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Research Article

STUDIES OF THE THERMODYNAMIC PROPERTIES OF THE MIXTURE OF ISOMERIC BUTYL ALCOHOL & WATER

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ABSTRACT

The molar heat capacities of the binary mixture compound of water and isomeric butyl alcohol were measured with an adiabatic calorimeter at the temp. 308.15 K. The ultra sonic absorption coefficients in the frequency of 2 MHz. sound velocity, density were measured in the aqueous solutions at various concentrations. It was speculated that a double relaxational equation of the Debye type is appropriate to represent the absorption data in the concentration range from 0.001 to 1.000 mol dm^{-3} while a single one is fitted in those less than 1.0 down to 0.79 mol dm^{-3} For explaining the ultrasonic relaxation phenomena, the analysis was carried out with a reaction model associated with solute-solvent interaction. From the concentration dependence of the relaxation frequencies, the rate and the thermodynamic parameter were evaluated for the two reaction. The thermodynamic function relative to a temperature of 308.15 K were derived based on the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

Keywords: Thermodynamic properties, Isomeric mixture.

INTRODUCTION

It is well known that the structure of water is strongly influenced by addition of non electrolytes. The quantitative interperation seems to be performed for dilute aqueous solutions[1]. However, in concentrated solutions, many questions still remain because of the lack of sufficient experimental data and theoretical aspects.

The ultrasonic absorption method which may be one of the chemical relaxation techniques is useful for obtaining the dynamical information taking place in solution along with the equilibrium properties. The interesting phenomena observed by ultrasonic absorption and velocity measurement in alcohol solutions are that the absorption coefficient divided by the square of the frequency and the sound velocity show their maxima as a function of concentration. When the absorption is measured as a function of frequency, relaxation process are observed although the relaxation parameters are considerably dependent on the alcohol structures[2-7].

On the other hand, some other analytical equations have been proposed to interpret the frequency dependence of the ultrasonic absorption in aqueous solution of alcohol[8,9]. A very recent study by Brai and Kaatze[10] show that the ultrasonic absorption in alcohol aqueous solutions are well represented by the sum of the equations due to Debye-type relaxation and those due to fluctuations. Our interpretation of the absorption, however, is based on an assumption that the absorption spectra are expressed by the Debye-type relaxational equation because of the following reason. First, the experimental condition is far from a critical temperature, and a lot of the measured absorption spectra are well represented by the Debye-type equation although the measurement frequencies are restricted in a limited range. Second, a single relaxational absorption is observed in solutions. Solutes of which consist of relatively small hydrophobic groups. Even though we use the conventional Debye-type equation, we do not have definite confidence that the fluctuation model is not applicable to the aqueous solutions. In order to analyze the concentration dependences of the ultrasonic relaxation characteristic, under these situations, a solute-solvent interaction model has been proposed along with a molecular aggregation reaction which is only observed when the solute consists of a relatively large hydrophobic group.

This means that the parameters of ultrasonic relaxation depend strongly on the balance between hydrophobicity and hydrophilicity in alcohol molecules. This has also been clearly confirmed in the study of aqueous solutions, the solutes of which are isomers[11-12]. We expect that a quantitative relation between the molecular structures of alcohols and the ultrasonic characteristic may be held and that the effect of alcohols on the water structure may be well established from the ultrasonic absorption data. In this paper, we present the ultrasonic absorption, velocity and density data in an aqueous solution of n-Butyl alcohol, iso-butyl alcohol, sec.-butyl alcohol, tert-.butyl alcohol.

MATERIALS AND METHODS

Experimental Details System

The isomeric butyl alcohols used were of Anala R grade samples and they were purified by usual methods[13-15].The boiling points of these liquids agree with the literature values indicating the alcohols use in the present study are of high purity. The ultrasonic velocity was measured at 308.15 k by a single crystal variable path multi frequency ultrasonic inter fero meter operating at 2 MHz. supplied by Mittal Enterprises, New Delhi, Model F-81. Water was circulated from thermostatically regulated bath around the sample holder with double wall to maintain the temperature of the solution constant with a precision of ± 0.10 C^0. The accuracy of the ultrasonic measurement in the ultrasonic interferometer was ±0.001ms^{-1}. The densities of all components were measured by a 10 ml specific gravity bottle calibrated with deionised double distilled water. The viscosities of solutions were measured by a calibrated Ostwald viscometer. The viscometer was immersed in a constant temperature water bath maintained within ±0.10 C^0 and the time of flow was determined.

