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ACOUSTIC AND EXCESS THERMODYNAMICAL STUDIES ON 1-ALKANOLS WITH DMA IN CYCLOHEXANONE AT DIFFERENT TEMPERATURES

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the mixtures of 1–alkanols, namely, 1–propanol,1–butanol, and 1–pentanol with N,N-dimethyl acetamide (DMA) in cyclohexanone at 303, 308 and 313K. The experimental data have been used to calculate the acoustical parameters, namely excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E). These excess values predict the dissociation of hydrogen bonded structure of 1- alkanols and also the rupture of hydrogen bonds in the associated structure of 1-alkanols when it is mixed with DMA. It is also interesting to note that the elevation of temperature too induces the rupture of hydrogen bonds of unlike molecules..

Keywords: rupture of hydrogen bonds, dipole-dipole interactions, excess free volume, polar liquids, aprotic

INTRODUCTION

In our earlier investigations, [1-2] we made an attempt by making use of an ultrasonic technique to explore the behavior of some of the amino acids as well as in organic liquid mixtures. In recent years much effort has been made with measurement and interpretation of the ultrasonic properties of liquids and liquid mixtures. The ultrasonic studies are of great importance in helping to understand the nature and extent of the patterns of molecular aggregation that exist in liquid mixtures, resulting from intermolecular interactions.[3-4] N-N dimethylacetamide (DMA) is normally belonging to the amide group due to its wide range applicability as solvent in chemical and biological processes. It is highly polar, aprotic solvent and its molecules are associated through dipolar interactions.[2] On the other hand, alkanols are polar liquids, strongly self-associated by hydrogen bonding to extents of polymerization that may differ depending upon temperature, chain length and position of the OH group. Alkanol size, chain length etc., (which is related through density and refractive index) are important parameters that must be taken into account to explain the behavior of the DMA, cyclohexanone with 1-alkanols mixtures.

The ultrasonic studies for the binary mixtures of N,N-dimethylformamide (DMF) with substituted benzenes[5] with alcohols[6] with branched alcohols[7] with aliphatic esters[8] with tetrahydrofuran[9] with Chloroethanes and Chloromethanes[10] and with Vinylpyrrolidine[11] are already reported in the literature. Further,an exhaustive survey of literature has shown that a few attempts have been made for the ultrasonic velocity data of ternary mixtures[12-13].However, no effort appears to have been made to collect the ultrasonic velocity data for the ternary mixtures of N,N-dimethylacetamide, cyclohexanone with 1-alkanols. Hence, an experimental study were carried out by the authors and reported N,N-dimethylacetamide (DMA) + cyclohexanone + 1-alkanols, namely 1-propanol, 1-butanol and 1-pentanol at different temperatures.

The following liquid systems were taken at 303,308 and 313K

System-I 1-propanol + cyclohexanone + DMA
System-II 1-butanol + cyclohexanone + DMA
System-III 1-pentanol + cyclohexanone + DMA

EXPERIMENTAL

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay were obtained from Sd fine chemicals India and E-merck, Germany as such without further purification. In all systems, the various concentrations of the ternary liquid mixtures were prepared in terms of mole fraction, out of which the mole fraction of the second component cyclohexanone ($X_2 = 0.4$) was kept fixed while the mole fractions of the remaining two components 1-alkanols (X_1) and DMA (X_3) were varied from 0.0 to 0.6. There is nothing significant in fixing the second component at 0.4. The density of pure liquids and liquid mixtures are determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.1mg (Model: SHIMADZU AX-200).An Ostwald's viscometer which is 10ml capacity is used for the viscosity measurement of pure liquids and liquid mixtures. The viscometer is calibrated with fresh conductivity water immersed in the water bath which is kept at the experimental temperature. The time of flow (t_W) of water and the time flow (t_S) of solution is measured with digital stop clock having an accuracy of 0.01s (Model: RACER HS-10W) An ultrasonic interferometer (Model: F81) supplied by M/s. Mittal Enterprises, New Delhi, having the frequency 3MHz with an overall accuracy of ± 2 ms^{-1} has been used for velocity measurement.

