_____

Acoustic Study of Intermolecular Interactions in Binary Liquid Mixture*s*

S. Thirumaran*, R. Murugan, N. Prakash

*Department of Physics (DDE), Annamalai University, Annamalainagar-608 002, India
_____

Abstract

The ultrasonic velocity, density and viscosity have been measured for the binary mixtures of 1-propanol with toluene, benzene and cyclohexane at 303K The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), acoustic impedance (Z) and molar volume (V_m). The excess values of some the above parameters are also evaluated and presented. A weak molecular interaction between the component molecules is observed in the present investigation. Also, the additionof non-polar component with polar 1-propanol causes dissociation of its hydrogen bonded structure. A weak magnitude of molecular association is observed in 1-prpoanol-cyclohexane system.

Key Words: Adiabatic compressibility, hydrogen bonding, intermolecular free length, dipole-dipole interaction.
_____

Introduction

Interaction studies in a system comprising aromatic hydrocarbon and polar liquid as components have attracted the attention of researchers in recent years. The significance of volumetric, acoustic and thermodynamic studies in mixtures have been used for understanding the intermolecular interactions by many researchers for interpreting different types of interactions, viz., But dipole-dipole,[1] and dipole-induced dipole[2-3] in polar-polar[4] and polar-non-polar systems,[5-6]. Increasing use of benzenes, toluene and 1-propanol in many industrial processes

_____

have greatly stimulated the need for extensive information on the acoustic and transport properties of these liquids and their mixtures. Commercial uses of benzene include synthesis of different intermediate compounds during the process of manufactures of plastics, dye stuffs, detergents and insecticides.[7-8]

1-propanol is used as a blending agent for petroleum naptha, resins and gums and also as an extractant in the production of vitamins, harmones, essentials oils, antibodies and sulphonated oils[9]. The above salient features of these liquids had motivated the authors to carry-out the present study of binary liquid mixtures of 1-propanol with toluene, benzene and cyclohexane at 303K.

The present work deals with the measurement of ultrasonic velocity and evaluation of the related parameters in the following binary liquid systems at 303 K

System-I	1-propanol	+ toluene
System-II	1-propanol	+ benzene
System-III	1-propanol	+ cyclohexane

Materials and Methods

In all the systems, the various concentrations are prepared by varying mole fraction from 0.1 to 0.9 so as to have thorough concentrations of 1-propanol (x_1) and toluene, benzene and cyclohexane $-(x_2)$ which have been measured at 303K. The ultrasonic velocity in liquid mixtures have been measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi, Model:F81) working at frequency 3MHz with an overall accuracy of $\pm$ 0.1 ms^{-1}. The density and viscosity are measured using a Pyckno meter and on Ostwald's Viscometer an accuracy of $\pm$0.1kg m^{-3} and $\pm$ 0.001 Nsm^{-2} respectively. All the precautions were taken to minimize the possible experimental error. The set-up is checked for standard liquids. The values obtained are compared with literature and found that they makes very well with each other. The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grade with minimum assay of 99.9% were obtained from Sd fine chemicals India and E-merck, Germany as such without further purification.

Theory

Using the measured data,
the Adiabatic compressibility (β) have been calculated.

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

Intermolecular free length (L_f) has been calculated from relation

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

_____

where K_T is a temperature dependent constant.
Free volume (V_f) has been calculated from relation,

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

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.
Internal pressure (π_i) has been calculated from relation,

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

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.

The excess values are calculated as,
$$A^E = A_{exp} - A_{id} \qquad \qquad ...(5)$$

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) of all the three liquid systems are given Table1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) of the above systems are tabulated in Table 2. Molar volume (Vm) and acoustic impedance (Z) of all the binary mixtures have been computed and reported in Table 3. The excess values of some these parameters have been evaluated and presented in Table 4.

