Study of Molecular Interactions in Binary Liquid Mixtures by Acoustical Method at 303K

P. PAUL DIVAKAR^{A*} B.V.RAO^B, and K. SAMATHA^A

^aUltrasonic Laboratories, Department of Physics,
Andhra University, Visakhapatnam – 530 003, India

^bDepartment of Engineering Chemistry
Andhra University, Visakhapatnam – 530 003, India

putla_paul@yahoo.co.in

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Abstract: Ultrasonic velocity and density measurements were made in two binary liquid mixtures Isopropyl acetate (IPA) and Isobutyl acetate (IBA) with cyclohexanone (CY) as a common component at 303K, at fixed frequency of 2MHz using single crystal variable path interferometer and specific gravity bottle respectively. The experimental data have been used to calculate the acoustic impedance, adiabatic compressibility, inter molecular free length and molar volume. The excess thermodynamic parameters have been evaluated and discussed in the light of molecular interactions.

Keywords: acoustic impedance, adiabatic compressibility, intermolecular free length, molar volume, molecular interactions.

Introduction

Ultrasonic investigations find extensive applications in characterising thermodynamic and physico-chemical behaviour of binary and ternary liquid mixtures. The measurement of ultrasonic velocities and parameters derived from it have been used in understanding the nature of inter molecular and intra-molecular interactions in binary liquid mixtures[1-6]. The study of intermolecular interactions play an important role in the development of molecular sciences.

Having wide usage in flavouring, perfumery, artificial essences, and cosmetics, esters become one of the industrially important class of liquids. Esters are also used as solvents in pharmaceutical and paint industries and as plasticizers in plastic industries. The commercial use of cyclohexanone includes synthesis of nylon. Hence a fundamental understanding of the mixing behavior of alkyl acetates (isopropyl and isobutyl) with cyclohexanone is important from a technical and engineering view point.

The present investigation deals with the study of molecular interaction in 2 binary liquid mixtures at 303 K.

System-I: cyclohexanone + Isopropyl acetate (CY+IPA)

System-II: cyclohexanone + Isobutyl acetate (CY+IBA)

Experimental

The velocity of ultrasonic waves in the liquid mixture have been measured using a single crystal variable path ultrasonic interferometer (Model-F81, Mittal Enterprises, New Delhi) measured at 303 K using 10 ml specific gravity bottle by the standard procedure with an accuracy of $\pm 0.1 \text{ kg m}^{-3}$. The constant temperature was maintained by using thermostat throughout the experiment.

Theoretical Aspects

Various Physical and thermodynamical parameters are calculated using the measured parameters, viz., the ultrasonic velocity (U) and density (ρ).

1. Acoustical Impedance	$Z = \rho U$	$\text{kg-m}^2/\text{sec}$
2. Adiabatic Compressibility	$\beta = 1/(\rho U^2)$	m^2/N
3. Intermolecular free length	$L_f = k (\beta)^{1/2}$	m

where k is a temperature dependent constant. It's value is 201.1209×10^{-8} at 303K.

4. Molar volume	$V_m = M_{\text{mix}} / \rho$	m^3/mole

where M_{mix} is the molecular weight of the mixture in which $M_{\text{mix}} = \sum m_i x_i$

Here m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively.

The excess values are calculated using the general formula, $A^E = A_{\text{exp}} - A_{\text{id}}$ where, $A_{\text{id}} = \sum A_i x_i$ where A_i is any acoustical parameter and x_i is the mole fraction of liquid component.

Results and Discussion

Table 1 shows the values of ultrasonic velocity (U), density (ρ) and excess acoustical impedance (Z^E), excess adiabatic compressibility (β^E), excess free length (L_f^E) and excess molar volume (V_m^E) for cyclohexanone + Isopropyl acetate / Isobutyl acetate at 303K.

From the Table-1, it is observed that ultrasonic velocity (U) and density (ρ) increases with increasing in the mole fraction of cyclohexanone in both the binary systems. This behavior can be attributed to intermolecular interactions in the systems studied [7-8] and may be due to the depolymerization of alkyl acetates caused by the addition of cyclohexanone.

Table 1. Experimental values of ultrasonic velocity (U), density (ρ) and excess acoustical impedance (Z^E), excess adiabatic compressibility (β^E), excess free length (L_f^E) and excess molar volume (V_m^E) for cyclohexanone + Isopropyl acetate / Isobutyl acetate at 303K.

