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Ultrasonic Velocity, Viscosity, Density and Excess Properties of Ternary Mixture of N-Methylcyclohexylamine+Benzene+1-Propanol

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Abstract: Ultrasonic velocity (U), viscosity (η), density (ρ) has been measured for ternary mixture of N-methylcyclohexylamine with 1-propanol using benzene as a solvent at three temperatures 303.15, 308.15 and 313.15 K, over the entire range of composition. Adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) have been calculated using experimental values of ultrasonic velocity (U), viscosity (η) and density (ρ). The results have been used to discuss the nature and strength of intermolecular interactions in the system. Excess values of the above said parameters were plotted against the mole fraction of N-methylcyclohexylamine over the entire composition range, indicates that the strong and weak hydrogen bonding interaction between the molecules of the mixture.

Key words: Ultrasonic velocity, ternary mixture, hydrogen bonding, intermolecular interaction

INTRODUCTION

Liquids, liquid mixtures (multicomponent) and solutions have found wide applications in chemical, textile, leather and nuclear industries, well explained by Acree (1984) and Prausnitz *et al.* (1986). The study and understanding of thermodynamic and transport properties of liquid mixtures and solutions are more essential for their application in these industries. Awasthi and Shukla (2003), Pimental and Maclellan (1960) and Marcus *et al.* (1952) have studied the IR, Raman Effect and dielectric properties of multicomponent (binary, ternary mixtures etc.) mixtures and solutions. Like other methods, the measurement of ultrasonic velocity in the liquid mixtures and solutions has also been found to be an important tool to study the physico-chemical properties of the mixtures and solutions.

Lagemann and Dunbar (1945) was the first to point out the interaction in liquids. Volker Hanel *et al.* (1998) have measured sound velocity and thickness of thin samples by time-resolved acoustic microscopy. Venkatesu *et al.* (2006) have evaluated the ultrasonic sound velocity and density for the ternary mixtures of N, N-dimethylformamide (DMF) and cyclohexanone with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol at 303.15K and predicted the possible molecular interaction between the unlike molecules.

The accurate thermodynamic properties of alcohols, in particularly propan-1-ol are of interest for different branches of science and engineering. Propan-1-ol is an important industrial chemical fluid. Furniss *et al.* (1989) have explained propan-1-ol is used as a solvent in the pharmaceutical industry. Hydrogen bonding is one of the most important types of intermolecular interactions play an important role in various physicochemical, biological and industrial processes.

Though a number of investigations were carried out in liquid mixtures having alcohol as one of the components, ternary mixtures with alcohols as one components as indispensable for the industrial rectification column to avoid the formation of azeotropes. Covington and Jones (1968) have confirmed that N-methylcyclohexylamine, are polar and self-associated through hydrogen bonding of their

amino groups. Further, the amine group in the amine tends to participate in hydrogen bonding interaction with the 1-propanol, which can act as electron donor. Literature survey indicates that there has been no temperature-dependent study of this system from the point of view of their ultrasonic and thermodynamic behaviour. Hence, study performed on the interaction of 1-propanol with N-methylcyclohexylamine using benzene as a non-polar solvent.

MATERIALS AND METHODS

The ultrasonic velocities in liquid mixtures have been measured using an ultrasonic interferometer (Model F81) supplied by Mittal Enterprises, New Delhi working at 3 MHz frequency with an accuracy of $\pm 0.1 \text{ m sec}^{-1}$. The temperatures were controlled by circulating water around the liquid cell from a thermostatically controlled water bath (accuracy $\pm 0.1^\circ\text{C}$). The temperature of the cell was measured using a thermocouple (at the crystal) and was found to be accurate to $\pm 0.25^\circ\text{C}$.

The chemicals used were of AR/Merck and S.D.Fine quality. All the chemicals were purified by standard procedures discussed by Perrin and Armarego (1988) before use.

The density and viscosity were measured using a pycnometer and an Ostwald's viscometer respectively with an accuracy of 3 parts in 10^5 for density and 0.001 Ns m^{-2} for viscosity at 303, 308 and 313 K.

Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following standard expressions discussed by Ali and Nain (2002) and Bahl and Bhat (2005):

$$\text{Adiabatic compressibility } \beta = (U^2 \rho)^{-1} \quad (1)$$

$$\text{Intermolecular free length } L_f = K_T \beta^{1/2} \quad (2)$$

$$\text{Free volume } V_f = \left[\frac{M_{\text{eff}} U}{\eta K} \right]^{3/2} \quad (3)$$

$$\text{Internal pressure } \pi_i = bRT \left[\frac{K\eta}{U} \right]^{1/2} \left[\frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}} \right] \quad (4)$$

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (5)$$

and

$$A_{\text{id}} = \sum x_i A_i \quad (6)$$

where, K_T is the temperature-dependent constant having a value 201.1209×10^{-8} in M.K.S. system, M_{eff} is the effective molecular weight, b is the cubic packing factor which is assumed to be 2 for all liquids and solutions, K is a constant equal to 4.28×10^9 in MKS system, independent of temperature for all liquids R is the gas constant; x is the mole fraction; A^E stands for excess property of any given parameter, A_{exp} is the experimental value and A_{id} is the ideal value.

RESULTS AND DISCUSSION

Measured values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i), at 303, 308 and 313 K for the ternary system of N-methylcyclohexylamine+benzene+1-propanol are given in Table 1 and 2. Representative graphs of excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E) as a function of concentration are presented in Fig. 3-6.

Table 1: Density (ρ), viscosity (η) and velocity (U) values of System: N- methylcyclohexylamine+benzene+1-propanol

Mole fraction		Temperature (K)								
		ρ (kg m ⁻³)			$\eta \times 10^3$ (Ns m ⁻²)			U (m sec ⁻¹)		
X ₁	X ₂	303	308	313	303	308	313	303	308	313
0.0000	0.7000	761.0	756.5	755.1	1.3247	1.1955	1.0707	1.221.3	1209.6	1184.6
0.1000	0.6000	766.5	762.8	768.6	1.4185	1.2783	1.1768	1251.0	1231.3	1215.3
0.2000	0.5000	775.6	767.6	773.5	1.4669	1.3051	1.2104	1282.0	1263.3	1242.0
0.3000	0.4000	778.4	778.5	776.8	1.4864	1.3162	1.2431	1299.0	1281.0	1269.0
0.4000	0.3000	786.2	780.8	781.1	1.4155	1.2925	1.1793	1317.3	1285.0	1276.3
0.5000	0.2000	790.1	784.8	786.2	1.2632	1.2279	1.1631	1323.0	1306.0	1286.0
0.6000	0.1000	794.3	786.3	791.8	1.2457	1.1553	1.0570	1335.6	1314.3	1290.3
0.7000	0.0000	804.5	790.7	796.2	1.1979	1.0971	1.0056	1345.0	1331.6	1308.6

Table 2: Adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of System: N-methylcyclohexylamine+benzene+1-propanol

Mole fraction		Temperature (K)											
		$\beta \times 10^{10}$ Pa ⁻¹			$L_f \times 10^{11}$ m			$V_f \times 10^3$ m ³ mol ⁻¹			$\pi_i \times 10^{-8}$ Pa		
X ₁	X ₂	303	308	313	303	308	313	303	308	313	303	308	313
0.0000	0.7000	8.8103	9.0349	9.4373	5.9225	6.0453	6.2367	0.5298	0.6091	0.6966	6.8996	6.6683	6.4724
0.1000	0.6000	8.3360	8.6472	8.8087	5.7608	5.9142	6.0255	0.5572	0.6360	0.7061	6.4721	6.2745	6.1896
0.2000	0.5000	7.8448	8.1632	8.3808	5.5885	5.7463	5.8773	0.6127	0.7142	0.7794	6.0223	5.7766	5.7311
0.3000	0.4000	7.6133	7.8277	7.9941	5.5055	5.6269	5.7401	0.6778	0.7967	0.8559	5.5800	5.3753	5.3257
0.4000	0.3000	7.3301	7.7566	7.8591	5.4021	5.6013	5.6914	0.8189	0.9044	1.0271	5.0564	4.9498	4.8226
0.5000	0.2000	7.2313	7.4705	7.6906	5.3655	5.4971	5.6301	1.0689	1.0940	1.1596	4.4616	4.4803	4.4710
0.6000	0.1000	7.0578	7.3622	7.5859	5.3008	5.4571	5.5916	1.2044	1.3164	1.4632	4.1449	4.0629	4.0043
0.7000	0.0000	6.8708	7.1322	7.3340	5.2301	5.3711	5.4980	1.3977	1.5710	1.7441	3.8396	3.7108	3.6588

All the measured parameters increase with increasing mole fraction of N-methylcyclohexylamine except viscosity. Such nonlinear variation in viscosity indicates the presence of intermolecular interaction between the components. Among the three components, N-methylcyclohexylamine and 1-propanol are expected to involve in strong interaction due to their polar nature.