It is observed that ultrasonic velocity (U) and density (ρ) decreases with increasing molar concentration of 1-propanol, whereas, the other parameter viscosity (η) shows reverse trend with the same rise of concentration of 1-propanol. This behavior at such concentrations is different from the ideal mixtures behavior can be attributed to intermolecular interactions in the systems studied[10-11]. The decreasing trend of ultrasonic velocity with mole fraction of alcohol is attributed to the depolymerization of polar alcohols[12] such as 1-propanol caused by the addition of non-polar components such as cyclohexane and benzene. Such a variation in sound velocity (U) in the systems is supported by that of adiabatic compressibility (β) and intermolecular free length (L_f), whose observations are in confirmation with the general trends of sound speed variation in several binary mixtures [13-14].

_____

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

Mole Fraction		Density	Viscosity	Ultrasonic Velocity
X_1	X_2	$\rho/(kg/m^3)$	$\eta/(\times 10^{-3} NSm^{-2})$	$U/(m/s)$
System – I				
0.1000	0.8999	844.7338	0.6292	1261.2
0.1999	0.8000	837.5025	0.6761	1252.5
0.3000	0.6999	830.2578	0.7220	1243.8
0.4000	0.5999	823.0266	0.7671	1235.1
0.4925	0.5075	815.7819	0.8112	1226.4
0.6000	0.3999	811.1362	0.9666	1219.4
0.6999	0.3000	806.4904	1.1231	1212.5
0.7999	0.2000	801.8312	1.1711	1205.5
0.8999	0.1000	797.1854	1.2349	1198.5
System – II				
0.1000	0.8999	854.05	0.6497	1248.9
0.2000	0.7999	848.9082	0.6753	1239.65
0.2999	0.7000	843.7507	0.7004	1230.39
0.4000	0.5999	838.6067	0.7253	1221.14
0.4999	0.5000	833.4493	0.7498	1211.88
0.5999	0.4000	825.0061	0.9401	1207.34
0.6999	0.3000	816.5495	1.1263	1202.79
0.7999	0.2000	808.1063	1.3111	1198.25
0.8999	0.1000	799.6497	1.4892	1193.7
System – III				
0.1000	0.8999	773.4913	0.9623	1217.1
0.1999	0.8000	771.0242	1.0157	1213.6
0.2999	0.7000	769.5570	1.0682	1210.1
0.3999	0.6000	767.0898	1.1201	1206.6
0.5000	0.4999	765.6226	1.1711	1203.3
0.5999	0.4000	763.1555	1.2611	1199.6
0.7000	0.2999	761.6883	1.3656	1196.1
0.8000	0.1999	759.2211	1.4608	1192.6
0.9000	0.1000	757.7539	1.5550	1189.1

The parameters such as adiabatic compressibility (β) and intermolecular free length (L_f) show reverse trend – both are found to be increased with the increasing molar concentration of 1-propanol in all the three liquid systems, which are tabulated in Table 1. In the three liquid systems, namely, in 1-propanol-benzene system, the adiabatic compressibility (β) and free length (L_f) increase with increasing molar concentrations of alcohol. Such an increase in β as well as L_f suggest that the hydrogen bonded association of alcohols breaks up gradually with addition of benzene.

