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Investigation of Molecular Interaction in Ternary Liquid Mixtures by Viscosity and Ultrasonic Velocity Measurement at 303, 308 and 313K

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the mixtures of cyclohexane with n-butyl acetate in 1-propanol, 1-butanol, 1-pentanol and 1-hexanol at 303, 308 and 313K. The experimental data have been used to calculate the acoustical parameters namely free volume (V_f), internal pressure (π_i), relaxation time (τ), molar volume (V_m) and excess values of V_f, π_i and V_m. These parameters especially excess functions are found to be more sensitive towards the nature and the extent of intermolecular interactions in the ternary liquid mixtures.

KEYWORDS : Free volume, internal pressure, relaxation time, molar volume, excess values

INTRODUCTION

Ultrasonic investigation finds extensive applications in characterizing aspects of thermodynamic and physico-chemical behaviour of binary and ternary mixtures. The measurements of density, ultrasonic speed and parameters derived from it have been used to understand the nature of intermolecular in binary and ternary mixtures (Wankhede et al., 2008). The non-reactilinear behaviour of ultrasonic velocity, compressibility and other thermodynamical parameters of liquid mixtures with changing mole fractions is attributed to the difference in size of the molecules and the strength of interactions (Iloukhani and Rostami, 2003). The investigation on the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been found to be an excellent qualitative and quantitative way to elicit information about molecular structure and intermolecular forces in liquid mixtures (Manisha Gupta et al., 2006).

Moreover excess thermodynamic properties are used as important parameters for understanding molecular interactions. The properties of liquid mixtures can be altered continuously within a reasonable range by varying composition of the mixture/solution till an optimum value of some desired parameter is attained. Pure liquid lack such flexibility. The study of properties of liquid mixtures finds direct applications in the fields of chemistry and biology (Saravanakumar et al., 2007). The study of molecular association in ternary mixtures having an alcohols as one component is of particular interest. Since alkanols are protic, highly associated through hydrogen bonding and this association decreases with increase in alkyl chain length in 1-alkanol (Anilkumar Nain, 2013).

The system of alkanols with alkyl acetate (butyl acetate) are of considerable interaction from the two counts.

Breaking of H-bonded structures of alkanols and

Formation of new H-bonded molecular complexes between alkanol and alkyl acetate (Oswal and Putta, 2001).

To the best of our knowledge ultrasonic studies on ternary mixtures of n-butyl acetate + cylcohexane + 1-alkanols at different temperatures are not reported in the literature. Hence, the aim of this work is to provide databases for the characterization of molecular interactions in the present ternaries and also to study the effect of alcohol chain length as well as temperature on molecular interactions during mixing.

THEORY

The various acoustical parameters such as free volume (V_f), internal pressure (π_i), relaxation time (τ), molar volume (V_m) and excess values of V_f, π_i and V_m were determined using the following equations (Asghar et al., 2010; Aravinth Raj et al., 2011; Dubey et al., 2010);

Where b is a constant which is 2 for cubic packing, R the gas constant

and T is the absolute temperature, K is the temperature independent constant (K = 4.28×10^9), M_{eff} is the effective molecular weight of the solution, X_1, X_2, X_3, and M_1, M_2, and M_3, are the mole fraction and molecular weight of pure liquids.

The excess parameters (A^E) of all the acoustic parameters were computed by the relation

$$A^E = A_{exp} - A_{id}$$

Where where Ai is any acoustical parameter and Xi is the mole fraction of the liquid component i.

MATERIALS AND METHODS

The chemicals used in the present work were Analytical Reagent (AR) grade with minimum assay of 99.9% were obtained from Sd fine chemicals India, which are used as such without further purification. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kgm⁻³. The purities of the above chemicals were checked by density (ρ) determination by pycnometer at 303, 308 and 313 K ± 0.1K which showed an accuracy of ± 0.1 mg on a electronic digital balance (model: SHIMADZU AX 200). The dynamic viscosities (η) were measured using Ostwald's viscometer (10 ml) calibrated with triple distilled water at all experimental temperatures. An electronic digital stopwatch with an accuracy of ± 0.01s was used for flow time measurement. The speed of sound waves were obtained by using ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of ± 2ms⁻¹. An electronically digital operated constant temperature bath (RAAGA Industries, Madras-61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. For preparing various concentration mixtures, the mole fraction of second component cyclohexane was kept constant (X_2=0.4) and the mole fractions of other two components were varied from 0.0 to 0.6.

