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Acoustic Studies on Primary Alcohols in P-Xylene with Nitrobenzene at 303K

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Abstract

The ultrasonic velocity, density and viscosity have been measured for the mixtures of 1–alkanols, namely, 1–propanol, 1–butanol, and 1–pentanol in p-xylene with nitrobenzene at 303 K. The experimental data's have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), and acoustic impedance (Z). The excess values of some of the above parameters are also evaluated and presented. A strong dipole-dipole interaction through hydrogen bonding between nitrobenzene and 1-alkanols is observed in the present investigation. The donor-acceptor complexation between p-xylene and nitrobenzene molecules is noticed. It is understood that the above two factors which clearly lead to an increase in adiabatic compressibility and intermolecular free length in the liquid mixtures.

Key Words: intermolecular free length, dipole-dipole interaction, hydrogen bonding, adiabatic compressibility, acoustic impedance, internal pressure

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Introduction

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative informations about the physical nature and strength of molecular interaction in the liquid mixtures [1-3]. Ultrasonic velocity in a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids, [4-8]. The variation of ultrasonic velocity and related parameters throw much light on the structural changes associated with the liquid mixtures having weakly interacting components [9,10] as well as strongly interacting components. The study of molecular association in organic ternary mixtures having alcohol as, one of the components is of particular interest, since alcohols are strongly self-associated liquid having a three dimensional network of hydrogen bond [11] and can be associated with any other group having some degree of polar attractions [12]. Although several investigations [13-15] were carried out in liquid mixtures having alcohol as one of the components, a systematic study in a series of primary alcohols in ternary systems has been scarcely reported. The ultrasonic studies for the binary mixtures of N,N-Dimethylformamide (DMF) with substituted benzenes [16-18] with branched alcohols with aliphatic esters [19-20] with Chloroethanes and Chloromethanes[21] and with Vinylpyrrolidine [22] are already reported in the literature.

An exhaustive survey of literature has shown that a few attempts have been made for the ultrasonic velocity data of ternary mixtures. [23-25].However, no effort appears to have been made to collect the ultrasonic velocity data for the ternary mixtures of nitro-benzene, p-xylene with 1-alkanols. Hence, the experimental studies were carried out by the authors and reported nitro-benzne + p-xylene + 1-propanol + 1-butanol, and 1-pentanol at 303 K.

The present ternary liquid systems used for study at 303K are:

System-I	1-propanol	+ p-xylene	+ nitrobenzene
System-II	1-butanol	+ p-xylene	+ nitrobenzene
System-III	1-pentanol	+ p-xylene	+ nitrobenzene

Materials and Methods

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9% were obtained from Sd fine chemicals India and E-merck, Germany. In all systems, the various concentrations of the ternary liquid mixtures were prepared in terms of mole fraction, out of which the mole fraction of the second component p-xylene (X_2 = 0.4) was kept fixed while the mole fractions of the remaining two (X_1 and X_3) were varied from 0.0 to 0.6. There is nothing significant in fixing the second component at 0.4. The density of pure liquids and liquid mixtures are determined using a specific gravity bottle by relative measurement method with a reproducibility of ± 0.01 kg.m^{-3} (Model: SHIMADZU AX-200).An Ostwald's viscometer of 10ml capacity is used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within ±0.01sec. An ultrasonic interferometer (Model: F81) supplied by M/s. Mittal Enterprises, New Delhi, working at a frequency of 3MHz with an overall accuracy of ± 2 ms^{-1} has been used for velocity measurement. An electronically digital constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is ± 0.1K.

Theory

Using the measured data, the following acoustical parameters have been calculated

Adiabatic Compressibility

$$\beta = \frac{1}{U^2 \rho} \qquad \ldots(1)$$

Intermolecular free length (L_f) has been calculated from relation,

$$L_f = K_T \sqrt{\beta} \qquad \ldots(2)$$

where K_T is a temperature dependent constant.

Free volume (V_f) has been calculated from relation,

$$V_f = \left(\frac{M_{eff} U}{K \eta} \right)^{3/2} \qquad \ldots(3)$$

where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma m_i x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

The internal pressure (π_i) can be found out as

$$\pi_i = bRT \left(\frac{K \eta}{U} \right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}^{7/6}} \right) \qquad \ldots(4)$$

K is a constant, T the absolute temperature, η the viscosity in Nsm^{-2}, U the ultrasonic velocity in ms^{-1}, ρ the density in Kgm^{-3}, M_{eff} the effective molecular weight.