Theory and Calculations

Using the measured data, the following acoustical parameters have been calculated

Adiabatic Compressibility

$$\beta = \frac{1}{U^2 \rho} \tag{1}$$

Intermolecular free length (L_f) has been calculated from relation,

$$L_f = K_T \sqrt{\beta} \tag{2}$$

where K_T is a temperature dependent constant.

Free volume (V_f) has been calculated from relation,

$$V_f = \left(\frac{M_{eff} U}{K \eta} \right)^{3/2} \tag{3}$$

where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma m_i x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

The internal pressure (π_i) can be found out as

$$\pi_i = bRT \left(\frac{K\eta}{U} \right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}^{7/6}} \right) \tag{4}$$

K is a constant, T the absolute temperature, η the viscosity in Nsm^{-2}, U the ultrasonic velocity in ms^{-1}, ρ the density in Kgm^{-3}, M_{eff} the effective molecular weight.

Excess parameter (A^E) has been calculated by using the relation

$$A^E = A_{exp} - A_{id} \tag{5}$$

where $A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameters and X_i the mole fraction of the liquid component.

RESULTS AND DISCUSSION

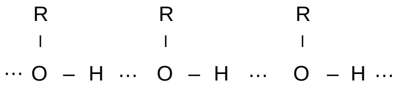
The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of all the pure liquids at 303, 308, and 313K are presented in Table 1 and the same for the three ternary systems are listed in Table 2. The excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E), and internal pressure (π_i^E) at the three different temperatures are reported in Table 3. The Figure-1 represents the variation of excess free volume (V_f^E) of all 1-alkonols with their corresponding mole fraction.

In all the mixtures, the ultrasonic velocity decreases with increase in mole fraction of alkanols. It is observed that as the number of hydrocarbon group or chain-length of alcohol increases, a gradual decrease in sound velocity is noticed. This behaviour at such concentrations is different from the ideal mixtures behaviour can be attributed to intermolecular interactions in the systems studied[14-15]. The dissociation of hydrogen bonded structure of 1-alkanols due to mixing of DMA with it may result in decrease in ultrasonic velocity.

Alkanols are liquids which are associated through the hydrogen bonding and in the pure state, they exhibit an equilibrium between the monomer and multimer species. Also, they can be associated with any other groups having some degree of polar attractions[2]. Due to polar nature of DMA and cyclohexanone and alkanols, the dipole-dipole interactions prevail in these mixtures. When the compounds are mixed, the changes that occur in association equilibria are evidently rupture of the hydrogen bonds[16] in pure cyclohexanone and alkanols and DMA-DMA dipole-dipole interactions and the formation of O-H…C=O and perhaps even O-H…..$N(CH_3)_2$ hydrogen bonds between the components.

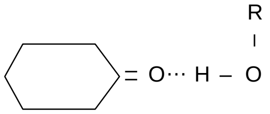
Mixing of DMA with alkanols would release the dipoles of alkanols due to the breaking of hydrogen bonds. As a result, the free dipoles released from the alkanols in association with DMA molecules forming strong hydrogen bonds, hence stronger molecular association existing between the DMA and alkanols molecules through hydrogen bonding[17]. Further, mixing of such DMA with 1-alkanols causes dissociation of hydrogen bonded structure of 1-alkanols and subsequent formation of (new) H-bond (C=O –H….O) between proton acceptor oxygen atom (with lone pair of electrons) of C=O group of DMA and proton of OH- group of 1-alkanols[18].

The 1–alkanols are associated through hydrogen bonding,



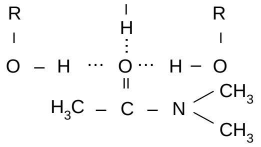
$$\cdots\underset{\substack{|\\R}}{}\overset{\substack{R\\|}}{O}-H\cdots\overset{\substack{R\\|}}{O}-H\cdots\overset{\substack{R\\|}}{O}-H\cdots$$

and, cyclohexanone–1–alkanols interactions are due to hydrogen bonding between the oxygen atom of the ketone (cyclohexanone) and the proton of hydroxyl group of alkanols.