RESULTS AND DISCUSSION

From the Table 1 it is observed that as the concentration of alcohols increases, free volume (V_f) decreases whereas, the internal pressure (π_i) increases. The decreasing V_f suggest that there is a specific interaction between the components of the mixtures. The observed decreasing values of V_f are due to close association between solute and solvent molecules (Kumara Sastry et al., 2012). The internal pressure value reflects the net cohesive / adhesive forces available in the medium. Such forces will drastically change if mole fraction of the components are changed. An inverse trend is observed in case of internal pressure as compared to free volume. The values of V_f decreases whereas, the π_i increases due to the various degree of dispersive interaction and the coloumbic interaction existing between the component molecules (Sumathi and Uma maheswari 2009) since π_i is a measure of intercomponent forces of attractions (Palaniappan 2001) its value is found to

decrease with temperature in all mixtures.

It is referred from the Table 2 that the relaxation time (τ) increases with increase in mole fraction of 1-alkanols. The viscous relaxation time shows the presence of molecular interaction by addition of 1-alkanols (Praharaj et al., 2012). The decreasing values of relaxation time with increasing temperature show a weak intermolecular forces existing between the component molecules with rise in temperature.

Fig. 1 gives the value of the excess free volumes (V_f^E) for the ternary liquid mixtures. The excess values are found to be positive in all the systems studied which indicates the existence of weak molecular interaction in the liquid mixtures (Rajagopal and Chenthilnath, 2010). In the study of liquid mixtures the variations of the excess internal pressure (π_i^E) may give some information regarding the nature and force existing between the molecules. The values of excess internal pressure are found to be negative for all the systems (Fig. 2) over the entire mole fraction range. It is interesting to note that the variation in the internal pressure values and their deviation behave exactly in a reverse trend as that of free volume. The negative values of π_i^E indicate that only dispersion and dipolar forces operating with complete absence of specific interaction (Sumathi and Uma maheswari, 2009) which also supports the present conclusion. Similar trends were observed in Manisha Gupta et al. (2006).

From the Fig. 3, it is observed the excess molar volume (V_m^E) for all the four ternary mixtures are positive, except at higher mole fraction in 1-propanol. As it is known the excess molar volume depends mainly on the intermolecular forces between components of the mixtures result from the contributions due to the physical, chemical and structural characteristics of the component liquids. The physical contributions comprise dispersion forces and non-specific physical (weak) interactions which lead to positive V_m^E values. The chemical contributions involve breaking up the associates present in the pure liquids, resulting in positive V_m^E values. These contributions also involves specific interactions such as formation of H-bonding charge transfer (donar-acceptor) complexes, and strong dipole-dipole interactions between the component molecules of the mixture, resulting in negative V_m^E values. The structural contributions are due to the geometrical fitting (favourable or unfavourable) of the molecules of very different molecular size into each other's structures resulting in negative or positive V_m^E values (Anil Kumar Nain, 2013).

Hence the observed positive values of V_m^E may be due to the disruption of the H-bonds between alcohol molecules and non-specific interactions are predominant over the less significant contribution from structural effects (Gonzalez et al., 2013) whereas the observed negative V_m^E values at higher mole fraction of 1-propanol indicate the presence of significant interactions between the component molecules, leading to a contraction in volume of the mixture, which results in negative V_m^E values for these mixtures (Anil Kumar Nain, 2013).

Conclusion

The results obtained for the present study indicate that the thermodynamic parameters are sensitive to the molecular interaction present in liquid mixtures. The positive values of V_f^E, V_m^E and negative value of π_i^E in all the three mixture reveals the presence of weak dipolar and dispersive interactions between the component molecules in the mixtures. The behaviour of all the excess parameters studied here support each other.

Table 1
Values of Free volume (Vf) and Internal pressure (πi) of cyclohexane and n-butylacetate in 1-alkanols