_____

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

Mole Fraction		Adiabatic compressibility $\beta/(\times 10^{-10}\,m^2\,N^{-1})$	Free length $L_f/(\times 10^{-10}\,m)$	Free volume $V_f/(\times 10^{-7}\,m^3\,mol^{-1})$	Internal pressure $\pi_i/(\times 10^6\,Nm^{-2})$
X_1	X_2				
System-I					
0.1000	0.8999	7.4424	0.5443	2.6874	350.28
0.1999	0.8000	7.6113	0.5505	2.2602	378.11
0.3000	0.6999	7.7855	0.5567	1.9145	407.51
0.4000	0.5999	7.9649	0.5631	1.6298	438.94
0.4925	0.5075	8.1501	0.5696	1.4010	469.17
0.6000	0.3999	8.2911	0.5745	0.9962	541.82
0.6999	0.3000	8.4341	0.5795	0.7373	614.84
0.7999	0.2000	8.5819	0.5845	0.6397	662.63
0.8999	0.1000	8.7330	0.5896	0.3924	720.09
System-II					
0.1000	0.8999	7.5069	0.5467	2.0061	430.79
0.2000	0.7999	7.6655	0.5524	1.8062	451.47
0.2999	0.7000	7.8289	0.5583	1.6300	472.94
0.4000	0.5999	7.9967	0.5642	1.4729	495.43
0.4999	0.5000	8.1696	0.5703	1.3329	518.9
0.5999	0.4000	8.3154	0.5754	0.7540	596.28
0.6999	0.3000	8.4652	0.5805	0.6606	670.3
0.7999	0.2000	8.6186	0.5858	0.5016	743.36
0.8999	0.1000	8.7763	0.5911	0.3947	815.03
System-III					
0.1000	0.8999	8.7275	0.5894	1.1873	458.73
0.1999	0.8000	8.8060	0.5921	1.0424	487.65
0.2999	0.7000	8.8739	0.5944	0.9189	518.48
0.3999	0.6000	8.9542	0.5971	0.8124	550.59
0.5000	0.4999	9.0206	0.5993	0.7204	585.04
0.5999	0.4000	9.1057	0.6021	0.6099	607.33
0.7000	0.2999	9.1767	0.6044	0.5112	684.46
0.8000	0.1999	9.2607	0.6072	0.4356	738.11
0.9000	0.1000	9.3333	0.6097	0.3731	795.99

Such addition of benzene causing breaking of hydrogen bonded association of alcohols leads to expansion in volume. Hence, an increase in molar volume (V_m) is observed which are tabulated in Table 3. Further, the loss of dipolar associations is observed due to non-polar component on one hand, on the other hand, the interaction of the type O—H--π between alcohol and electrons of aromatic ring of benzene can be expected. The increase in the former type of interaction leads to expansion in volume. Similar results were noticed by the earlier workers [15].

_____

Further, the decrease in free volume and increase in internal pressure with rise in concentration of alkanol in all the systems clearly show the increasing magnitude of interactions[16]. Further, the increase in internal pressure (π_i) generally indicates association through hydrogen bonding. Similar results were observed by earlier workers [17].

Table - 3 Values of molar volume (V_m) and acoustic impedance (Z) at 303K

Mole Fraction		Molar volume	Acoustic impedance
X_1	X_2	$V_m/(\times 10^{-3}\,m^3\,mol^{-1})$	$Z/(\times 10^6\,Kg\,m^2\,s^{-1})$
System-I			
0.1000	0.8999	0.0794	1.0654
0.1999	0.8000	0.0829	1.0490
0.3000	0.6999	0.0864	1.0327
0.4000	0.5999	0.0899	1.0165
0.4925	0.5075	0.0936	1.0005
0.6000	0.3999	0.0964	0.9891
0.6999	0.3000	0.0994	0.9779
0.7999	0.2000	0.1024	0.9666
0.8999	0.1000	0.1053	0.9554
System-II			
0.1000	0.8999	0.0774	1.0666
0.2000	0.7999	0.0788	1.0523
0.2999	0.7000	0.0802	1.0381
0.4000	0.5999	0.0816	1.0241
0.4999	0.5000	0.0829	1.0100
0.5999	0.4000	0.0845	0.9961
0.6999	0.3000	0.0862	0.9821
0.7999	0.2000	0.0878	0.9683
0.8999	0.1000	0.0893	0.9545
System-III			
0.1000	0.8999	0.9414	0.0825
0.1999	0.8000	0.9357	0.0855
0.2999	0.7000	0.9312	0.0884
0.3999	0.6000	0.9256	0.0914
0.5000	0.4999	0.9213	0.0942
0.5999	0.4000	0.9155	0.0972
0.7000	0.2999	0.9111	0.0999
0.8000	0.1999	0.9054	0.1029
0.9000	0.1000	0.9010	0.1057

Further, in all three liquid systems, the value of acoustic impedance (Z) is found to be decreased, which are listed in Table 3. 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 1-propanol. 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 term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures.

The excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) for all the three liquid systems are furnished in Table 4. It is learnt that the dispersion forces are responsible for possessing positive excess values, while dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values[18].

Table – 4 Excess values of adiabatic compressibility (β), free length (L_f) free volume (V_f) internal pressure (π_i) and acoustic impedance for

Mole Fraction		Excess Adiabatic compressibility β^E/($\times 10^{-10}$ m^2 N^{-1})	Excess Free length L_f^E/($\times 10^{-10}$ m)	Excess Free volume V_f^E/($\times 10^{-7}$ m^3 mol^{-1})	Excess Internal pressure π_i^E/($\times 10^6$ Nm^{-2})	Excess Acoustic impedance Z^E/($\times 10^6$)
X_1	X_2					
System-I						
0.1000	0.8999	0.1111	0.0052	0.4621	-59.15	-0.0138
0.1999	0.8000	0.1009	0.0050	0.2413	-83.7	-0.0151
0.3000	0.6999	0.0956	0.0048	0.1024	-106.8	-0.0162
0.4000	0.5999	0.0958	0.0048	0.0243	-127.8	-0.0173
0.4925	0.5075	0.1144	0.0053	-0.0137	-146.1	-0.0193
0.6000	0.3999	0.0635	0.0034	-0.1961	-129.8	-0.0143
0.6999	0.3000	0.0274	0.0020	-0.2486	-109.1	-0.0104
0.7999	0.2000	0.0041	0.0006	-0.1396	-113.8	-0.0065
0.8999	0.1000	0.0323	0.0007	-0.1804	-108.7	-0.0026
System - II						
0.1000	0.8999	0.0435	0.0019	0.1659	-38.61	-0.0001
0.2000	0.7999	0.0376	0.0018	0.1298	-63.71	-0.0007
0.2999	0.7000	0.0365	0.0019	0.1172	-87.96	-0.0011
0.4000	0.5999	0.0396	0.0021	0.1241	-111.3	-0.0013

_____

0.4999	0.5000	0.0480	0.0024	0.1477	-133.5	-0.0017
0.5999	0.4000	0.0293	0.0017	-0.2674	-101.9	-0.0018
0.6999	0.3000	0.0145	0.0011	-0.1970	-73.67	-0.0020
0.7999	0.2000	0.0033	0.0006	-0.1922	-46.38	-0.0020
0.8999	0.1000	0.0036	0.0001	-0.1353	-20.48	-0.0021
System - III						
0.1000	0.8999	0.0748	0.0026	-0.0598	-14.49	0.0080
0.1999	0.8000	0.0121	0.0004	-0.1069	-30.87	0.0012
0.2999	0.7000	0.0399	0.0014	-0.0090	-45.39	-0.0043
0.3999	0.6000	0.1045	0.0035	-0.1411	-58.62	-0.0110
0.5000	0.4999	0.1551	0.0052	-0.1351	-69.56	-0.0163
0.5999	0.4000	0.2244	0.0075	-0.1478	-92.57	-0.0231
0.7000	0.2999	0.2796	0.0092	-0.1485	-60.83	-0.0286
0.8000	0.1999	0.3478	0.0115	-0.1262	-52.52	-0.0353
0.9000	0.1000	0.4037	0.0134	-0.0910	-40.03	-0.0408

In the present study, the excess values of adiabatic compressibility (β^E) and free length (L_f^E) exhibit positive deviations over the entire range of composition in all the three liquid binary systems. The positive values of β^E is attributed to the breaking of homopolymerisation with addition of non-polar aromatic compounds. (toluene, benzene) Similar observations found in the binary systems of Miyanaaga *et.al.,*[19] and Oswel *et.al.* [20]. The positive deviation of excess free length (L_f^E) also suggests that there is a possibility of some weak interactive forces (dipole-induced dipole) in all the three liquid systems. Such an observation is quite obvious in the cases of non-polar with polar mixtures. Similar types of observations were reported by Miyanaga *et.al.* [19]

The excess internal pressure (π_i^E) values are furnished in the Table 4. The excess values of internal pressure is often described in terms of molecular interaction in liquid mixtures, whose negative deviations in all the three liquid systems over the entire range of composition clearly suggest that the dispersive forces or weak dipole-induced dipole types of forces are existing between the system components.