The following studies by earlier workers clearly support our present investigation. Ultrasonic velocity in binary mixtures of Methyl isobutyl ketone (MIBK) with aliphatic alcohol is investigated by Das *et. al.,*[19] and was discussed in terms of hydrogen bond formation between the ketone and alcohols. Also, Selvakumari[20], pointed out from the study of ternary mixtures of Methyl iso-butyl ketone (MIBK) with 1-alkanols in benzene that there is formation of hydrogen bonding between the ketone and 1-alkanols.

Further addition of N, N-dimethylacetamide (DMA)) with mixtures causes dissociation of hydrogen bonded structure of 1-alkanols as well as decrease in interaction between Ketone (cyclohexanone) and alkanols. The subsequent formation of new hydrogen bonding between proton acceptor oxygen atoms of $>C=O$ group of DMA and proton of – OH group of 1-alkanols[18]. $\left[>C=O\cdots H-O-\right]$.



In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The effect of deviation depends upon the nature of the constituents and composition of the mixtures. The excess values of adiabatic compressibility (β^E), intermolecular free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) for all the three liquid systems are furnished in Table 3. In the present investigation, it is observed that all the excess values of all the parameters exhibit positive deviation over the entire range of composition in all three liquid systems The positive excess values of adiabatic compressibility(β^E) and free length (L_f^E) in all the three liquid systems indicate that the dispersion forces (or weak forces) are dominant in these systems.[21-22] Such a domination of dispersion forces in these systems can be attributed to the fact that the component molecules may have different molecular size. Further, the increase in temperature however makes the free length to increase as expected due to the thermal expansion of the liquids. It is interesting to note that such a rise in temperature also induces the rupture of hydrogen bonds between unlike molecules

It is noticed from the Table 3, that the excess values of free volume (V_f^E) are positive for all the three ternary liquid systems over the entire composition range. A plausible qualitative explanation on the behavior of these mixtures has been suggested. Mixing of DMA with 1-alknaols causes dissociation of hydrogen bonded structure of 1-alkanols and subsequent formation of (new) H-bond [C=O …..H-O] between proton acceptor oxygen atom (with lone pair of electrons) of C=O group of DMA and proton of OH group of 1-alkanols.The first (dissociation) effect leads to possessing of positive values of (V_f^E), whereas, the second effect leads to the negative values. The observed positive (V_f^E) values for the three liquid ternary systems further suggest that, the effect due to rupture of H-bonded associates of 1-alkanols dominate over that of H-bonding between unlike molecules. ie DMF-alkanols interaction is weaker than DMA-DMA or alkanol-alkanol interactions. From Table 3, it is noticed that the excess values of (V_f^E) are more positive for System II (1-butanol-cyclohexanone- DMA) than other system suggesting that the strength of the hydrogen bon formed should follow the order: 1-propanol > 1-pentanol >1-butanol. This may be convincingly explained by considering DMA as a proton acceptor, forms hydrogen bond more favourably with 1-proponal (a good proton donor) as compared to other alkanols.[23-24] The findings of the authors is also supported by Fort and Moore [25] according to which, V_f^E becomes increasingly positive with decreasing strength of the interaction

Also, the decreasing excess values of free volume in all the systems with increasing concentration of DMA resulting in weakening of hydrogen bonding interaction between ketone (cyclohexanone) and alcohols and also due to dissociation of alcohol molecules. The observed positive values of excess free volume also suggest that the DMA – alkanols interaction is weaker than the alkanol-alkanol and alkanols-ketone (cyclohexanone) interactions. The possessing of positive values of excess internal pressure in all the mixtures clearly confirms this prediction.

