Acoustic and Excess Thermoacoustic Study of Polar - Polar and Polar -Non Polar Binary Liquid Mixtures

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ABSTRACT

The ultrasonic velocity (u) and density (ρ) have been measured for binary mixtures of 1-Chlorobutane with benzene and nitrobenzene in different molar concentrations at temperature of 303.16 K and frequency of 2 MHz The data of u and ρ have been used to evaluate excess adiabatic compressibility (βE) and excess volume (VE) to study molecular interaction. The study reveals that interaction is maximum in the category polar- polar mixture.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Molecular interaction.

I. INTRODUCTION

Ultrasonic velocity and related data of pure liquid and liquid mixtures are found to be the most effective, powerful and reliable tool in testing the thermodynamics properties of liquids & liquid mixtures. In many industries, liquid mixtures rather than single components, liquid systems are used in processing and product formulations. Several attempts [1-3] have been made to use ultrasonic data in computing the thermodynamic parameters of mixtures. It has been reported by many workers [4,7,8] that, occurrence of complex formation can be explained successfully by excess parameters such as excess velocity, excess adiabatic compressibility, excess intermolecular free length etc. In the present study excess adiabatic compressibility and excess volume of binary mixture of 1- Chlorobutane with benzene and nitrobenzene has been evaluated to study molecular interaction in the mixtures.

II. EXPERIMENTAL

Ultrasonic interferometer model F-81 of fixed frequency 2 MHz having accuracy ± 0.03% and hydrostatic plunger method having accuracy ± 0.05% were used for measurement of ultrasonic velocity and density of pure liquids and its solution of different mole concentrations from 0.1, 0.2, ------0.9 at different temperatures. The calibration of the apparatus was done with air and deionizer double-distilled water.

III. RESULT AND DISCUSSION

Adiabatic compressibility (βa) has been evaluates from the experimental values of ultrasound velocity (u) and density (ρ) of pure liquids by using the relation

$$\beta_a = \left(U^2 \rho\right)^{-1}$$

The excess ultrasonic parameters[4-5] has been claimed to be an aid in characterization of molecular interactions that are present in solutions and liquid mixtures.

Excess parameter can be evaluated as :

$$Z^E = Z_{\exp} - Z_{ideal}$$

Where , $Z_{\exp}$ = Experimental value and Z_{ideal} = expected or ideal value of the parameter. Excess volume (VE), excess adiabatic compressibility (βaE) and excess velocity (UE) have been calculate by using the relations :

$$V^E = V_{\exp} - V_{ideal} \text{ and}$$

$$\beta_a^E = \left(\beta_a\right)_{\exp} - \left(\beta_a\right)_{ideal}$$

It also give an idea about deviation of experimental values from ideal or expected values. The presence of hetero-molecular AB interactions is reflected through the excess parameter such as excess compressibility [β_a^E] and excess volume [V^E]. For understanding the nature and strength of hetero-molecular interactions, only two parameters β_a^E and V^E are considered simultaneously. Excess volume and excess compressibility can be positive or negative hence the following possibilities of variation of excess parameters can be considered and may be called as broad classification

(1) $V^E < O$ $\beta_a^E < O$
(2) $V^E > O$ $\beta_a^E < O$
(3) $V^E < O$ $\beta_a^E > O$
(4) $V^E > O$ $\beta_a^E > O$

If the component liquids in binary mixture are A and B , then pure liquids A and B may exist as $A_{liq} = $ (A, A·A, A·A·A, ------)
$B_{liq} = $ (B, B·B, B·B·B, -----------------)
$(AB)_{mixture} = $ (A·B, A·B·B, A·A·B, ---------------)

In hetero–molecular interactions, both the types of molecules take part in causing the interaction.

Velocity of ultrasonic waves is a sensitive function of space filling factor n according to Cornahan. If n increases , ultrasonic velocity also increases. In mixture of liquids , space filling factor may change due to change in "V" (volume) or change in 'b' (Vander – Waals constant) or both. The change in 'b' would be due to change in intermolecular geometry (macro geometry). While change in V would be due to a change in intermolecular cluster geometry (micro geometry). Small changes in volume cause significant changes in velocity of ultrasonic waves. Volume of the liquid mixture depends upon the structural arrangement in liquid as well as on intermolecular interaction. An increase in the strength of the hetero–