Mole fraction		V_f/(× 10⁻⁷ m³mol⁻¹)			π_i / (× 10⁶ pa)		
		Temperature (K)					
X_1	X_3	303	308	313	303	308	313
System I: 1-propanol + cyclohexane + n-butyl acetate							
0.0000	0.5999	2.977	3.089	3.337	302.0	301.7	298.1
0.1000	0.5000	2.679	2.803	3.017	322.0	321.8	318.5
0.1999	0.4000	2.416	2.542	2.682	345.4	344.5	343.4
0.3000	0.3000	1.989	2.171	2.286	382.8	377.0	375.9
0.4000	0.2000	1.627	1.753	1.941	425.9	421.6	412.4
0.5000	0.1000	1.262	1.335	1.464	484.9	481.9	472.9
0.6000	0.0001	0.7832	0.867	1.007	593.1	580.1	559.7
System II: 1-butanol + cyclohexane + n-butyl acetate							
0.1000	0.5000	2.691	2.892	3.111	317.3	313.3	309.9
0.2001	0.4000	2.248	2.357	2.625	345.6	344.2	336.6
0.2999	0.3000	1.871	2.101	2.287	376.9	367.4	362.7
0.4001	0.1999	1.412	1.654	1.851	413.6	425.8	399.6
0.4999	0.0999	1.101	1.201	1.281	475.1	467.9	464.2
0.6000	0.0000	0.734	0.823	0.961	559.2	545.3	523.5
System III: 1-pentanol + cyclohexane + n-butyl acetate							
0.0999	0.4999	2.630	2.831	3.094	316.0	312.2	309.4
0.1995	0.4000	2.337	2.458	2.686	332.8	331.9	326.8
0.2998	0.3000	1.841	1.963	2.205	365.4	362.6	353.5
0.4000	0.2000	1.430	1.564	1.726	404.6	397.7	390.5
0.5000	0.1001	0.977	1.168	1.376	466.4	444.9	427.3
0.5992	0.0000	0.671	0.780	0.934	536.5	517.1	492.5
System IV: 1-hexanol + cyclohexane + n-butyl acetate							
0.1001	0.5001	2.660	2.789	2.974	311.4	309.5	307.4
0.2000	0.4000	2.048	2.193	2.451	340.6	336.8	328.6
0.2999	0.2999	1.592	1.771	1.979	372.0	363.5	355.3
0.3999	0.1999	1.252	1.356	1.584	405.5	399.8	385.1
0.5000	0.1000	0.869	1.016	1.117	460.4	442.2	434.7
0.6000	0.0000	0.566	0.667	0.762	532.8	510.0	494.6

Table 2
Values of relaxation time (τ) and molar volume (Vm) of cyclohexane and n-butylacetate in 1-alkanols

Mole fraction		τ/ (× 10⁻¹²)s			V_m / m³ mol⁻¹		
		Temperature (K)					
X_1	X_3	303	308	313	303	308	313
System I: 1-propanol + cyclohexane + n-butyl acetate							
0.0000	0.5999	0.7601	0.7591	0.7345	0.1249	0.1257	0.1262
0.1000	0.5000	0.7751	0.7683	0.7451	0.1195	0.1198	0.1201
0.1999	0.4000	0.7850	0.7740	0.7611	0.1133	0.1134	0.1138
0.3000	0.3000	0.8409	0.8091	0.7979	0.1069	0.1073	0.1076
0.4000	0.2000	0.9024	0.8756	0.8358	0.1007	0.1010	0.1016
0.5000	0.1000	0.9961	0.9794	0.9424	0.0941	0.0947	0.0953
0.6000	0.0001	1.276	1.215	1.124	0.0884	0.0889	0.0892
System II: 1-butanol + cyclohexane + n-butyl acetate							
0.1000	0.5000	0.7859	0.7664	0.7479	0.1221	0.1230	0.1235
0.2001	0.4000	0.8499	0.8428	0.8001	0.1175	0.1183	0.1188
0.2999	0.3000	0.9209	0.8708	0.8382	0.1131	0.1137	0.1138
0.4001	0.1999	1.062	0.9747	0.9232	0.1084	0.1091	0.1094
0.4999	0.0999	1.198	1.151	1.126	0.1042	0.1046	0.1050
0.6000	0.0000	1.485	1.406	1.302	0.0999	0.1004	0.1012

System III: 1-pentanol + cyclohexane + n-butyl acetate							
0.0999	0.4999	0.8101	0.7886	0.7711	0.1242	0.1250	0.1256
0.1995	0.4000	0.8540	0.8449	0.8119	0.1219	0.1224	0.1227
0.2998	0.3000	0.9755	0.9552	0.8989	0.1194	0.1199	0.1204
0.4000	0.2000	1.118	1.076	1.027	0.1163	0.1170	0.1172
0.5000	0.1001	1.397	1.262	1.158	0.1137	0.1144	0.1147
0.5992	0.0000	1.725	1.592	1.451	0.1112	0.1117	0.1125
System IV: 1-hexanol + cyclohexane + n-butyl acetate							
0.1001	0.5001	0.8146	0.8109	0.7913	0.1263	0.1276	0.1279
0.2000	0.4000	0.9566	0.9348	0.8867	0.1258	0.1267	0.1274
0.2999	0.2999	1.118	1.062	0.9989	0.1250	0.1258	0.1261
0.3999	0.1999	1.283	1.246	1.143	0.1239	0.1246	0.1250
0.5000	0.1000	1.605	1.477	1.412	0.1229	0.1238	0.1241
0.6000	0.0000	2.094	1.923	1.781	0.1223	0.1233	0.1237