X_1 Mole Fraction of CY	X_2 Mole Fraction of IPA/ IBA	U m/sec	ρ Kg/m ³	Z^E X10 ⁻³ Kg-m ² /sec	β^E X 10 ⁻¹¹ m ² / N	L_f^E X 10 ⁻¹² m	V_m^E X 10 ⁻⁷ m ³ / mole
Cyclohexanone + Isopropyl acetate							
0.0000	1.0000	1096.9	861.6	0.000	0.0000	0.0000	0.0000
0.1123	0.8877	1108.9	865.9	-2.811	2.2907	0.9966	5.3801
0.2218	0.7782	1123.9	871.1	-5.143	3.9700	1.7666	9.3857
0.3284	0.6716	1141.1	876.7	-7.109	5.2782	2.3851	12.716
0.4321	0.5679	1159.1	882.5	-8.850	6.4862	2.9430	15.651
0.5329	0.4671	1192.2	891.8	-8.700	5.3772	2.6265	14.033
0.6312	0.3688	1230.8	902.1	-7.773	3.8942	2.0970	11.272
0.7270	0.2730	1270.8	912.4	-6.543	2.7106	1.6028	8.6419
0.8202	0.1798	1313.2	922.8	-4.896	1.6959	1.0992	5.9985
0.9113	0.0887	1359.1	933.5	-2.713	0.7736	0.5565	3.1611
1.0000	0.0000	1408.0	944.6	0.000	0.0000	0.0000	0.0000
Cyclohexanone + Isobutyl acetate							
0.0000	1.0000	1134.8	860.1	0.0000	0.0000	0.0000	0.0000
0.1259	0.8741	1152.6	866.5	-2.1876	1.2302	0.6227	3.0717
0.2452	0.7548	1169.2	872.8	-4.2353	2.5718	1.2541	6.1261
0.3579	0.6421	1185.6	879.1	-6.0656	3.8237	1.8206	8.9598
0.4642	0.5358	1201.7	884.8	-7.7083	5.1011	2.3849	12.398
0.5652	0.4348	1219.6	891.5	-8.8823	5.9748	2.7717	14.297
0.6610	0.3390	1256.4	902.1	-7.6509	4.3294	2.1623	11.048
0.7521	0.2479	1296.1	913.2	-5.8555	2.6513	1.4648	7.4111
0.8389	0.1611	1333.9	923.8	-4.0912	1.4773	0.8986	4.6051
0.9213	0.0787	1371.1	934.4	-2.0984	0.6249	0.4253	1.9982
1.0000	0.0000	1408.0	944.6	0.0000	0.0000	0.0000	0.0000

As shown in Table 1, the excess adiabatic compressibility β^E values are increasing with increase in mole fraction of CY, reaches maximum at 0.43 mole fraction and then begins to decrease with further increase in mole fraction of CY, more over the values are positive in both the systems studied. This positive trend indicates the presence of weak interaction between the molecules of components of the liquid mixtures. However, the magnitude of β^E values are less positive in the case of the Isobutyl acetate system than that of Isopropyl acetate system. This indicates that the less interaction in the former system. The possible reason may be because of two types of effects. One is the increase of electron density in the O-H bond and the other is the steric effect. These two effects decrease the strength of the intermolecular hydrogen bond formation in the systems under study.

The intermolecular free length L_f has been calculated by using semi-empirical relation given by Jacobson [9]. The excess free length L_f^E follows the same trend as that of β^E in both the systems. These values are positive because of the fact that the sound waves cover only short distance due to decrease in free length ascribing the dominant nature of dispersive forces. Fort et.al [10] indicated that the positive values of excess free length

should attribute to dispersive forces and negative excess values should be due to charge transfer and hydrogen bond formation. In present study the positive contribution of L_f^E in both systems shows a weak interaction [11] between the molecules of alkyl acetates and cyclohexanone.

The excess molar volume V_m^E values are positive over the entire composition range in both the binary mixtures. The value is maximum at 0.5 mole fraction for IPA and at 0.6 mole fraction for IBA. This suggests that the component molecules are not so close in the liquid mixtures as that of in the pure liquids forming the mixtures, indicating the weak interaction between component molecules. Another reason may be the presence non-specific physical interaction and unfavorable interaction between unlike molecules[12]. This leads to expansion of volume during mixing.

The whole discussion is well supported by the excess acoustic impedance Z^E . The Z^E values are negative over the entire mole fraction range and it is maximum at about 0.5 mole fraction of cyclohexanone. The negative trend of Z^E clearly suggests that there is a weak molecular interactions existing between the unlike molecules. The reason may be that the rupture of the hydrogen bond chain of alkyl acetates dominates over that of the hydrogen bond formed between the unlike molecules.

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. Also it is found that bond breaking predominates over the other type of molecular interactions.

Further it is noticed that the weak interactions are more in the binary mixture of CY + IBA than in CY + IPA binary liquid mixture. This can be attributed to the increase of chain length in IBA.

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