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Thermodynamic Study of Binary mixture of Butanol and n-Heptane at Different Temperatures and Concentration.

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ABSTRACT

An analysis of different thermodynamic properties as a function of temperature provides valuable information about their characteristics. The concentration and temperature dependence of acoustic and volumetric properties of multi component liquid mixtures has proved to be a useful indicator of the existence of significant effect resulting from intermolecular interactions. The thermo-physical parameters such as density (ρ), ultrasonic velocity (U) and viscosity (η) have been measured at 2 MHz frequency in the binary mixtures of Butanol and n-Heptane over entire range concentration at temperature 298K-308K using ultrasonic Pulse overlap technique. The experimental data have been used to calculate acoustical parameter namely adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG. The present paper represents shows the nonlinear variation of ultrasonic velocity and the thermo-acoustical parameters lead to In the present study the dipole-dipole interaction of pure 1-Butanol molecule is stronger than induced dipole –induced dipole interaction of pure n-Heptane molecule.

Keywords: Ultrasonic velocity, acoustical parameters, molecular interactions, binary mixtures, concentration in mole fraction, Butanol and n-Heptane.

INTRODUCTION

The ultrasonic study of liquid plays an important role in understanding the nature and strength of molecular interactions [1-3]. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman Effect, Nuclear Magnetic Resonance, Ultra Violet and ultrasonic method [4-6]. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids, owing to its ability of characterizing physio-chemical behavior of the medium. The ultrasonic velocity data for binary liquid mixtures have been used for by many researchers [7-11]. In present paper we have calculate the ultrasonic Density (ρ), Velocity (U) and Viscosity (η) of the binary mixture of Butanol and n-Heptane over entire range concentration at temperature 298K-308K using ultrasonic Pulse overlap technique. From these experimental values, number of thermodynamics parameters, namely adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG) were calculated. The variations of these parameters with concentrations were found to be useful in understanding the nature molecular interactions between the components.

METHODOLOGY

The ultrasonic velocity in the liquid mixtures have been measured using a Pulse echo overlap technique working at frequency 2MHz with an overall accuracy of ± 0.1 ms^{-1}, an electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of a steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a 10 ml specific gravity bottle with an accuracy of ± 0.1 Kgm^{-3}. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with accuracy 0.001 NSm^{-2}. The viscometer was calibrated before used. The time of flow of water (t_w) and time flow of solution (t_s) was measured with digital stop watch having an accuracy ±1x10^{-6} NSm^{-2}.

RESULTS AND DISCUSSION

The experimental measured values of density (ρ), ultrasonic velocity (U), viscosity (η) and thermodynamic parameters like adiabatic compressibility (β_a), intermolecular free length (L_f) and free volume (V_f) of binary liquid mixtures (1-Butanol + n-Heptane) at temperature range 298K-308K and at frequency 2MHz are presented in **table-1&2**. Internal pressure (π_i), relaxation time (τ) and Gibb's free energy(ΔG) of binary liquid mixtures (1-Butanol + n-Heptane) at temperature range 298K-308K and at frequency 2MHz are presented in **table-3**.

Density is an important concept with respect to buoyancy, purity and packaging. It varies with temperature and pressure. It is observed that density increases with increase in molar concentration of 1-Butanol in n-Heptane. Increase in density decreases the volume, indicating association in component molecules. The density of binary liquid mixture may be increase due to hydrogen bonding is predominant in case of 1-Butanol. Increasing temperature of the mixture decreases its density (ρ). The decrease in density (ρ) with increase in temperature indicates decrease in cohesive force.

Ultrasonic velocity is the speed in which sound propagates in a certain materials. It is observed that ultrasonic velocity increases with increase in molar concentration of 1-Butanol in n-Heptane, indicating the increase in stiffness of the mixture and hence association [12]. The association in the constituent molecules may involve due to dipole-dipole interaction or hydrogen bonding is predominant in case of 1-Butanol. The association due to stronger dipole-dipole interaction of pure 1-Butanol than the induced dipole – induced dipole interaction of pure n-Heptane molecule.

The viscosity is a physical property in understanding the structure as well as molecular interaction occurring in the aqueous system. Entropy measures the disorder of medium. It also depends on the temperature. Higher the disorder more will be entropy. It is observed that viscosity increases with increase in molar concentration of 1-Butanol in n-Heptane indicating strong molecular interaction. The

viscosity gives the strength of molecular interaction between interacting molecules. Increase in temperature of the mixture increases disorder of the medium and hence entropy increases. As entropy increases, viscosity of the binary mixture decreases.

Adiabatic compressibility is a measure of intermolecular association or dissociation or repulsion. It is observed that adiabatic compressibility decreases with increase in molar concentration of 1-Butanol in n-Heptane indicating strong intermolecular interaction between 1-Butanol and n-Heptane. This also shows associating tendency of the component molecules. This is because of the fact that dipole-dipole interaction of pure 1-Butanol stronger than the induced dipole – induced dipole interaction of pure n-Heptane molecule. The observed decrease of adiabatic compressibility with increase in concentration indicates the enhancement of degree of association in the component molecules. The decrease in free length is a result of dipole-dipole and induced dipole – induced dipole interaction between 1-Butanol and n-Heptane indicating association.