Excess parameter (A^E) has been calculated by using the relation

$$A^E = A_{exp} - A_{id} \qquad \ldots(5)$$

where $A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameters and X_i the mole fraction of the liquid component.

Results and Discussion

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) at for all the three liquids systems at 303K are tabulated in Table 1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), and acoustic impedance (Z) of the three systems are given in Table 2. The respective some of the excess values of these above parameters have been evaluated and presented in the Tables 3 & 4.

Table 1 Values of Density(ρ), Viscosity(η) and Ultrasonic Velocity(U) of System–I at 303K

Mole Fraction		**DENSITY** $\rho/(kg/m^3)$	**VISCOSITY** $\eta/(\times 10^{-3}\ NSm^{-2})$	**VELOCITY** U/(m/s)
X_1	X_3			
0.0000	0.6000	1040.8	1.0120	1329.9
0.0998	0.5000	1034.2	0.9958	1325.0
0.2000	0.4000	1028.8	0.9612	1320.9
0.2999	0.2999	1023.4	0.9462	1316.7
0.4000	0.1999	1018.0	0.9317	1314.5
0.4999	0.0998	1012.7	0.9218	1312.4
0.5999	0.0000	1010.6	0.9053	1309.4
FOR SYSTEM-II				
0.0000	0.5999	1041.7	1.3406	1317.8
0.1000	0.5000	1037.7	1.3156	1315.7
0.2001	0.3999	1033.3	1.2806	1313.0
0.2999	0.2999	1024.2	1.2513	1305.8
0.3999	0.1998	1015.4	1.2301	1300.4
0.5000	0.0999	1006.7	1.2008	1295.7
0.6000	0.0000	1001.5	1.1729	1292.2

FOR SYSTEM-III				
0.0000	0.5904	1043.49	1.3430	1327.4
0.0998	0.5000	1040.77	1.3196	1323.0
0.1843	0.4467	1038.61	1.2970	1320.9
0.2999	0.2999	1036.47	1.2745	1317.9
0.4000	0.1998	1033.11	1.2564	1314.9
0.5000	0.0998	1029.63	1.2316	1312.4
0.6000	0.0000	1025.30	1.2106	1310.6

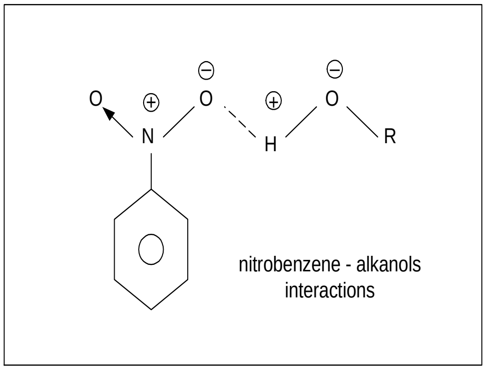
In all the three ternary liquid systems, the ultrasonic velocity decreases with increasing molar concentration of 1-alkanols. This behaviour at such concentrations can be attributed to intermolecular interactions in the system [26]. The variation of ultrasonic velocity in a mixture depends upon the increase (or) decrease of intermolecular free length after mixing the components. On the basis of a model, for sound propagation proposed by Eyring and Kincaid [27], ultrasonic velocity should decrease, if the intermolecular free length increase and vice-versa. This is, in fact observed in the present investigation for all the three liquid systems.

Table 2 Adiabatic compressibility (β), Free length (L_f) Free volume (V_f) Internal pressure (π_i) and Acoustic impedance (Z) of System –I at 303 K

Mole		**Adiabatic compressibility** $\beta/(\times10^{-10}\ m^2\ N^{-1})$	**Free length** $L_f/(\times10^{-10}\ m)$	**Free volume** $V_f/(\times10^{-7} m^3\ mol^{-1})$	**Internal pressure** $\pi_i/(\times10^6\ Nm^{-2})$	**Acoustic impedance** $Z/(\times10^6\ kg\ m^2\ s^{-1})$
X_1	X_3					
0.0000	0.6000	5.4324	0.4650	2.1347	371.95	1.3841
0.0998	0.5000	5.5083	0.4683	1.9999	392.84	1.3702
0.2000	0.4000	5.5707	0.4709	1.9221	412.54	1.3589
0.2999	0.2999	5.6360	0.4737	1.7825	439.60	1.3475