RESULT AND DISCUSSION

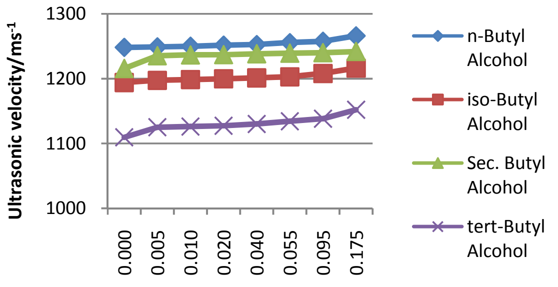
A coustical parameters such as adiabatic compressibility, inter molecular free length, Rao constant, absorption coefficient, free volume, cohesive energy, internal pressure and molecular interaction parameter with respect to velocity were calculated from the ultrasonic velocity, density and viscosity values using standard equation[16-18] and the measured values of ultrasonic velocity, density and viscosity at 308.15 k are given in Table-1 and the corresponding plots of ultrasonic velocity versus mole fraction of water for the four isomeric alcohols are given in fig.1 from these plots, It is evident that there is a slight increase in ultrasonic velocity values with the addition of water in systems containing n-butyl alcohol, iso-butyl alcohol and secondary butyl alcohol up to x_1 =1.000 and above this concentration the increase is more..

However, in water-tertiary butyl alcohol system there is a steep increase in ultrasonic velocity value even at x_1=2.000. A second steep increase is observed at x_1=4.600. This indicates that the interaction differ in the tertiary-butyl alcohol system. The increase in ultrasonic velocity with mole fraction of water (x_1) suggests that there are attractions between the alcohol molecules and water at all compositions. In these systems two different type of interaction are presents. They are attraction between similar molecules (either alcohol or water) and the other is attraction between dissimilar molecules[19-21]. Uniform decrease in adiabatic compressibility values (Table-2 and fig-2) with mole fraction of water suggests that in the first three system there are strong attractions between alcohol and water molecules. But in tertiary butyl alcohol system, adiabatic compressibility values decrease considerably.

Table 1: Ultrasonic velocity, density and viscosity for water-n butyl alcohol, water iso.-butyl alcohol, water- sec .butyl alcohol and water-tert.butyl alcohol system at 308.15 K

Molefraction		**n-Butyl**	**iso-Butyl**	**Sec. Butyl**	**tert-Butyl**		**n-Butyl**	**iso-Butyl**	**Sec. Butyl**	**tert-Butyl**		**n-Butyl**
iso-Butyl	**Sec. Butyl**		**tert-Butyl**									
x_1	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**
0.000	1248.2	1194.1	1215.7	1109.5	794.3	786.4	789.1	765.4	2.87	3.91	3.28	-
0.005	1249.2	1197.5	1235.5	1125.1	795.1	787.3	790.2	764.7	2.73	3.75	3.26	4.85
0.010	1250.1	1198.7	1236.7	1126.3	796.3	787.9	790.9	767.5	2.71	3.71	3.25	4.61
0.020	1251.7	1199.9	1237.1	1127.4	797.5	788.1	791.3	768.1	2.70	3.66	3.22	4.57
0.040	1252.8	1201.3	1238.5	1130.2	798.4	789.6	792.9	769.1	2.69	3.63	3.19	4.49
0.055	1255.8	1203.0	1239.4	1134.4	799.4	790.4	793.7	770.2	2.69	2.69	3.58	4.46
0.095	1257.8	1208.1	1240.1	1138.3	800.5	791.4	794.2	771.8	2.68	2.68	3.54	4.41
0.175	1266.2	1216.3	1241.9	1152.1	802.5	793.4	797.2	774.0	2.67	2.67	3.44	4.36
1.000	1513.2	1513.2	1513.2	1513.2	984.0	984.0	984.0	984.0	1.00	1.00	1.00	1.00

Ultrasonic velocity (U)ms^{-1} Density (P) kg/m^3 Viscosity(ή)/10^{3}nsm^{-2}



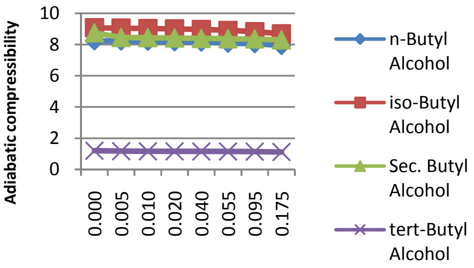
Mole Fraction of water (x_1)

Fig. 1: Plots of Ultrasonic Velocity versu x_1 of Isomericbutyl alcohol at 308.15 k.