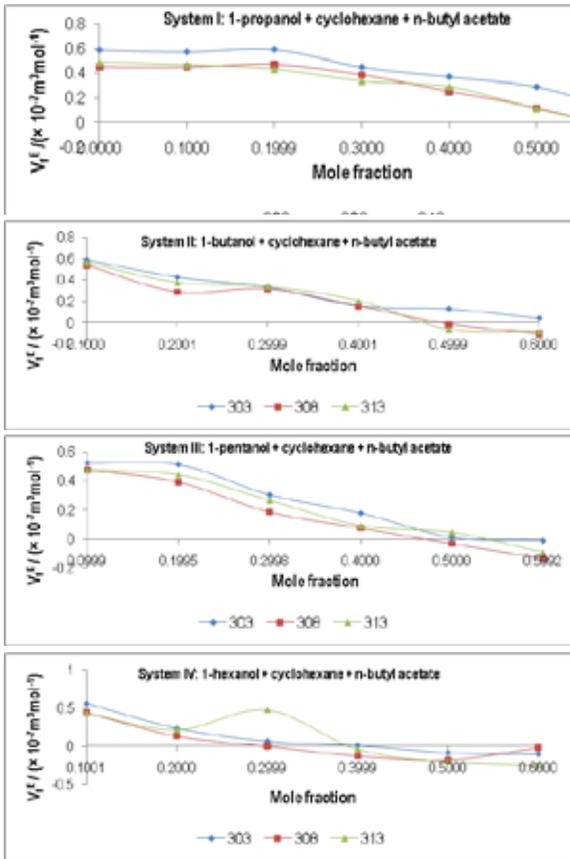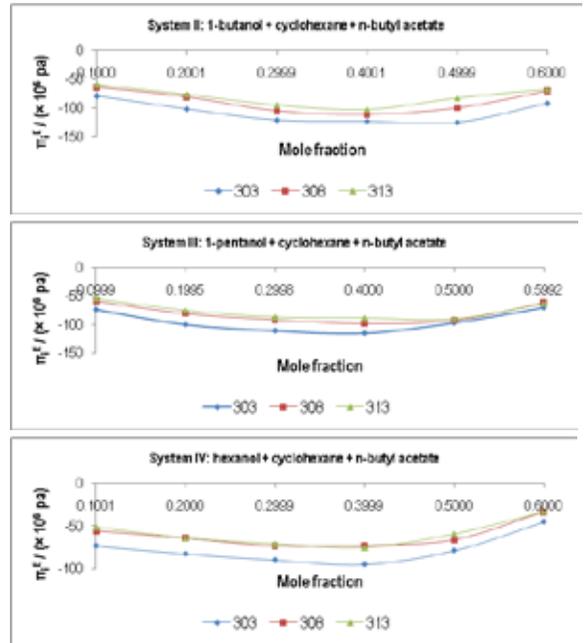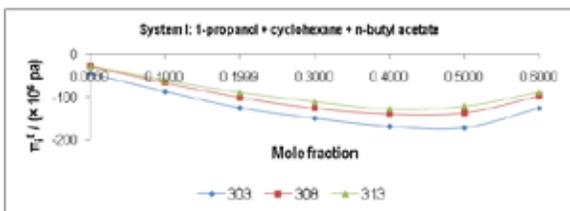Fig. 2: Excess internal pressure vs mole fraction of 1-alkanols

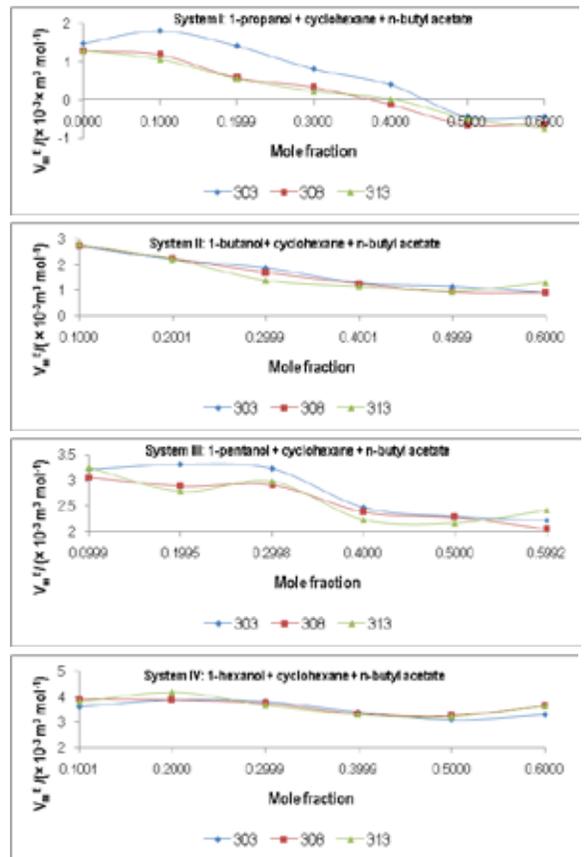Fig. 1: Excess free volume vs mole fraction of 1-alkanols

Fig. 3: Excess molar volume vs mole fraction of 1-alkanols

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