The above conclusion is further strengthened by the excess acoustic impedance (Z^E) values which are tabulated in Table 4. Such values of excess acoustic impedance Z^E in all the three liquid binary systems over the entire range composition show negative deviations confirming that weak magnitude of interactive forces existing between the system components. This is further attributed to dissociation of self-association of 1-propanol lead to the negative values of Z^E. The variation of Z^E in all the binary liquid mixtures reveals that dispersive forces are more prominent and there is a possibility of weak dipole-induced dipole types of forces acting between the unlike molecules. Similar observations were found in acetone-benzene and acetone-cyclohexane systems by Yadav *et.al.* [21]

_____

Conclusion

From ultrasonic velocity, related acoustical parameters and their excess values it is concluded that there exists a weak molecular association between the component molecules in the mixtures. Further the addition of non-polar component with polar 1-propanol leads to breaking of its hydrogen bonded association . This results in subsequent weak molecular interaction (dipole-induced dipole) existing between the unlike molecules. Comparing the three binary liquid systems, the weak magnitude of molecular association is identified in 1- propanal- cyclohexane system. (System - III)

References

[1] S Thirumaran; P Anbuselvi; *Asian Journ Chem,* **2009**, *21(9), 7261.*

[2] S Thirumaran ; Deepesh George ; *ARPN Journ of Engg & Appl Sci*. **2008**, 27D(2), 281.

[3] Zielikewiez, J., *Journ Chem Thermodyn*., **26** (1994) 959.

[4] S Thirumaran; J Ramesh; *Rasayan Journ chem,* **2009,** vol 2 (3), 733.

[5] S Thirumaran; K Ramya; *Asian Journ Chem*. **2009,** 21(8), 6359.

[6] S Thirumaran; J Earnest Jayakumar, *Ind.Journ pure & Appl. Phys,* **2009,** 47, 265.

[7] Lide D R , *C.R.C. Handbook of Chemistry 81st Edn* (Boca Raton, New York) **2001.**

[8] Dean J A *Lange's Handbook of Chemistry, 13th Edn Mcgraw Hill,* New York **1987.**

[9] Monic A J Alcohots, (Chapman Reinhold Inc New York) **1968.**

[10] Tiwari K, Patra C, & Chakravorthy V, *Acoust Lett,* 19 **(1995)** 53.

[11] Kannappan AN & Palaniappan L, *Ind Journ Phys*., 73B **(1999)** 531.

[12] S Thirumaran; M Suguna; SR Selvi; *Research Journ Chem & Envioron,* **2009,** 13 (3), 81.

[13] Rao T S, Veeriah, Rao G S, Ramachandran D, & Rambabu C, *Ind J. Chem.,* 42A **(2003)** 1876.

[14] Nikam P S Kapade V M & Hassan M, *Journ Pure & Appl Ultraso*, 22 **(2000)** 16.

[15] Reddy N Y, Naidu P S & Prassad K R, *Ind Jou Pure & Appl Phys.,* 32 **(1994)** 958.

[16] Anbananthan, D, *J. Accoust. Soc. India,* 7 **(1979)** 123.

[17] Pandey J D, Hassan N A, Shukla J N, & Dey R, *Acoust Lett.,* 23 **(1999)** 06.

[18] Alculea Palofax M, *Ind Journ Pure & Appl Phys*. 31 **(1993)** 90.

[19] Miyanaga S, Tamura K, & Murakami S, *Themochmica Acta,* 198 **(1992)** 237.

[20] Oswel S L, Oswel P, & Dove J P, *Journ Mol Liq.,* 94 **(2001)** 203.

[21] Yadav R, & Yadav SS, *Ind Jour Chem.,* 20A **(1981)** 221.