CONCLUSION

Hence from the present investigation, it very obvious that there exists an interaction between DMA (Proton acceptor) and 1-alkanols is due to hydrogen bonding and also there is dissociation of associated structure of 1-alkanols and decrease in interaction (hydrogen bonding) between cyclohexanone and 1-alkanols. The observed positive excess values of free volume indicate that the effect due to rupture of hydrogen bonded association of 1-alkanols and decrease in interaction between ketone and 1-alkanols dominate over that of hydrogen bonding between DMA-1-alkanols. Further, it is observed that the elevation of temperature also induces the rupture of hydrogen bonds between the unlike molecules.

Table-1:The values of density (ρ), viscosity (η) and velocity (U) of pure liquids

Liquids	DENSITY $\rho/(kg/m^3)$			VISCOSITY $\eta/(\times10^{-3}\,NSm^{-2})$			VELOCITY U/(m/s)		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
N-N, dimethyl acetamide (DMA)	934.6	929.5	926.8	0.9000	0.8056	0.7734	1444.0	1440.0	1430.0

Cyclohexanone	936.5	930.6	926.6	1.7372	1.6191	1.4308	1407.7	1397.4	1393.8
1-propanol	794.3	782.1	778.6	1.7150	1.4315	1.2542	1193.8	1190.5	1187.7
1-butanol	794.1	790.7	787.6	1.9887	1.8528	1.5765	1237.1	1232.8	1227.9
1-pentanol	801.8	797.1	794.6	2.6496	2.3087	2.0753	1266.4	1242.9	1233.0

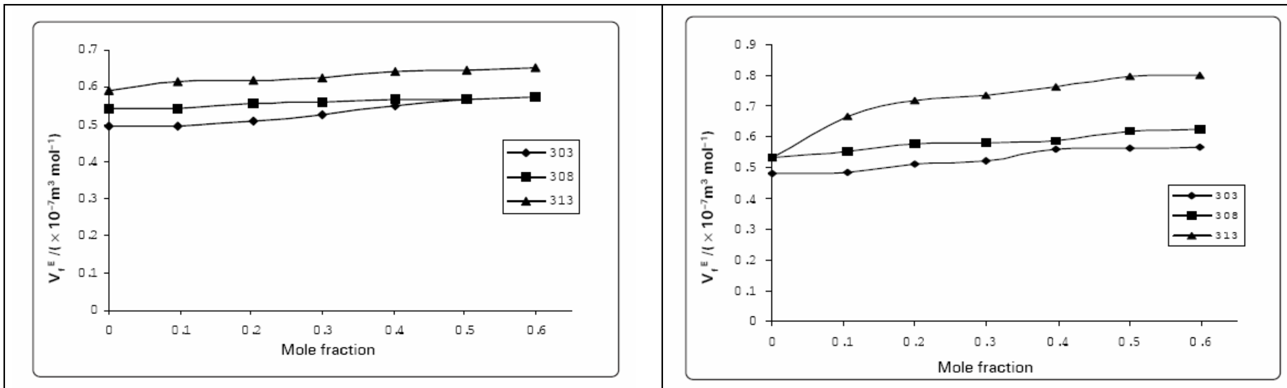
Table-2:The values of density (ρ), viscosity (η) and velocity (U) for Systems I, II and III for