Table 2: Adiabatic Compressibility, Linear free length and molecular interaction parameter values for water -n-butyl alcohol, water iso-butyl alcohol, water –sec. butyl alcohol and water - tert.butyl alcohol system at 308.15 k.

Molefraction	**n-Butyl**	**iso-Butyl**	**Sec. Butyl**	**tert-Butyl**		**n-Butyl**	**iso-Butyl**	**Sec. Butyl**	**tert-Butyl**		**n-Butyl**	**iso-Butyl**
Sec. Butyl		**tert-Butyl**										
x_1	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**	**Alcohol**
0.000	8.24	9.08	8.75	1.20	0.573	0.603	0.583	0.643	-	-	-	-
0.005	8.23	9.05	8.45	1.17	0.573	0.603	0573	0643	-0.031	-0.079	-0.050	-0.066
0.010	8.21	9.02	8.44	1.16	0.573	0.603	0.573	0.643	-0.160	-0.184	-0.157	-0.182
0.020	8.18	9.00	8.42	1.16	0.573	0.603	0.573	0.643	-0.470	-0.307	-0.283	-0.316
0.040	8.16	8.96	8.39	1.15	0.563	0.593	0.573	0.633	-0.512	-0.450	-0.429	-0.464
0.055	8.09	8.91	8.37	1.15	0.563	0.593	0.573	0.633	-0.662	-0.528	-0.511	-0.543
0.095	8.06	8.82	8.36	1.14	0.563	0.593	0.573	0.623	-0.761	-0.611	-0.598	-0.627
0.175	7.94	8.68	8.30	1.11	0.563	0.593	0.573	0.623	-0.814	-0.689	-0.689	-0.700
1.000	4.58	4.58	4.58	0.63	0.433	0.433	0.433	0.433	-	-	-	-

Adiabatic Compressibility (β)/10^{-10}m^{2}N$_{-1}$ Linear Free Length (L_f)A Molecular interaction Parameter(X_U)



Mole Fraction of water (x_1)

Fig. 2: Plots of adiabatic compressibility versu x_1 of Isomericbutyl alcohol at 308.15 k.

This suggests that there may be weak attraction between tertiary butyl alcohol (similar) molecules due to steric effect. Water molecules strongly attract tertiary butyl alcohol molecules through strong intermolecular hydrogen bond. The trend in linear free length value also supports this. which is given in Table. 2. The trends in ultrasonic velocity, adiabatic compressibility and linear free length are similar in all the four systems above x_1=1.900 indicating similar type of attraction and higher mole fraction of water.

The values of free volume, available volume and cohesive energy values for the four systems are given in table 3. The decrease in free volume and available volume with increase in the concentration of water indicates strong intermolecular attraction between dissimilar molecules even at low composition of water. The decrease in available volume and free volume is significant in the four systems except in tertiary butyl alcohol systems. This is in support of the suggestion that the attraction between similar molecules is weak in tertiary butyl alcohol due to large alkyl group.

Table 3: Available volume, free volume and cohesive energy values for water -n-butyl alcohol, water-sec. butyl alcohol and water- tert. butyl alcohol system at 308.15 k.

Molefraction x_1	n-Butyl Alcohol	iso-Butyl Alcohol	Sec. Butyl Alcohol	tert-Butyl Alcohol	n-Butyl Alcohol	iso-Butyl Alcohol	Sec. Butyl Alcohol	tert-Butyl Alcohol	n-Butyl Alcohol	iso-Butyl Alcohol	Sec. Butyl Alcohol	tert-Butyl Alcohol
0.000	4.67	4.77	4.74	5.02	2.12	1.27	1.64	-	80.5	98.0	88.7	-
0.005	4.53	4.62	4.59	4.86	2.09	1.29	1.62	0.86	80.2	96.3	88.1	110.3
0.010	4.34	4.43	4.40	4.65	1.98	1.24	1.54	0.86	80.5	96.3	88.5	108.3
0.020	4.06	4.15	4.12	4.33	1.83	1.15	1.43	0.81	81.0	96.7	99.1	108.5
0.040	3.64	3.71	4.69	3.88	1.57	1.01	1.24	0.71	82.5	98.1	90.3	110.0
0.055	3.32	3.39	3.36	3.53	1.39	0.91	1.12	0.65	83.5	99.0	91.2	111.9
0.095	2.88	2.93	2.92	3.06	1.15	0.87	0.93	0.55	85.5	100.3	93.0	112.5
0.175	2.30	2.33	2.32	2.42	0.85	0.61	0.73	0.44	88.5	102.4	95.0	113.2
1.000	0.81	0.81	0.81	0.81	1.71	1.71	1.71	1.71	50.0	50.0	50.0	50.0