The coefficient of viscosity initially increases up to 0.3 mole fraction of N-methylcyclohexylamine and then decreases; this may be due to solute-solvent interactions between the molecules. The decrease in viscosity is due to steric effect and may be explained that, as the concentration increases the association of N-methylcyclohexylamine increases or steric crowding is more so that the intermolecular interaction between the N-methylcyclohexylamine and 1-propanol is weakened thereby decreasing viscosity. And also, as N-methylcyclohexylamine (149°C) is having a high boiling point, the energy between the molecules of amine is so high that the molecular bonds of N-methylcyclohexylamine cannot be ruptured, whereas for 1-propanol, it is not so. The increasing mole fraction of amine supports non-rupturing of components and hence, increase in viscosity up to 0.3 mol fraction. There is a uniform decrease in viscosity with temperature indicating loosening of intermolecular forces due to thermal agitation of molecules in the liquid at high temperatures.

As amines are basic in nature due to the presence of unshared electron pair on nitrogen atom which accepts proton; the readiness with which the lone pair of electrons is available for co-ordination with a proton determines the relative strength of amines. Thus due to +I effect of alkyl group, the nitrogen atom becomes rich in electron with the result, the lone pair of electrons on nitrogen atom in amines is more easily available than in ammonia and thus amines are stronger bases than ammonia. However, it is important to note that the relative basic character of amines is not in total accordance with the inductive effect i.e., T>S>P, but it is in the following order:

Secondary>Primary>Tertiary

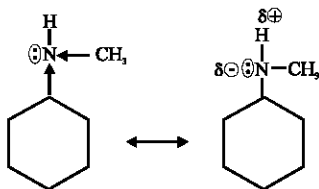


Fig. 1: Formation of partial dipoles due to +I effect

The anomalous behaviour of the tertiary amines is due to the presence of three bulky (alkyl) groups which shield the lone pair of electrons on nitrogen (steric effect) and hence it is not readily available for protonation derived by Agarwal and Agarwal (1996).

In the view of the discussions above, it may be pointed out that the concept used in the present work coincide with N-methylcyclohexylamine (secondary amine), so that there are some possibilities of interactions between 1-propanol and N-methylcyclohexylamine. In N-methylcyclohexylamine the methyl group and cyclohexyl group exerts +I effect. As a result of this effect, the negative and positive charge is partially generated on nitrogen and hydrogen respectively as shown in Fig. 1.

As ρ increases, the number of particles in a given region is increased and this leads to quick transfer of sound energy and thus velocity also increases, this result is in accordance with Arul *et al.* (2001). It can be observed from Table 1, that the ultrasonic velocity is found to increase with the increase in N-methylcyclohexylamine concentration. The increase in ultrasonic velocity in any mixture indicates the maximum association among the molecules of a mixture.

An examination of Table 2 shows that intermolecular free length increases with rise in temperature is identified in the ternary mixtures. This increase in intermolecular free length leads to an increase in compressibility with rise in temperature (Table 2). These results are supported by Pandey *et al.* (1994) view that a temperature increase results increase of intermolecular distance in liquids, thereby increasing the distance between surfaces of two molecules. The increase in intermolecular free length with rise in temperature results in a decrease in density and velocity in the ternary mixtures and this fact is supported by the results of the experimental observations given in Table 1. The mathematical relations for adiabatic compressibility ($\beta = (U^2\rho)^{-1}$) show that they must exhibit opposite behaviour and this behaviour is observed in all the liquid mixtures studied (Table 2).

Ultrasound waves are high frequency mechanical waves. Their velocities in a medium depend inversely on density and the compressibility of the medium reported by Hykes *et al.* (1985). The rapid decrease of adiabatic compressibility (β) with increase of concentration in N-methylcyclohexylamine clearly indicates the formation of a large number of tightly bound systems. Since the velocity increases with concentration and the density does so, the compressibility must decrease with increase in concentration. Such reduction in compressibilities has been found in the solution due to N-methylcyclohexylamine molecules. The decreased compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length as observed in Table 2. At lower concentration of N-methylcyclohexylamine in 1-propanol the molecules are not closer and thus intermolecular free length (L_f) is high. In the more concentrated solution the molecules come closer and segment-segment interaction will exist, thereby decreasing the intermolecular free length and hence internal pressure decreases. A continuous decrease in β or L_f is a clear evidence for the existence of strong interactions. Such strong interaction may be due to charge transfer, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc. The interdependence of L_f and U has been evolved from a model for sound propagation proposed by Kincaid and Eyring (1938).