0.4000	0.1999	5.6852	0.4756	1.6460	470.33	1.3381
0.4999	0.0998	5.7337	0.4778	1.4978	507.41	1.3289
0.5999	0.0000	5.7715	0.4793	1.3669	549.91	1.3232
FOR SYSTEM-II						
0.0000	0.5999	5.5283	0.4691	1.3808	782.21	1.3727
0.1000	0.5000	5.5678	0.4708	1.3274	806.95	1.3651
0.2001	0.3999	5.6138	0.4727	1.2888	828.69	1.3567
0.2999	0.2999	5.7267	0.4774	1.2333	856.76	1.3373
0.3999	0.1998	5.8241	0.4815	1.1675	892.78	1.3204
0.5000	0.0999	5.9171	0.4853	1.1139	925.50	1.3043
0.6000	0.0000	5.9802	0.4879	1.0587	964.12	1.2940
FOR SYSTEM-III						
0.0000	0.5904	5.4389	0.4653	1.3711	785.27	1.3851
0.0998	0.5000	5.4894	0.4675	1.3588	792.62	1.3769

0.1843	0.4467	5.5183	0.4687	1.3562	799.15	1.3719
0.2999	0.2999	5.5549	0.4703	1.2928	827.49	1.3659
0.4000	0.1998	5.5984	0.4721	1.2516	849.44	1.3584
0.5000	0.0998	5.6392	0.4738	1.2205	867.72	1.3512
0.6000	0.0000	5.6783	0.4754	1.1894	888.67	1.3437



As ultrasonic velocities of all the three liquid systems decrease with increasing mole fraction of primary alkanols, the adiabatic compressibility (β) and intermolecular freelength (L_f) show the reverse trend. i.e., both the parameters increase with increase of molar concentration of 1-alkanols.

Such an increase in adiabatic compressibility and intermolecular free length with increasing mole fraction of alkanols indicate significant interactions between nitrobenzene and alkanol molecules forming hydrogen bonding through dipole-dipole interaction.

Since alkanols are liquids which are associated through hydrogen bonding and in the pure state, they exhibit an equilibrium between multimer and monomer species. Further, when Nitrobenzene is mixed with alkanols, the NO_2 group can interact with –OH group[28,29]. The aromatic derivatives set up on interaction between the π-electrons cloud and the hydroxyl group. Of course, this interaction is of minor intensity compared with hydrogen bonding, but they lead to formation of intermolecular complexes[30]. It may be further interpreted as by taking account of electron withdrawing capacity of $–NO_2$group which acts as an electron – acceptor towards the π-electrons of p-xylene. This is due to the fact that $-CH_3$ group of p-xylene is an electron – donating group through induction, which enhances the π-electron density of the p-xylene ring. This makes the donation of π-electrons (of p-xylene) for $-NO_2$ group easier forming donor – acceptor complex between p-xylene and nitrobenzene molecules. Similar results were noticed by earlier workers[31] supports the present investigation. Thus, dipole-dipole interaction through hydrogen bonding between nitrobenzene and alkanols as well as donor–acceptor complexation between p-xylene and nitrobenzene molecules which, clearly enhance the increase in adiabatic compressibility and intermolecular free length. Similar results[32] were observed by earlier workers.

Further, a decrease in free volume (V_f) and an increase in internal pressure (π_i) is noticed with rise in molar concentration of alkanols in all the systems which clearly shows the increasing magnitude of interactions[33] which are furnished in Table 2. Further, in all three liquid systems, the values of acoustic impedance (Z) is found to be decreased, which are listed in Table 2. When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it is observed that these acoustic impedance (Z) values decrease with increasing concentration of n-alkanols. Such a decreasing values of acoustic impedance (Z) further supports the possibility of molecular interactions between the unlike molecules.

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The effect of deviation depends upon the nature of the constituents and composition of the mixtures.

Table 3 Excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) of System–I at 303 K

Mole Fraction		**Excess adiabatic compressibility $\beta^E/(\times10^{-10}m^2N^{-1})$**	**Excess free length $L_f^E/(\times10^{-10}$ m)**	**Excess free volume $V_f^E/(\times10^{-7}$ $m^3mol^{-1})$**	**Excess internal pressure $\pi_i^E/(\times10^6Nm^{-2})$**
X_1	X_3				
0.0000	0.6000	-0.1206	-0.0098	-0.3160	-269.19

0.0998	0.5000	-0.2811	-0.0059	-0.3536	-360.44
0.2000	0.4000	-0.7007	-0.0227	-0.3347	- 453.70
0.2999	0.2999	-1.1135	-0.0389	-0.3770	-538.90
0.4000	0.1999	-1.5447	-0.0563	-0.4164	-620.90
0.4999	0.0998	-1.9736	-0.0730	-0.4668	-696.04
0.5999	0.0000	-2.4169	-0.0909	-0.5013	-766.28
FOR SYSTEM-II					
0.0000	0.5999	-0.2163	-0.0140	-1.0701	-148.13
0.1000	0.5000	-0.1511	-0.0412	-1.0273	-66.57
0.2001	0.3999	-0.5125	-0.0159	-0.9699	-11.03
0.2999	0.2999	-0.8065	-0.0278	-0.9302	-81.85
0.3999	0.1998	-1.1158	-0.0400	-0.8999	-145.05
0.5000	0.0999	-1.4304	-0.0533	-0.8573	-211.81
0.6000	0.0000	-1.7748	-0.0675	-0.8167	-272.52