Available Volume $V_a/10^6 m^3$ Free volume(v)/$10^{-8} m^3$ Cohesive energy (CE) ks/mol^{-1}

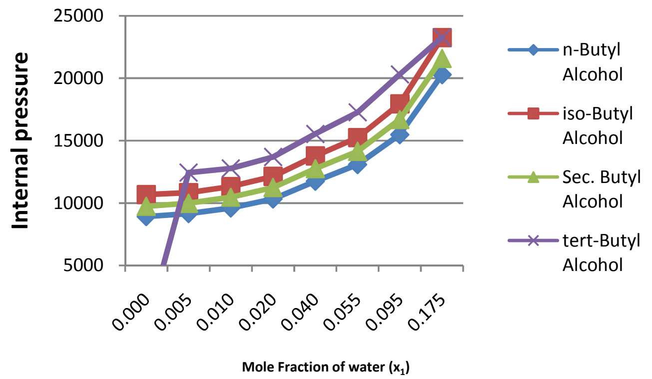


Fig. 3:Plots of Internal pressure versu x_1 of Isomericbutyl alcohol at 308.15 k.

The addition of water may affect the cohesive forces of attraction between alcohol and water molecules. This may be reflected in the internal pressure. The values of internal pressure, Rao constant and absorption coefficient and internal pressure values for the four systems are given in table 4 and the corresponding plots of internal pressure versus mole fraction of water for four isomeric butyl alcohols are given in fig.3. From the graph it is evident that there is an increase in internal pressure with increase in the mole fraction of water in all the four system. At a given composition, the internal pressure is less for n-butyl alcohol system than isobutyl alcohol system at the same temperature. This suggest that with increase in the length of the hydro-phobic alkyl chain, the attraction between alcohol and water decreases. In secondary butyl alcohol, there are two alkyl groups around the alcohol group, which decrease the attraction. This is indicated by the lower internal pressure value in this system. Interestingly, tertiary butyl alcohol with three alkyl groups around alcohol group should decrease the attraction. On the contrary, higher internal pressure values in this system are indicative of stronger attraction between the dissimilar molecules in this system. It may be due to weaker cohesive forces existing in tertiary butyl alcohol due to steric effect. The decrease in Rao constant value with increase in mole fraction also indicates the attraction between dissimilar molecules in all the four system. There is uniform decrease in the absorption coefficient values with increase in molefraction, which also suggests strong interaction between the components even at low concentration of water.

Table 4: Rao constant, absorption Coefficient and internal pressure value for water -n-butyl alcohol, water- iso.butyl alcohol ,water - sec. butyl alcohol and water - tert.butyl alcohol system at 308.15 k.

Molefraction x_1	n-Butyl Alcohol	iso-Butyl Alcohol	Sec. Butyl Alcohol	tert-Butyl Alcohol	n-Butyl Alcohol	iso-Butyl Alcohol	Sec. Butyl Alcohol	tert-Butyl Alcohol	n-Butyl Alcohol	iso-Butyl Alcohol	Sec. Butyl Alcohol	tert-Butyl Alcohol
0.000	9.95	9.90	9.93	9.96	5.16	8.20	6.55	-	8912	10675	9733	-
0.005	9.65	9.61	9.67	9.66	5.06	7.84	6.21	1.35	9154	10831	9980	12435
0.010	9.25	9.21	9.27	9.24	5.02	7.71	6.16	1.29	9599	11321	10466	12773
0.020	8.66	8.63	8.69	8.65	4.97	7.59	6.09	1.26	10327	12137	11243	13692
0.040	7.76	7.72	7.78	7.73	4.94	7.48	6.01	1.23	11751	13776	12760	15543
0.055	7.08	7.05	7.09	7.04	4.88	7.33	5.93	1.21	13081	15245	14144	17272
0.095	6.13	6.10	6.14	6.11	4.85	7.14	5.86	1.16	15484	17957	16693	20312
0.175	4.87	4.85	4.87	5.27	4.73	6.80	5.61	0.57	20287	23266	21593	23275
1.000	2.19	2.19	2.19	2.19	0.91	0.91	0.91	0.21	28454	28454	28454	28454

