature with increasing mole fraction (mf) of benzene in all the systems. The coefficients of viscosity initially increases up to 0.5 mole fraction of benzene and then decreases for methanol system but for the other two systems, a continuous decrease with increasing mole fraction of benzene is noticed. An elevated boiling point (80.0°C for benzene, whereas 64.6°C for methanol) or a higher density is a clear indication of the extent of interaction. Benzene denser than the considered alcohols, exhibit more chemical bonds and are more susceptible for any changes in the medium. Thus the chances of benzene to exercise more interactions, though it is nonpolar, are evident. Such inherent interactions of benzene and the associative nature of methanol may be attributed to the increasing nature of sound velocity.

It is evident that the addition of benzene to the alcohol leads to the compactness of the medium. As one of the components is polar whereas the other is nonpolar, the chances for compactness are restricted only to temporary effects and not dipole type or charge transfer. The Kekule structure

Table 1: Values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) at 303 K

Mole fraction of A	$\rho$ (kg m <sup>-3</sup> )			$\eta \times 10^3$ (Nsec m <sup>-2</sup> )			U (m sec <sup>-1</sup> )		
	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
0.1000	782.5	788.5	798.3	0.522	0.908	1.454	1116.7	1151.1	1197.6
0.1996	790.2	802.9	801.2	0.549	0.800	1.218	1140.0	1165.2	1204.0
0.2998	796.3	812.5	811.6	0.579	0.764	1.131	1155.7	1170.6	1211.5
0.4028	805.7	819.0	819.0	0.589	0.711	0.905	1181.6	1179.3	1218.7
0.5007	814.6	826.7	826.3	0.593	0.662	0.825	1198.6	1192.3	1221.3
0.6066	829.0	835.0	835.0	0.588	0.628	0.719	1214.6	1208.3	1224.3
0.7110	835.4	843.1	840.0	0.577	0.600	0.675	1223.3	1219.1	1230.0
0.8010	849.8	851.3	851.1	0.576	0.589	0.630	1236.6	1234.6	1238.3
0.9006	856.2	857.6	859.4	0.575	0.579	0.609	1249.9	1251.3	1243.6
1.0000	868.2	868.1	868.1	0.573	0.573	0.573	1282.2	1282.2	1282.2

A: Benzene; B: Methanol; C: Ethanol; D-1: Propanol

of benzene and the resonating electrons make it to be available for the formation of temporary dipoles. In case if no electrons are available, then the saturated molecule as a whole supports the inherent dispersive interactions. Thus benzene molecules are found to possess either the permanent dispersive nature or temporary dipole nature or both.

Alcohols in general can interact and dissolve both polar and nonpolar components. The hydrocarbon chain acts as hydrophobic that can dissolve the nonpolar and the hydroxyl group as hydrophilic which can dissolve the polar components. The chain length of the hydrocarbon is one among the many parameters that decides the extent of interactions. This makes it clear that whether benzene has given its Kekule electrons or not, intermolecular interactions are evident in between the benzene and alcohol combination.

As the hydrophobic group in methanol is shorter and being linear, the physical area associated with the group is also less and hence methanol is having very low coefficient of viscosity. The addition of benzene, a three dimensional molecule, favourably offer additional area in different planes and hence the coefficient of viscosity increases initially. As benzene fraction becomes 0.5 M, the compactness of the benzene molecules restricts the availability of area in different planes and hence the coefficient of viscosity decreases. Further at higher mole fractions, the delocalization of C-C benzene bonds are available more and they freely interacts with the methylene or hydroxyl group of methanol (Peters, 1982), beyond 0.5 mf of benzene, again viscosity decreases. For the other two systems as the hydrophobic chain itself can offer considerable area of contact and the addition of benzene disturbs the existing area and hence coefficient of viscosity shows a continuous decreasing trend. Moreover, the presence of more number of methylene groups supports the interactions of benzene that leads to reduce the existing particle-particle friction and thus viscosity shows continuously decreasing trend. All these trends clearly indicate the presence of inter molecular interactions (Narendra *et al.*, 2011).

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  $\beta$  and  $L_f$  behave similar in nature whereas,  $V_f$  and  $\pi_1$  shows opposite trend to each other.

As benzene molecules are basic in nature due to the presence of p electrons (Deshpande and Bhatgadde, 1968) the possibilities of interactions between the alcohol and benzene are definite. Such interactions bring the components close to each other and hence  $\beta$  and  $L_f$  is of decreasing magnitude.