X_1	X_3	DENSITY $\rho/(kg/m^3)$			VISCOSITY $\eta/(\times10^{-3}\,NSm^{-2})$			VELOCITY U/(m/s)		
		303K	308K	313K	303K	308K	313K	303K	308K	313K
System I: 1-propanol + cyclohexanone + DMA										
0.0000	0.5999	935.9	930.9	928.7	1.3112	1.2225	1.1125	1420.8	1414.8	1409.1
0.0968	0.5046	923.6	917.4	913.4	1.3201	1.2311	1.1148	1383.7	1378.5	1374.9
0.2038	0.3983	904.6	903.4	901.3	1.3296	1.2447	1.1572	1363.2	1356.0	1352.4
0.3003	0.3004	894.4	8938	890.8	1.3330	1.2684	1.1723	1345.2	1339.2	1333.4
0.4018	0.2000	882.2	881.1	878.5	1.3347	1.2912	1.1938	1336.2	1333.8	1332.6
0.5022	0.0967	875.1	873.6	871.6	13377	1.3112	1.2092	1311.0	1308.6	1282.2
0.6055	0.0000	864.9	862.4	858.6	1.3489	1.3208	1.2201	1295.4	1291.8	1290.0
System II: 1-butanol + cyclohexanone + DMA										
0.0000	0.5993	937.4	934.3	930.7	1.3148	1.2121	1.0734	1412.4	1393.8	1387.2
0.1060	0.4957	917.9	912.3	911.6	1.3670	1.2570	1.1122	1389.6	1387.2	1377.6
0.1997	0.4005	906.1	905.1	902.3	1.3777	1.2680	1.1138	1368.6	1365.6	1360.8
0.2991	0.3012	891.4	889.8	887.3	1.4186	1.3514	1.1418	1351.8	1347.6	1343.4
0.3963	0.2027	882.8	881.6	874.8	1.4318	1.3699	1.1674	1345.8	1337.4	1334.4
0.5012	0.0988	875.1	872.5	866.7	1.4791	1.3850	1.1814	1330.2	1324.2	1316.4
0.5989	0.0000	868.4	864.5	857.1	1.5117	1.4045	1.2180	1305.6	1300.8	1297.2
System III: 1-pentanol + cyclohexanone + DMA										
0.0000	0.5993	935.6	934.7	931.6	1.2130	1.1968	1.1212	1408.8	1402.8	1395.0
0.1005	0.4989	920.1	919.2	914.1	1.2800	1.2655	1.1240	1384.2	1380.2	1377.0
0.2031	0.3980	902.9	901.3	894.9	1.3522	1.3324	1.1772	1367.4	1345.8	1343.2
0.3007	0.3014	891.9	889.4	884.1	1.4092	1.3864	1.2218	1357.8	1340.2	1340.2
0.3993	0.2013	882.7	874.0	873.2	1.4732	1.4294	1.2884	1341.0	1338.0	1332.0
0.4994	0.1023	869.5	867.9	862.3	1.5253	1.4613	1.3151	1326.6	1291.2	1289.4
0.6008	0.0000	865.7	863.6	860.1	1.6134	1.5076	1.4638	1324.0	1276.4	1275.0

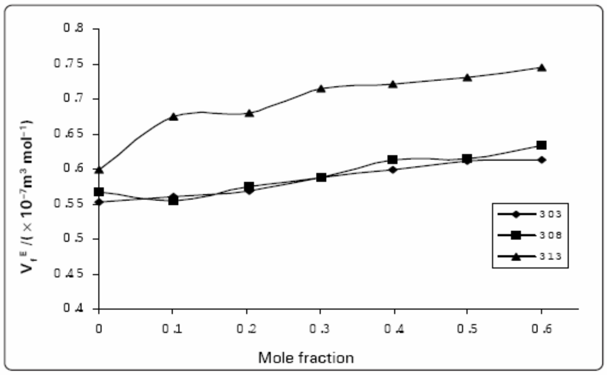
Table-3:Excess Values of adiabatic compressibility (β^E), free length (L_f^E), freevolume (V_f^E), and internal pressure (π_i^E) at 303 K for