FOR SYSTEM-III					
0.0000	0.5904	-0.1661	-0.0140	-1.0670	-152.24
0.0998	0.5000	-0.1880	-0.0029	-0.9918	-40.36
0.1843	0.4467	-0.3693	-0.0103	-0.8195	-63.07
0.2999	0.2999	-0.8536	-0.0305	-0.8556	-147.76
0.4000	0.1998	-1.1762	-0.0439	-0.7959	-237.37
0.5000	0.0998	-1.5012	-0.0575	-0.7263	-330.55
0.6000	0.0000	-1.8279	-0.0711	-0.6563	-421.18

In the present investigation, the excess values of adiabatic compressibility (β^E), excess freelength (L_f^E), excess free volume (V_f^E), and excess internal pressure (π_i^E) are negative in all the three systems over the entire range of composition. Sri Devi et.al.[34] suggests that the negative excess values has been due to the closely packed molecules which account for existence of strong molecular interaction and positive excess values to weak interaction between unlike molecules.The sign of adiabatic compressibility (β^E) and excess freelength (L_f^E) play a vital role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole-dipole interactions[35] and dipole-induced dipole interactions interstitial accommodation and orientational ordering[36] leading to more compact structure-making, which enhances excess adiabatic compressibility (β^E) and excess freelength (L_f^E) to have negative values.

Table 4 Excess values of molar volume (V_m^E) and acoustic impedance (Z^E) of System–I at 303K

Mole Fraction		**Excess Molar volume V_m^E /(×10^{-3} m^3 mol^{-1})**	**Excess acoustic impedance Z^E/(×10^6 kg m^2 s^{-1})**
X_1	**X_3**		
0.0000	0.6000	-0.0002	0.0804
0.0998	0.5000	-0.0025	0.0172
0.2000	0.4000	-0.0054	0.0480
0.2999	0.2999	-0.0084	0.1138
0.4000	0.1999	-0.0112	0.1812
0.4999	0.0998	-0.0142	0.2492
0.5999	0.0000	-0.0177	0.3200
FOR SYSTEM-II			
0.0000	0.5999	-0.0001	0.0917
0.1000	0.5000	-0.0032	0.0272
0.2001	0.3999	-0.0065	0.0367

0.2999	0.2999	-0.0092	0.0894
0.3999	0.1998	-0.0121	0.1449
0.5000	0.0999	-0.0150	0.2008
0.6000	0.0000	-0.0184	0.2625
FOR SYSTEM-III			
0.0000	0.5904	-0.0030	0.0629
0.0998	0.5000	-0.0038	0.0184
0.1843	0.4467	-0.0057	0.0157
0.2999	0.2999	-0.0113	0.1093
0.4000	0.1998	-0.0150	0.1712
0.5000	0.0998	-0.0187	0.2332
0.6000	0.0000	-0.0223	0.2948

Further, excess negative values of adiabatic compressibility (β^E) and excess freelength (L_f^E) in the present investigation is an indication of strong interaction in the liquid mixtures[37]. The negative excess value of internal pressure in all the three systems clearly confirms this prediction. Moreover, the values of excess molar volume (V_m^E) (in Table 4) exhibit negative values over the entire range of composition in all the three liquid systems clearly suggest that the existence of strong interactive forces present in the mixtures. Also, the negative values increase with increasing molar concentration of alkanols again support the systems studied are tending towards the strong molecular association between the unlike molecules. Further, it is again well supported by the excess values of acoustic impedance (Z^E) in Table 4. are all positive in all the liquid systems over the entire range of composition. The positive excess values of Z^E clearly suggest that there is a strong molecular interaction existing between the unlike molecules.

Conclusion

From the present investigation, it is eventually concluded that existence of strong dipole-dipole molecular interaction through hydrogen bonding between nitrobenzene and 1-alkanols. Followed by, the donor – acceptor complexation is observed between p-xylene and nitrobenzene molecules. Both the above factors which clearly enhance an increase in adiabatic compressibility (β) as well as intermolecular free length (L_f) in the liquid mixtures.

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