Rao Constant (R)/10^{-4} Absorption Coefficient $(\propto / f^2)10^{-13} Npm^{-1}s^{-1}$ Internal Pressure (π / atm)

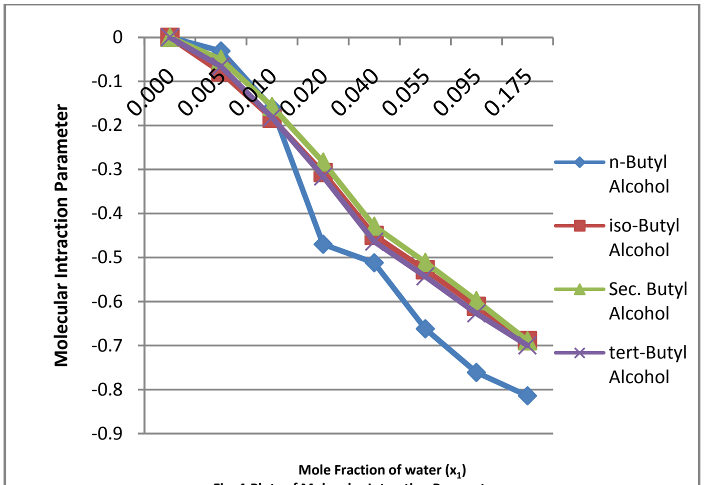


Fig. 4:Plots of Molecular Intraction Parameter versu x_1 of Isomericbutyl alcohol at 308.15 k.

Molecular interaction parameter values as a function of ultrasonic velocity are calculated for the four systems. Molecular interaction parameter values with respect to velocity versus mole fraction of water for the four isomeric butyl alcohols with different mole fraction of water are given in Fig.4 Negative values of molecular interaction parameter with respect to velocity at all compositions at 308.15k indicate the presence of strong attractive forces between the components. Cohesive energy (Table3) in a binary system is a measure of attractive forces between the particles of the components. Cohesive energy values are calculated for the four systems as a function of mole fraction of water. In a given system at a given temperature the cohesive energy decrease in the beginning and increase with increase in the mole fraction of water. This suggests that there are strong intermolecular hydrogen bonds between alcohol and water molecules. as a result the associated alcohol molecules are separated and then they are hydrated. It may be mentioned here that there is a steep increase in cohesive energy values above a particular concentration, which may be the concentration at which the attraction between dissimilar molecules predominates. Another observation is that if we compare cohesive energy at the concentration at which there is a sharp increase in cohesive energy value, the cohesive energy values are in the order n-butyl alcohol < secondary butyl alcohol < isobutyl alcohol < tertiary butyl alcohol. This trend shows that increase in the length of alkyl chain decrease the molecular interaction. However, in tertiary butyl alcohol system the former aspect predominates and hence there are strong attraction between water molecules and tertiary butyl alcohol molecules.

Interesting observations are made in the ultrasonic studies on binary systems of water and four isomeric butyl alcohol. The intermolecular attraction between the components depends on the mutual association of similar molecules and their dissociation due to attraction between dissimilar molecules. In n-butyl alcohol system the mutual association is the dominant factor when the mole fraction of water is above 0.2. Below this concentration, there are attraction between dissimilar molecules which may be due to strong intermolecular hydrogen bond. The strength of the bond depends on the length of the alkyl chain and the branching in the alkyl group. Increase in the chain length may enhance hydrophobic character and there are weak interaction between n-butyl alcohol and water. In isobutyl alcohol and secondary butyl alcohol there are relatively strong interaction. This may be due to the inductive effect of the alkyl groups. Interestingly, in tertiary butyl alcohol system, the steric effect should reduce the inter molecular attraction. But at the same time inductive release of electrons by the three-methyl group may increase the negative charge density on oxygen atom and consequently the attraction between tertiary butyl alcohol and water molecules is increased.

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