molecular forces manifesting in a decrease in adiabatic compressibility (β_a) of a mixture would tend to reduce the size of cluster, hence decrease in the total volume of the mixture. If there is one minimum, there would be one stable cluster or two minima will indicate two relatively stable clusters. The process leading to the stable clusters would be equilibrium at these concentrations. The above association would occur due to the presence of active subgroup in A type and an active subgroup in B type molecules. If minimum is closer to higher concentration of A, then interaction AA > BB. If it lies closer to higher concentration of B, then BB > AA. While a symmetrical variation would indicate AB .> AA as well as AB > BB as the relative strength of interaction. All systems in present study fall in the category $V^E < O$ and $\beta_a^E < O$, hence there are attractive interaction causing association between A and B type of molecules. The forces present in the mixtures are attractive in nature causing their association between dissimilar molecules.

Figure -1 shows the negative variation of V^E and figure-2 shows the negative variation of β_a^E with composition respectively for the systems 1-Chlorobutane + Benzene ,1-Chlorobutane + Nitrobenzene.The data in given in table 1.

Considering the solutions of 1-Chlorobutane with hydrocarbon that is Benzene there is strong interaction. In this, the variation of both V^E and β_a^E is symmetrical depicting strong AB – type interactions. A stable cluster is recommended at x = 0.6. 1-Chlorobutane is a polar molecule so 1-Chlorobutane + Benzene is a mixture Table 1-Mole fraction(x),sound speed (u), density (ρ), excess volume (V^E), excess adiabatic compressibility (β^E) at 303.16K

Table 1

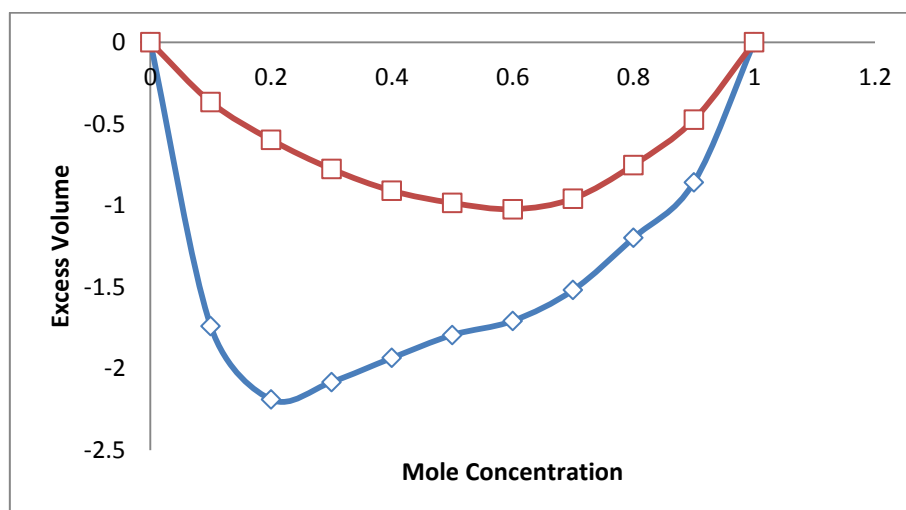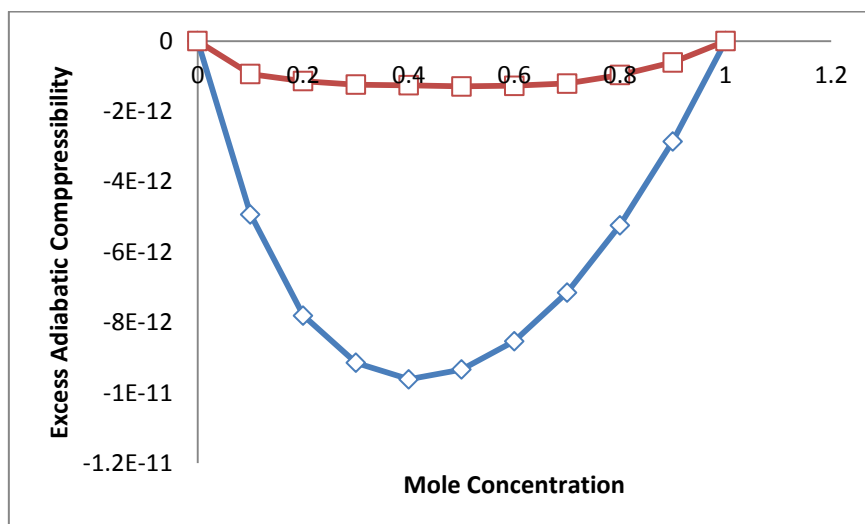| 1-Chlorobutane + Benzene					1-Chlorobutane + Nitrobenzene				
x	u	ρ	V^E	β^E	X	u	ρ	V^E	β^E
	m/s	$Kg/m^3 \times 10^3$				m/s	$Kg/m^3 \times 10^3$		
0	1096.41	0.87538	0	0	0	1096.41	0.87538	0	0
0.1	1116.57	0.87522	-0.36718	-9.388E-13	0.1	1131.63	0.92194	-1.7405	-4.9E-12
0.2	1133.56	0.87492	-0.59838	-1.139E-12	0.2	1168.67	0.95802	-2.19007	-7.8E-12
0.3	1150.65	0.87449	-0.77718	-1.242E-12	0.3	1204.54	0.98907	-2.08297	-9.1E-12
0.4	1167.86	0.87411	-0.91063	-1.259E-12	0.4	1239.68	1.01966	-1.93531	-9.6E-12
0.5	1185.98	0.87368	-0.98533	-1.29E-12	0.5	1273.72	1.05024	-1.79475	-9.3E-12
0.6	1204.48	0.87338	-1.0237	-1.27E-12	0.6	1307.5	1.081311	-1.70822	-8.5E-12
0.7	1223.88	0.87257	-0.95853	-1.208E-12	0.7	1340.48	1.11123	-1.51936	-7.1E-12
0.8	1243.33	0.87086	-0.75294	-9.648E-13	0.8	1372.35	1.13959	-1.19957	-5.2E-12
0.9	1262.87	0.86885	-0.47554	-6.061E-13	0.9	1402	1.16754	-0.85929	-2.9E-12
1	1282	0.8653	0	0	1	1431.59	1.18931	0	0

