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Ultrasonic studies on ternary liquid systems at different temperatures

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ABSTRACT

The measurement of ultrasonic velocity, density and viscosity has been made for the ternary liquid mixtures of 1-pentanol and 1-hexanol with decane in cyclohexane at different temperatures (303 K, 308 K and 313 K). Acoustic parameters such as adiabatic compressibility, intermolecular free length, free volume and internal pressure have been evaluated. Weak molecular interaction taking part between the unlike molecules of solute in each mixture have been studied through these acoustical parameters and their excess values.

Keywords: Acoustic parameters, adiabatic compressibility, intermolecular free length, free volume, internal pressure.

INTRODUCTION

The properties of liquid mixtures are very important as a part of studies of thermodynamic, acoustic and transport aspects. The compositional dependence of thermodynamic properties has proved to be very useful tool in understanding the nature and extend of molecular aggregation resulting from intermolecular interaction between components. This type of study is a powerful means of characterizing the various aspects of physico-chemical behavior of liquid mixtures [1-4]. Ultrasonic methods have used by many researchers [5-7] to investigate the structural properties of pure liquid and liquid mixtures. Ultrasonic velocity together with density and viscosity data furnish a wealth of information about the sum total of interactions between ions, dipoles, H-bonding, multipolar and dispersion forces [8,9]. The use of alcohol in preparing a number of compounds like aldehydes, ketones, acids, alkenes, alkanes, alkynes, halides, etc. is well known. Since ultrasonic velocity and related parameters provide better insight into the molecular environment in liquid mixtures, it is to study the molecular association occurring between decane and 1-pentanol/1-hexanol in a non-polar solvent cyclohexane using ultrasonic technique. Moreover, literature survey indicates that no ultrasonic study on these ternary systems has been reported. Therefore, the present study was under taken in order to have a deeper understanding of the intermolecular interaction between the components of the above ternary mixtures.

MATERIALS AND METHODS

The mixture of various concentrations in mole fraction was prepared by taking purified AR grade samples at all temperatures. In all the mixtures, the mole fraction of the second component, decane ($x_2 = 0.3$) was kept fixed, while the mole fraction of the remaining two (x_1 and x_3) were varied from 0.0 to 0.7 so as to have the mixtures of different compositions.

Ultrasonic velocity for the mixtures was measured by using a Pulse Echo Interferometer operating at a frequency of 1 MHz and with accuracy ±0.01%. The cell temperature was maintained using a thermostat having accuracy ±0.01K. The density of mixtures was measured using a specific gravity bottle with an accuracy of ±0.1kgm^{-3}.

The viscosity measurements have been carried out by using an Ostwald's viscometer (10 ml capacity). The overall accuracy of the measurement of viscosity is ±0.001 Nsm^{-2}.

THEORY

From the measured values of the ultrasonic velocity (U), density (ρ) and viscosity (η). The following acoustical parameters were calculated:

i) Adiabatic compressibility (β) = $1/U^2 \rho$ (1)
ii) Intermolecular free length (Lf) = $K_T \beta^{1/2}$ (2)

where K_T is the temperature dependent constant. The values of K_T for different temperatures were taken from the work of Jacobson [10].

iii) Free volume (V_f) = $[\, M_{eff}\, U / \eta K]^{3/2}$ (3)

where M_{eff} is the effective molecular weight ($M_{eff} = \sum m_i x_i$ in which m_i is the molecular weight and x_i is the mole fraction of the Ith component). K is a constant, equal to 4.28 x 10^9 independent of temperature for all liquids [8].

iv) Internal pressure (π_i) = bRT $[K\eta/V]^{1/2}$ $[\rho M_{eff}^{7/6}]$ (4)

where b stands for the cubic packing factor, K the temperature independent constant, R the gas constant, T the absolute temperature.

EXCESS VALUES

Excess parameters A_E by definitions represent the difference between the parameters of real mixture (A_{exp}) and those corresponding to an ideal mixture (A_{id}) as

$$A_E = A_{exp} - A_{id}$$

$A_{id} = \sum A_i x_i$, where A_i ia any acoustical parameter and x_i the mole fraction of the liquid component.