X_1	X_3	Excess Adiabatic compressibility $\beta^E/(\times10^{-10}\,m^2\,N^{-1})$			Excess Free length $L_f^E/(\times10^{-10}\,m)$			Excess Free volume $V_f^E/(\times10^{-7}m^3\,mol^{-1})$			Excess Internal pressure $\pi_i^E/(\times10^6\,Nm^{-2})$		
		303K	308K	313K	303K	308K	313K	303K	308K	313K			
System I: 1-propanol + cyclohexanone + DMA													
0.0000	0.5999	4.0360	4.0935	4.1310	0.3611	0.3674	0.3709	0.4938	0.5427	0.5908	605.93	589.69	579.25
0.0968	0.5046	4.3979	4.4661	4.5048	0.3795	0.3842	0.3874	0.4941	0.5433	0.6150	571.27	562.98	542.27
0.2038	0.3983	4.6911	4.7499	4.7757	0.3887	0.3940	0.3989	0.5080	0.5551	0.6188	550.71	547.17	536.92
0.3003	0.3004	4.9216	4.9700	5.0274	0.3980	0.4030	0.4090	0.5250	0.5585	0.6243	523.98	520.17	514.68

0.4018	0.2000	5.1452	5.1474	5.1535	0.4018	0.4085	0.4128	0.5503	0.5670	0.6411	495.78	493.42	490.60
0.5022	0.0967	5.2297	5.4145	5.9621	0.4165	0.4205	0.4352	0.5658	0.5682	0.6458	482.01	473.92	477.92
0.6005	0.0000	5.6331	5.6785	5.8221	0.4393	0.4398	0.4401	0.5722	0.5734	0.6516	456.63	454.35	452.96
System II: 1-butanol + cyclohexanone + DMA													
0.0000	0.5993	4.0179	4.2102	4.2219	0.3563	0.3645	0.3712	0.4802	0.5336	0.5336	607.36	596.17	568.48
0.1060	0.4957	4.3121	4.3460	4.4136	0.3682	0.3725	0.3795	0.4845	0.5528	0.6672	566.20	549.78	525.93
0.1997	0.4005	4.5624	4.5744	4.6183	0.3782	0.3826	0.3874	0.5119	0.5771	0.7163	515.87	501.09	494.02
0.2991	0.3012	4.8093	4.8384	4.8782	0.3882	0.3926	0.3976	0.5223	0.5800	0.7353	494.02	492.92	455.58
0.3967	0.2027	4.9245	4.9916	5.0531	0.3942	0.3987	0.4057	0.5583	0.5868	0.7642	460.75	454.58	423.87
0.5012	0.0988	5.1284	5.1861	5.2915	0.4022	0.4067	0.4158	0.5630	0.6175	0.7966	433.20	427.61	396.50
0.5989	0.0000	5.4258	5.4860	5.5689	0.4121	0.4188	0.4260	0.5683	0.6246	0.8006	412.41	404.11	377.36
System III: 1-pentanol + cyclohexanone + DMA													
0.0000	0.5993	3.3986	3.9876	4.0442	0.3517	0.3550	0.3593	0.5521	0.5672	0.5984	576.23	572.71	570.29
0.1005	0.4989	4.2672	4.2674	4.2978	0.3626	0.3630	0.3715	0.5605	0.5543	0.6745	529.42	528.85	511.60
0.2031	0.3980	4.5181	4.6767	4.7219	0.3736	0.3731	0.3877	0.5689	0.5751	0.6796	486.43	481.38	469.59
0.3007	0.3014	4.6763	4.8107	4.8256	0.3796	0.3796	0.3918	0.5877	0.5879	0.7136	449.09	442.94	431.00
0.3993	0.2013	4.8946	4.9240	4.9830	0.3876	0.3832	0.3999	0.5983	0.6124	0.7203	418.15	416.65	401.05
0.4994	0.1023	5.1298	5.4619	5.5036	0.3876	0.3933	0.4239	0.6109	0.6143	0.7306	386.81	391.59	370.74
0.6008	0.0000	5.1843	5.6583	5.6811	0.3995	0.4013	0.4263	0.6122	0.6333	0.7442	364.72	360.20	350.38



Excess free volume Vs mole fraction of System-I
Excess free volume Vs mole fraction of System-II



Excess free volume Vs mole fraction of System-III

Fig.-1:Excess free volume ($\mathbf{V_f^E}$) of 1-alaknols Vs mole fractions

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