Figure 1. Mole fraction versus excess volume of (1-chlorobutane + benzene □), (1-chlorobutane + nitrobenzene ◊)

of polar – nonpolar molecules. The 1-Chlorobutane is definitely inducing dipoles and causing attractive interactions thereby decreasing the volume. In mixtures of 1-Chlorobutane with Nitrobenzene, excess volume and excess adiabatic compressibility both are negative as shown in figure (2) Nitrobenzene is a polar liquids and have considerable dipole moment 4.22D. Hence this is a mixture of polar – polar liquids.

Decrease in the volume in this system indicates the association between unlike molecules. Addition of Nitrobenzene to 1-Chlorobutane causes more and more attraction such that these molecules may be filling the interstitial spaces available in the first liquid. 1-Chlorobutane and Nitrobenzene both are strongly polar liquids, hence dipole – dipole force are present. From the figure 1 , it can be concluded that AA interactions are stronger than BB interactions and AB interactions are found to be absent i.e. 1-Chlorobutane is more dominant than Nitrobenzene in causing this type of interactions. A cluster / aggregate

is seen to be formed at x = 0.6. This cluster may not be stable as it is

Figure 2. Mole fraction versus excess adiabatic compressibility of 1-chlorobutane + benzene □) , (+nitromobenzene ◊)

not supported by $\beta_a{}^E$ variation. The overall interaction is of attractive type due to dipole – dipole forces. For the lower concentration of Nitrobenzene molecules in 1-Chlorobutane, they may be filling the interstitial space reducing the volume of the mixture. But as concentration of Nitrobenzene is increased, both the types of molecules interact equally in the later part of x. Negative $\beta_a{}^E$ supports the finding of excess volume.

In the system of 1-Chlorobutane with Nitrobenzene, there are strong interactions as suggested from figure - 2 . The interactions are of AA type. A cluster / aggregate is seen to be formed at x = 0.6. This cluster may not be stable as it is not supported by $\beta_a{}^E$ variation. The overall interaction is of attractive type due to dipole – dipole forces. For the lower concentration of Nitrobenzene molecules in 1-Chlorobutane, they may be filling the interstitial space reducing the volume of the mixture. But as concentration of Nitrobenzene is increased, both the types of molecules interact equally in the later part of x. The strength of interaction is of order of (Chlorobutane + Nitrobenzene) > (1-Chlorobutane + Benzene) .The strength of interaction in polar- polar liquid is greater than that of polar –non polar liquid.

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