RESULTS AND DISCUSSION

The experimental values of density, viscosity and velocity at temperatures 303 K, 308 K and 313 K for the pure components and for the system 1-pentanol/1-hexanol are given in Table 1. The calculated values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at different temperatures for the pure components and for the mixtures are presented in Table 2. The respective excess values at the said temperatures have been calculated and shown in Figs 1-8.

It is found that the ultrasonic velocity increases with increasing concentration of 1-alkanols. As the number of hydrocarbon groups increases, the sound velocity is found to increase, as it is evident from the Table 1. However as temperature increases, the ultrasonic velocity decreases in the systems. The structural changes of molecules in the mixture take place due to the existence of electrostatic field between the interacting molecules. Thus the structural arrangement of molecules results in the effect of adiabatic compressibility (β), which shows an inverse behavior as compared to the ultrasonic velocity (Table 2).

Cyclohexane belongs to alicyclic hydrocarbon. The packing of carbon atoms in this even numbered alkane group allows the maximum intermolecular attraction [11] and therefore these molecules are highly inert towards electrophile or nucleophile at ordinary temperature.

Table 1. Density (ρ), Viscosity (η) and velocity (U)

Mole fraction		ρ kg m^{-3}			$\eta \times 10^3$ Nsm^{-2}			U ms^{-1}		
		Temperature (K)			Temperature (K)			Temperature (K)		
x_1	x_3	303	308	313	303	308	313	303	308	313
system I : 1- pentanol + decane + cyclohexane										
0.1009	0.5999	756.3	742.9	738.2	0.8806	0.7839	0.6840	1212.2	1199.3	1184.5
0.1999	0.5001	757.9	745.5	741.0	0.9548	0.8805	0.7700	1214.7	1202.3	1186.5
0.2997	0.3999	762.1	750.4	746.4	1.0730	0.9524	0.8770	1216.8	1203.0	1190.1
0.4002	0.3002	765.6	754.9	750.2	1.1880	1.0569	0.9806	1217.7	1208.3	1193.2
0.5003	0.1999	770.4	761.3	756.4	1.2739	1.1835	1.0935	1223.4	1214.3	1199.7
0.6022	0.0995	773.0	764.1	758.5	1.4074	1.2999	1.1657	1227.8	1221.4	1204.9
0.7000	0.0000	775.3	767.9	766.3	1.6145	1.4182	1.2946	1231.7	1224.9	1210.5
System II : 1- hexanol + decane + cyclohexane										
0.1008	0.5995	761.7	754.6	750.5	0.9367	0.8239	0.7610	1232.6	1217.8	1199.2
0.2014	0.4991	766.5	760.2	754.4	0.9920	0.9137	0.9060	1235.4	1221.9	1203.0
0.3001	0.3999	769.7	763.9	760.6	1.0992	1.0210	0.9291	1238.6	1224.8	1206.9
0.4003	0.2998	772.9	767.5	764.9	1.2555	1.1566	1.0688	1245.5	1232.3	1213.0
0.5002	0.1998	777.0	771.6	768.2	1.4785	1.3662	1.2592	1251.1	1237.3	1218.8
0.5960	0.1008	780.8	774.8	771.7	1.7001	1.5077	1.3253	1257.5	1242.4	1220.6
0.7001	0.0000	787.5	782.5	778.3	1.9810	1.7305	1.5777	1269.2	1251.8	1225.8

The primary alkanols are having a characteristic carbocation. The stability of a charged system is increased by the dispersal of the charge. Therefore, any factor that tends to spread out the positive charge of the electron-deficient carbon and distribute it over the rest of the ion must stabilize the carbocation. Thus, these carbocations will be stabilized by electron donating substituent's and will be rendered less stable by electron withdrawing substituent's. The alkyl group, attached to the carbon atom bearing positive charge, exerts an electron –releasing inductive effect and thus reduces the positive charge of the carbon atom to which it is attached, in doing so, the alkyl group itself becomes positive [11]. Hence, weak interactions such as dispersive type or temporary dipoles are expected between the molecules. Further, the increase in chain length involves more number of alkyl group, these interactions are expected to be more pronounced in higher members.