Table 2: Values of adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), free volume ( $V_f$ ) and internal pressure ( $p_i$ ) at 303 K

Mole fraction of A	$\beta \times 10^{10} (\text{Pa}^{-1})$			$L_f \times 10^{11} (\text{m})$			$V_f \times 10^7 (\text{m}^3 \text{mol}^{-1})$			$p_i \times 10^{-8} (\text{Pa})$		
	B	C	D	B	C	D	B	C	D	B	C	D
0.0000	10.592	10.033	8.831	6.493	6.320	5.926	0.699	0.435	0.328	10.38	9.40	8.80
0.1000	10.248	9.571	8.733	6.388	6.172	5.896	0.784	0.481	0.409	9.05	8.36	8.01
0.1996	9.737	9.181	8.610	6.226	6.044	5.853	0.897	0.611	0.559	8.04	7.36	7.14
0.2998	9.402	8.981	8.394	6.118	5.977	5.779	0.988	0.824	0.657	7.30	6.73	6.65
0.4028	8.889	8.779	8.220	5.946	5.909	5.718	1.154	0.966	0.690	6.54	6.10	5.79
0.5007	8.544	8.509	8.113	5.829	5.816	5.680	1.328	1.335	1.015	5.94	5.53	5.38
0.6066	8.201	8.202	7.989	5.701	5.710	5.636	1.557	1.596	1.215	5.39	5.06	4.90
0.7110	7.999	7.980	7.868	5.638	5.631	5.593	1.818	1.853	1.558	4.88	4.70	4.62
0.8010	7.695	7.706	7.662	5.529	5.533	5.519	2.033	2.085	1.787	4.57	4.41	4.36
0.9006	7.377	7.450	7.523	5.412	5.439	5.468	2.294	2.328	2.196	4.23	4.10	4.19
1.0000	7.006	7.006	7.006	5.273	5.273	5.323	2.609	2.609	2.609	3.92	3.92	3.92

A: Benzene; B: Methanol; C: Ethanol; D-1; Propanol

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  $\pi_i$  is found with increasing mole fraction of benzene. As cited already, benzene is better structured than alcohol and further if a given mole fraction of alcohol is replaced by same mole fraction of benzene as in the present case, number of benzene molecules will be less due to its higher molecular weight. Thus, on increasing the mole fraction of benzene, total number of components in the system is reduced. This also suggests the observed increase in  $V_f$  even though specific intermolecular interactions are present. Moreover, the transient Kekule electrons of benzene and the methylene or hydroxyl group of alcohol can mutually form induced dipoles and this temporary 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  $\pi_i$  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 is lower than methanol systems whereas at higher mole fraction it exhibits maximum. However, in the case of  $\pi_i$  values, the lower member, methanol systems always exhibit maximum values. The symmetry that exists in the single methyl group that maintains the nature of methanol is highly disturbed by the resonating electrons of benzene. This situation seems to be highly counteracted by the presence of more methylene groups in higher members. Thus  $V_f$  variations by the added benzene is high at lower mole fraction of benzene in methanol system. Further, it is a well known fact that the hydrophilic and the hydrophobic groups, of ethanol in particular, can effectively interact with the polar and nonpolar groups. Hence, considering benzene anyway as a weak polar due to its resonating electrons or as nonpolar due to its closed ring structure, ample chances are there for the existence of temporary dipole or dispersive type interactions. All the variations observed in  $V_f$  and  $\pi_i$  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 in similar systems (Pandey *et al.*, 2004). The presented excess parameters in Fig. 1 and 2 for these binary systems reveal that,  $\beta^E$  and  $V_f^E$  are negative for ethanol system at lower mf and show a specific trend.

In the case of methanol and 1-propanol systems,  $\beta^E$  shifts remain in positive side whereas for ethanol system it goes to negative side also. For ethanol system, a dip exists at 0.2 M fraction of benzene. The existence of negative value of these parameters clearly confirms the presence of