The extent of free volume (V_f) offers the knowledge of type of interaction. In the present case, an increasing trend of V_f with decreasing trend of π_i is found with increasing mole fraction of N-methylcyclohexylamine. As N-methylcyclohexylamine is more well-structured than 1-propanol

and further if a given fraction of 1-propanol is replaced by same mole fraction of N-methylcyclohexylamine as in the present case, only less number of N-methylcyclohexylamine will be existed due to its higher molecular weight (113.20) than 1-propanol (60.09). Thus, on increasing the mole fraction, total number of components in the system is reduced. This leads to the observed increase in V_f even though specific intermolecular interactions are present. Moreover, the methyl group of N-methylcyclohexylamine and methyl or hydroxyl group of 1-propanol can mutually form dipoles and this dipolar interaction also supports the existence of more space between the components. This is always attributed with a reduction of internal pressure as noticed.

The increase of V_f with temperature may be attributed to more depolymerization of N-methylcyclohexylamine molecules as well as to destabilization of dipolar order of 1-propanol, hence increase in free volume (V_f) of mixture. Further, the increases of free volume (V_f) results into more efficient packing of 1-propanol molecules into the free volume or cavities of N-methylcyclohexylamine.

Further, in order to examine the nature and strength of molecular interaction in the system, excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E) have also been evaluated and shown in Fig. 3-6. The dispersion forces should make positive contributions to excess values while dipole-dipole, dipole-induced dipole, charge-transfer interaction and hydrogen bonding between unlike components should make negative contribution. The strength of the interaction between the components increases when excess value trend to become increasingly negative.

The excess parameters β^E and L_f^E become more negative as the complex formation reaches to a saturation values at certain concentration. At 0.3 mole fraction of N- methylcyclohexylamine in both β^E and L_f^E clearly indicates, in the ternary system the hydroxy group of 1-propanol has more electronegative center i.e., oxygen which form strong intermolecular interaction with the positive center of N-methylcyclohexylamine (Fig. 2) and the presence of intermolecular hydrogen bonding in the above ternary system is confirmed by means of the viscosity results displayed in the Table 1. The presence of strong hydrogen bonding which becomes maximum when the minima of β^E and L_f^E occur i.e., 0.3 mole fraction. This is in conformity with the earlier result of Fort and Moore (1965) on the study of complex formation in mixtures.

The specific variation shown by V_f^E and π_i^E , in which they exhibit negative values and shows a dip formation at 0.3 mole fraction for V_f^E , it becomes positive and at 0.4 mole fraction for π_i^E indicate apart from the strong H-bonding, relatively weak hydrogen bonding (π ---H) between π -electrons of benzene ring and proton of 1-propanol. Thus, stronger H-bonds are formed between N-methylcyclohexylamine and 1-propanol than between benzene and 1-propanol molecules and hence, more negative excess values are observed. Further, it is also evident from Fig. 3-6 that their excess