Among the three components, cyclohexane is not expected to involve in any interactions either with decane or with 1-alkanol due to its inertness. Even though, decane is unsaturated, it behaves like a saturated compound ordinarily [11]. Moreover, the presence of decane molecules as electron donor will give higher stability to the carbocation of the 1-alkanols and hence they cannot provide any strong interaction. Further the addition of alkyl group in higher members will reduce the possible interaction between the components of the mixture.

Table 2. Adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i)

Mole fraction		$\beta \times 10^{10}$ Pa^{-1}			$L_f \times 10^{10}$ m			$V_f \times 10^7$ m^3 mol^{-1}			$\pi_i \times 10^{-6}$ Pa		
		Temperature (K)			Temperature (K)			Temperature (K)			Temperature (K)		
x_1	x_3	303	308	313	303	308	313	303	308	313	303	308	313
system I : 1- pentanol + decane + cyclohexane													
0.1009	0.5999	8.9982	9.3587	9.6551	0.5985	0.6153	0.6308	1.8669	2.1874	2.6342	336.0	319.9	304.3
0.1999	0.5001	8.9423	9.2795	9.5862	0.5967	0.6126	0.6286	1.6788	1.8668	2.2379	347.0	336.2	320.4
0.2997	0.3999	8.8624	9.2082	9.4594	0.5940	0.6103	0.6244	1.4219	1.6715	1.8613	367.1	349.4	341.3
0.4002	0.3002	8.8088	9.0732	9.3626	0.5922	0.6058	0.6212	1.2284	1.4470	1.5889	385.1	367.2	360.2
0.5003	0.1999	8.6725	8.9082	9.1855	0.5876	0.6003	0.6153	1.1145	1.2308	1.3609	399.4	389.7	381.3
0.6022	0.0995	8.5815	8.7727	9.0812	0.5845	0.5957	0.6118	0.9748	1.0896	1.2572	417.0	405.0	390.5
0.7000	0.0000	8.5020	8.6795	8.9058	0.5818	0.5925	0.6059	0.8025	0.9667	1.0889	444.2	421.6	411.2
System II : 1- hexanol + decane + cyclohexane													
0.1008	0.5995	8.6412	8.9358	9.2654	0.5865	0.6012	0.6179	1.7922	2.1336	2.3486	337.9	322.1	315.9
0.2014	0.4991	8.5482	8.8105	9.1594	0.5833	0.5970	0.6144	1.6935	1.8845	1.8644	342.1	333.5	328.4
0.3001	0.3999	8.4687	8.7264	9.0261	0.5806	0.5941	0.6099	1.4956	1.6428	1.8512	353.2	346.2	337.2
0.4003	0.2998	8.3405	8.5800	8.8853	0.5762	0.5891	0.6052	1.2665	1.4097	1.5498	370.3	362.0	355.1
0.5002	0.1998	8.2223	8.4656	8.7632	0.5721	0.5852	0.6009	1.0226	1.1323	1.2510	394.7	386.0	378.4
0.5960	0.1008	8.0992	8.3616	8.6977	0.5678	0.5816	0.5987	0.7246	1.0068	1.1897	439.4	398.2	382.0
0.7001	0.0000	7.8829	8.1554	8.5509	0.5602	0.5744	0.5937	0.7068	0.8481	0.9440	440.9	420.0	410.4

As decane is highly relatively higher dielectric constant (2.1) and being an electron donor than cyclohexane (2.02) [12], the interaction between the molecules of decane with cyclohexane is found to be weaker than the interaction with primary alkanols. Since dispersive interactions are dominant between decane and cyclohexane, the same type of interaction may also occur between the primary alkanols and cyclohexane due to the non-polar nature of cyclohexane and its inertness towards electron donors. The addition of 1-alkanols with the mixture leads to a compact structure due to the presence of dipolar or dispersive type interactions. This contributes to a decrease in free length (Table 2) and hence compressibility. The regular fall in free length with the mole fraction of alkanols may be attributed to the close approach of the molecules [13]. The increase in the free length with mole fraction in the case of lower members is due to the loose packing of the molecules inside the shield, which may be brought about by weakening of molecular interactions.