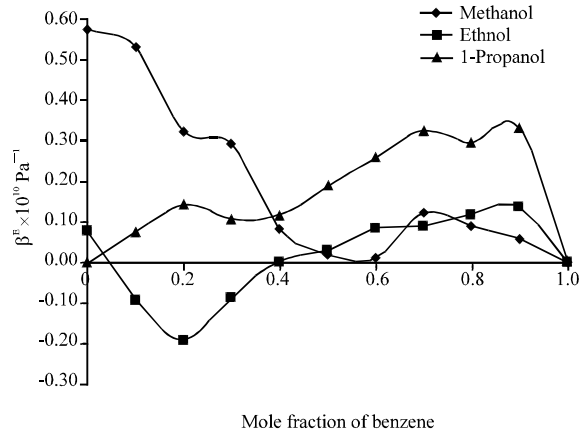


Fig. 1: Mole fraction vs. excess adiabatic compressibilities at 303 K

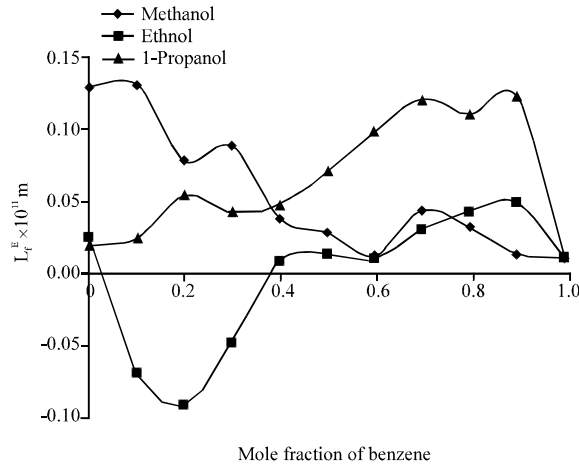


Fig. 2: Mole fraction vs. excess intermolecular free lengths at 303 K

strong intermolecular interaction (Arul *et al.*, 2008) in butanol systems though other systems are also having specific interactions. It is to be noted that, though all the alcohols are having hydrophobic and hydrophilic groups, it is only the ethanol that can show excellent dissolution of polar and nonpolar molecules. This may be due to the exact preferential hydrogen bonding network of the ethanol (Kolling, 1996). Further it is quite reasonable to think that the p electrons of benzene and the H atom of the hydrophobic group can interact favourably and forms hydrogen bond that can support the existing induced dipole-dipole interactions. This leads to the suggestion or relative stronger degree of interaction in ethanol system. This is attributed to the observed negative excess value of the adiabatic compressibility in ethanol system.

It is interesting to note that methanol system approaches the ideality nearly at 0.6 mf of benzene whereas for ethanol system it is nearly at 0.4 mf and 1-propanol has no ideality tendency. As the hydroxyl group is common in all the three, the observed deviations may be attributed to the presence of more methylene groups. This decreasing mf of benzene with increasing chain length of alcohol to approach ideality reveals that the methylene groups are having considerable

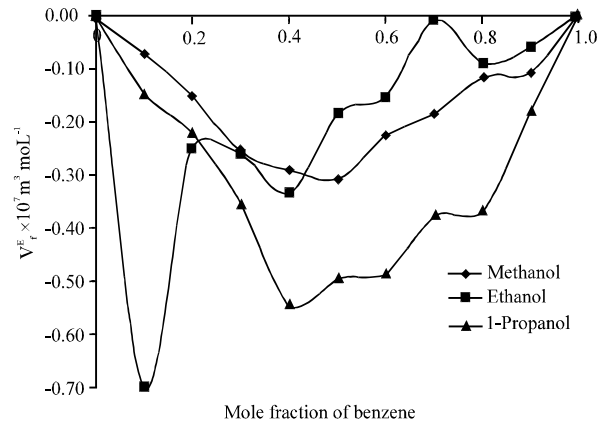


Fig. 3: Mole fraction vs. excess free volumes at 303 K

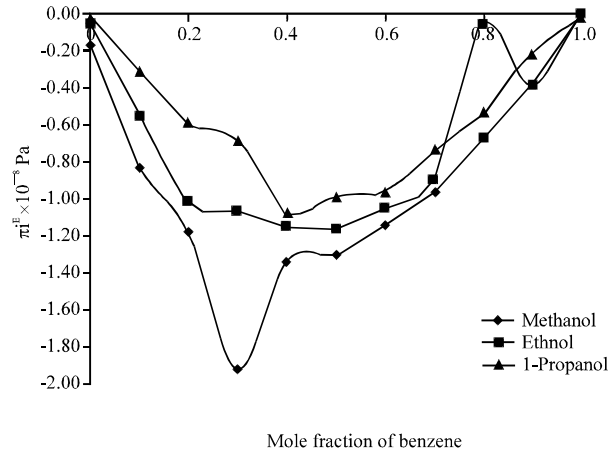


Fig. 4: Mole fraction vs. excess internal pressures at 303 K

interactions and so the components are made inactive mutually to reach ideality at the specified mole fractions. However, the estimated high excess values at higher mf of benzene in 1-propanol system may be attributed to the predominant interactions of its methylene group. This suggests that the methylene group is also fully saturated by the excessive benzene molecules and so the chances of inducement of dipoles are remote in this system. These are reflected in the observed  $L_f^E$  values.

The trend shown by  $V_f^E$  and  $\pi_i^E$  in methanol mixtures (Fig. 3-4) are interesting that they are fully negative and follow a specific trend. The existence of strong dip at 0.2 mf of benzene in ethanol system clearly indicates the dissolution of the complete benzene molecule i.e. the polar and nonpolar components by ethanol. Further, an unanimous dip seems to occur at 0.5 mole fraction of benzene in methanol and at 0.4 mf in other two systems, clearly shows that the existing interactions are strong and are not dispersive but induced dipole-dipole type (Kannappan and Santhi, 2006). This confirms the earlier prediction that the symmetry existing in the alcohol systems are highly disturbed by the added benzene molecules. The observed random fluctuations in the values of  $V_f^E$  and  $\pi_i^E$  clearly convey that induced dipole-dipole interactions exist in all the systems.

## CONCLUSION

Existence of specific interaction of strong magnitude is noticed in all the systems. Induced dipole-dipole interactions are found to be present in all the systems. Molecular symmetry in the alcohols is disturbed by the added benzene. Ethanol is found to offer more interactions with benzene than methanol or 1-propanol.

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