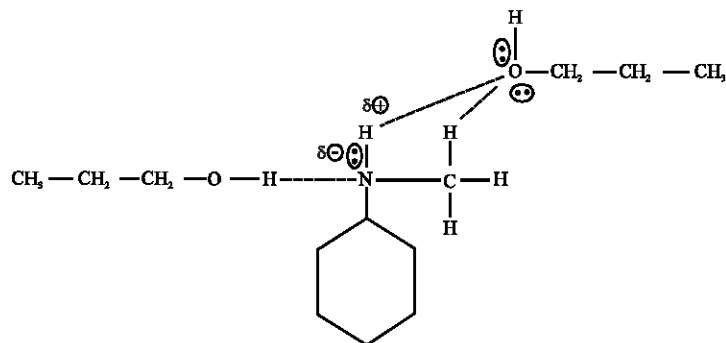


Fig. 2: Formation of hydrogen bonding with 1-propanol

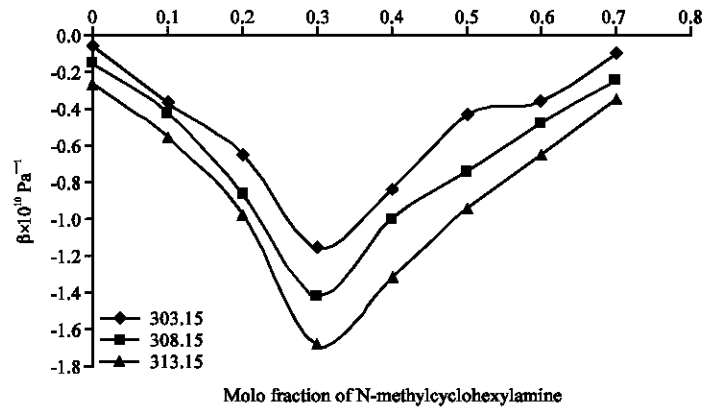


Fig. 3: Mole fraction versus excess adiabatic compressibility

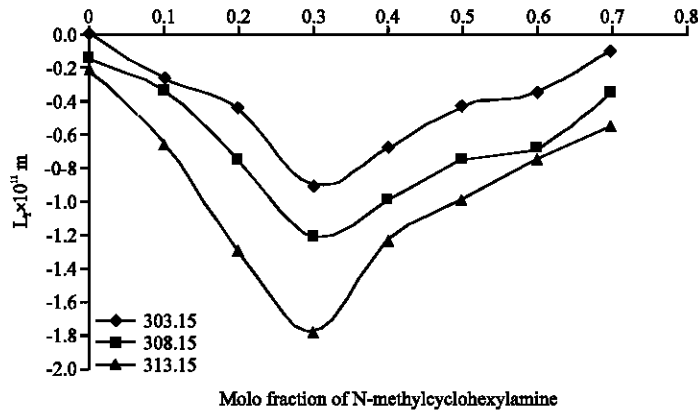


Fig. 4: Mole fraction versus excess free length

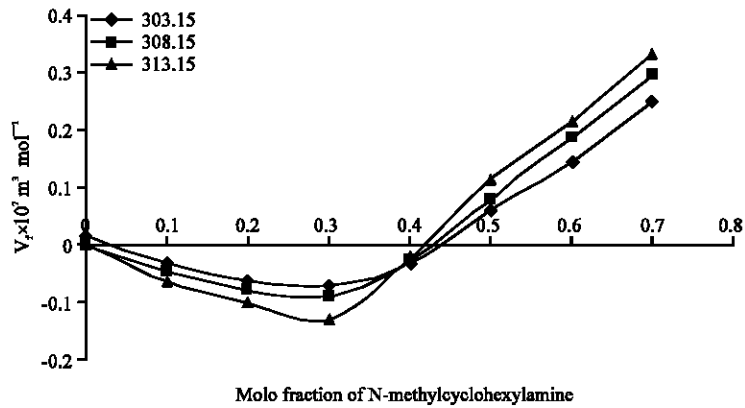


Fig. 5: Mole fraction versus excess free volume

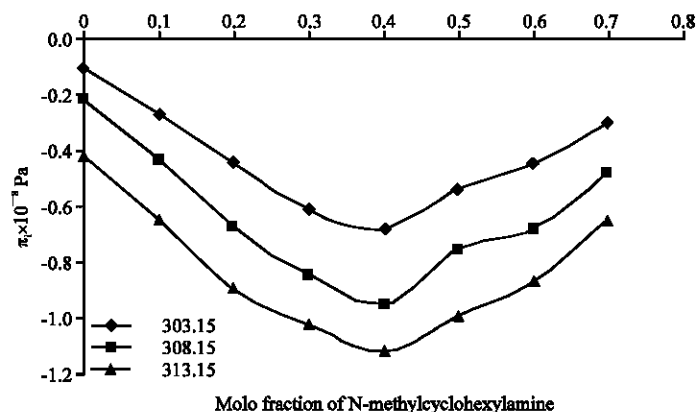


Fig. 6: Mole fraction versus excess internal pressure

values become more negative with increase in temperature of the system. Increase in temperature promotes the breaking of associates present in the pure liquids releasing more and more free dipoles of unlike molecules in the mixture which interact with each other forming greater number of H-bonds among the interacting molecules. As a result, the excess values become more negative with rise in temperature.

CONCLUSION

A strong intermolecular H-bonding interactions exist between N-methylcyclohexylamine and 1-propanol due to +I effect exerted by methyl and cyclohexyl group in N-methylcyclohexylamine and weak H-bonding between 1-propanol and benzene molecules.

From the acoustical parameters it is concluded that intermolecular hydrogen bonding interactions are very strong at 0.3 mol fraction of N-methylcyclohexylamine.

The temperature variation of the ternary mixtures indicates that the strength of intermolecular interaction increases with rises in temperature.

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