According to Erying and Kincaid [14], the regular fall in free length causes a rise in sound velocity in the mixture. This is also in accordance with expected decrease in adiabatic compressibility following an increase in the sound velocity in the mixtures studied. Further, this trend is an indication of clustering together of the molecules into same cage like agglomerates due to associative effect of the polar group predominating over the other types of interactions [15].

As the inert solvent, cyclohexane causes breakup of H-bonds in alcohol aggregates, the free space between the component molecules increases [16], leading to a decrease in velocity of increase in compressibility at lower mole fractions of alcohols. However, as the mole fraction of cyclohexane decreases, the rapture of hydrogen bonds is restricted and hence the free space between the component molecules decreases. These two opposing effects compensate each other to different degrees throughout the entire mole fraction range in the mixtures containing lower alcohols. The free space decreases as the chain length of the alcohol increases. This suggests that the increase in the size of the alcohol changes the concentration of closely packed aggregates. As result, liquid mixtures become lesser and lesser compressible with increase in chain length of the alcohol. These effects are reflected in the observed free length variations. The rise in temperature makes the free length to increase, as expected due to the thermal expansion of the liquid medium [17]. Thus, it is clear that the intermolecular free length is the determining factor to the nature of variation of the sound velocity in the mixtures and also lends a support to the presence of specific molecular interaction between the components of liquid mixture [18].

From Table 2, a decrease in free volume and an increase in internal pressure with increase in concentration of 1-alkanol is observed respectively, which may be attributed to the increase in magnitude of interactions [19]. As the dipole moment of cyclohexane is zero [12], the decrease in free volume shows that the clustering is not due to H-bonding but may be due to dispersive interactions. It is primarily due to the formation of spherical cage-like structures owing to the closer packing of the molecule [20]. The same is found to exhibit a reverse behavior with rise in temperature.

In order to highlight the presence of interaction between the molecules, it is essential to study the excess parameters. The deviation of a parameter from the ideal behavior is a measure of the interaction between the molecules, which may be due to either adhesive or cohesive forces [21]. They can give an idea about the non-ideality of the system as a consequence of associative or other types of interactions [15].

The excess adiabatic compressibility β^E (Figs. 1 & 5) and excess free length L_f^E (Figs. 2 & 6) are positive in these systems at all temperatures, indicating weak interactions between the components of mixtures. The observed values of these parameters indicate that the dissociation of the alcohol aggregates predominates over association between unlike molecules. The positive excess adiabatic compressibility shows again a weak interaction between the unlike molecules in the systems studied, which is in agreement with the investigation of Sivanarayana et al [22]. It is evident from this study that the addition of third component weakens the strength of interaction and the ternary mixtures tend to approach ideal behavior, as reported by Rastogi [23]. Accordingly, the decrease in excess free length with increase of either continuously or after attaining maxima, indicates the presence of specific interaction between the different sizes of molecules. The rise in the value of these parameters with temperature reveals further weakening of interaction. The values of excess free volume in 1-alkanols (Figs. 3 & 7) are positive in lower concentration and decrease with increase in concentration of 1-alkanols. This is due to the weakening of interaction between the molecules of the mixture. Such a behavior is also noticed by Ali et al [1] and by Rastogi [24] in some ternary liquid mixtures. The negative excess internal pressure in all the mixtures (Figs.4 & 8) is clearly confirms this prediction.

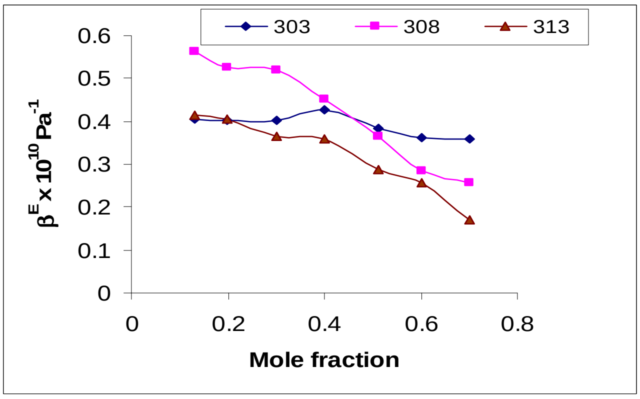

Fig. 1

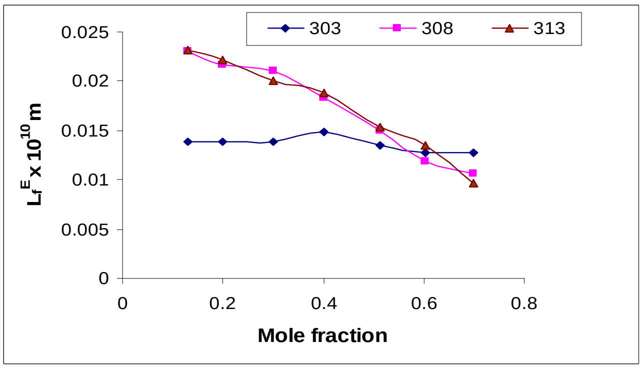

Fig. 2

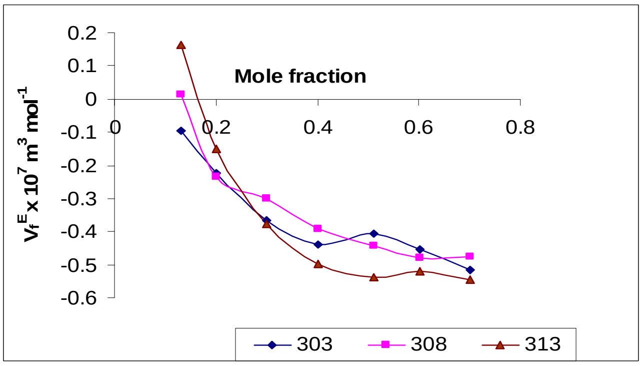

Fig. 3

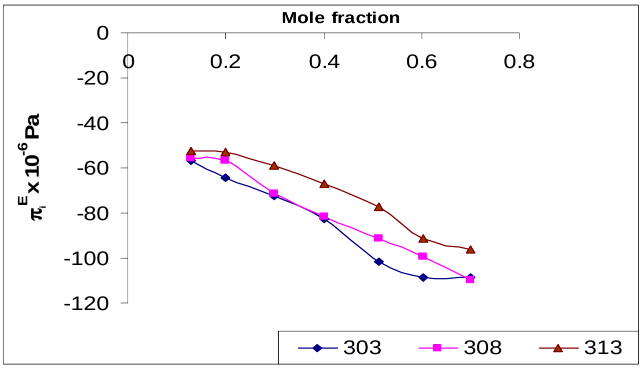

Fig. 4

Fig. 1-4. System I Mole fraction Vs Excess values of adiabatic compressibility, free length, free volume, and Internal pressure respectively

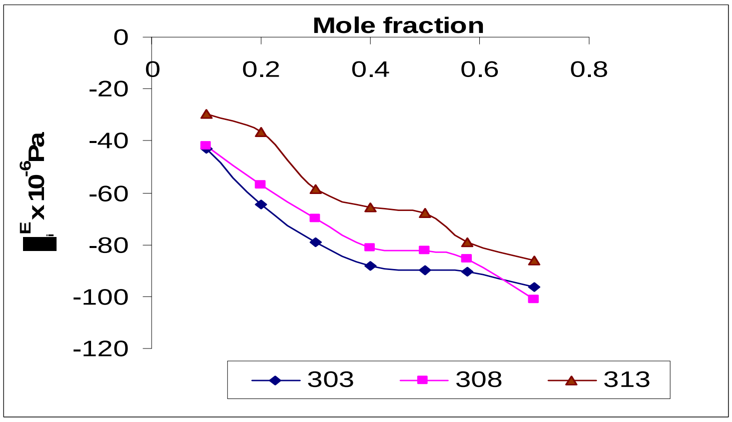

Fig. 5

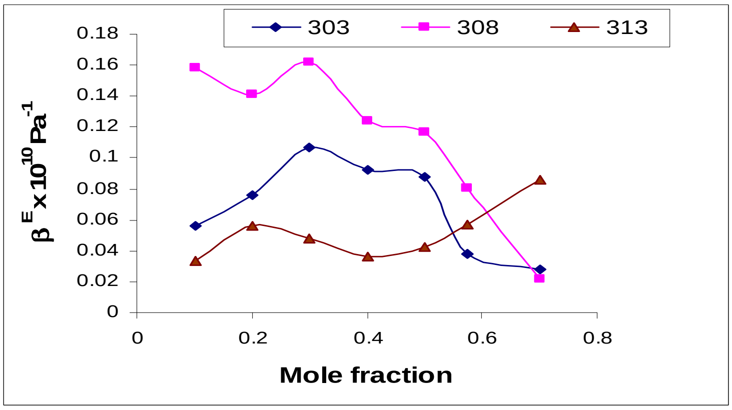

Fig. 6

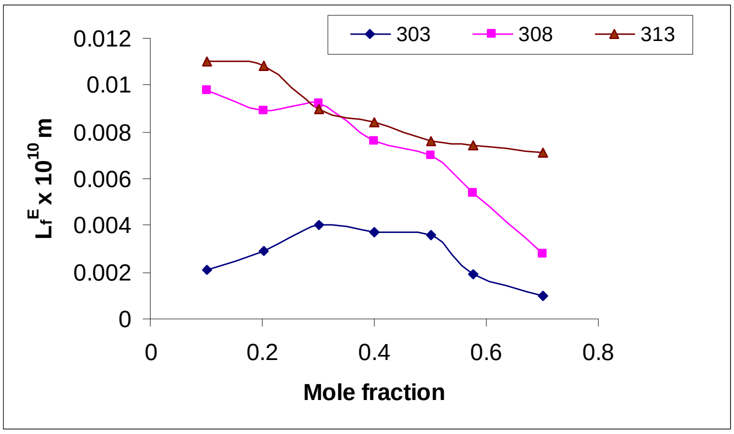

Fig. 7

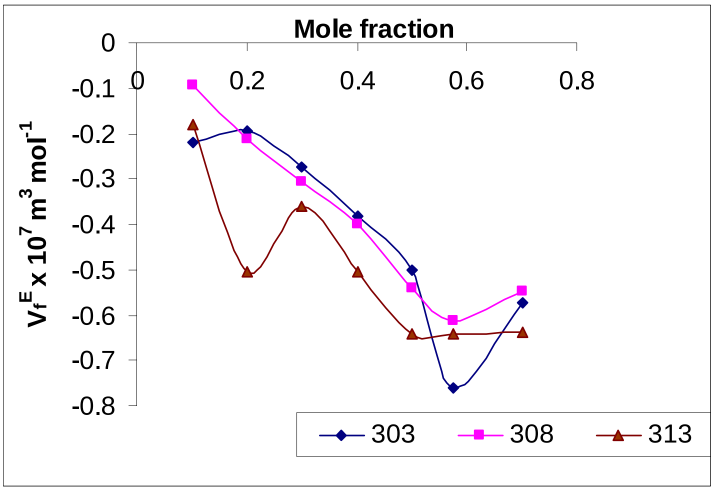

Fig. 8

Fig. 5-8. System II Mole fraction Vs Excess values of adiabatic compressibility, free length, free volume, and Internal pressure respectively

CONCLUSION

The derived acoustical parameters and their positive excess values hint to the presence of dispersive interactions between the components molecules in the mixtures studied.

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