Table 1: The experimentally measured values of density (ρ), ultrasonic velocity (U) and viscosity (η) with respect to mole fraction of Butanol at temperature range 298K-308K and at 2MHz frequency.

Mole Fraction (X)	ρ (Kgm^{-3})			U (ms^{-1})			η*10^{-3} (NSm^{-2})		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
0.0	657.98	655.43	650.61	1112	1100	1092	0.342	0.315	0.282
0.1	667.09	665.55	657.68	1080	1056	1020	0.378	0.340	0.285
0.2	676.20	672.63	665.76	1084	1060	1044	0.384	0.358	0.322
0.3	690.38	684.77	677.88	1120	1072	1052	0.434	0.391	0.353
0.4	695.44	691.85	684.95	1128	1084	1056	0.452	0.415	0.373
0.5	705.56	703.99	700.11	1144	1092	1084	0.528	0.483	0.439
0.6	720.74	715.11	711.22	1152	1100	1096	0.681	0.611	0.540
0.7	734.92	730.28	727.39	1164	1108	1100	0.696	0.626	0.570
0.8	752.12	746.47	740.52	1180	1116	1104	0.715	0.642	0.582
0.9	760.22	758.61	754.66	1188	1148	1124	0.724	0.653	0.594
1.0	784.52	779.85	773.86	1232	1196	1156	0.868	0.770	0.684

TABLE-2: - Calculated values of adiabatic compressibility (βa), free length (L_f) and free volume (V_f) with respect to mole fraction of Butanol at temperature range 298K-308K and at 2MHz frequency.

Mole Fraction (X)	βa *10^{-10} (m^2N^{-1})			L_f*10^{-10} (m)			V_f *10^{-7} (m^3mol^{-1})		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
0.0	12.29	12.60	12.88	0.6941	0.7101	0.7216	6.622	7.383	8.615
0.1	12.85	13.47	14.61	0.7098	0.7341	0.7684	5.254	5.941	7.355
0.2	12.58	13.23	13.78	0.7024	0.7275	0.7461	4.947	5.311	6.081
0.3	11.54	12.70	13.32	0.6728	0.7129	0.7338	4.149	4.542	5.132
0.4	11.30	12.30	13.09	0.6656	0.7014	0.7272	3.776	4.044	4.569
0.5	10.82	11.91	12.15	0.6515	0.6902	0.7007	2.921	3.117	3.560
0.6	10.45	11.55	11.70	0.6402	0.6799	0.6876	1.928	2.113	2.536
0.7	10.04	11.15	11.36	0.6274	0.6679	0.6775	1.810	1.969	2.240
0.8	9.548	10.75	11.07	0.6118	0.6559	0.6690	1.690	1.825	2.080
0.9	9.320	10.00	10.48	0.6044	0.6325	0.6509	1.594	1.764	1.970
1.0	8.397	8.960	9.660	0.5737	0.5988	0.6250	1.216	1.394	1.581

Table 3: Thermo-acoustic parameters like, internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG), with respect to mole fraction of Butanol at temperature range 298K-308K and at 2MHz frequency.

Mole Fraction (X)	**π_i*10^6 (Nm^{-2})**			**τ *10^{-12} (Sec.)**			**ΔG *10^{-20} (KJ/mol)**		
	298K	**303K**	**308K**	**298K**	**303K**	**308K**	**298K**	**303K**	**308K**
0.0	199.34	194.96	187.32	0.561	0.530	0.485	0.4152	0.4068	0.3863
0.1	221.16	215.52	202.41	0.648	0.612	0.556	0.4677	0.4605	0.4380
0.2	232.00	229.56	221.53	0.644	0.632	0.592	0.4658	0.4725	0.4620
0.3	254.09	249.32	241.69	0.668	0.662	0.628	0.4791	0.4902	0.4846
0.4	268.54	265.95	257.85	0.681	0.681	0.651	0.4863	0.5004	0.4977
0.5	301.21	299.28	289.95	0.763	0.767	0.711	0.5278	0.5449	0.5314
0.6	358.08	351.25	334.8	0.949	0.943	0.842	0.6079	0.6216	0.5955
0.7	379.26	372.38	361.63	0.931	0.931	0.864	0.6009	0.6170	0.6050
0.8	401.57	395.94	383.27	0.910	0.921	0.860	0.5923	0.6129	0.6033
0.9	421.67	413.88	404.16	0.899	0.872	0.831	0.5880	0.5924	0.5906
1.0	482.05	466.58	452.38	0.972	0.920	0.882	0.6166	0.6127	0.6129

The free volume (V_f) and internal pressure is a measure of intermolecular attraction between the component molecules. It is observed that free volume decreases (V_f) and internal pressure (π_i) increases with increase in molar concentration of 1-Butanol in n-Heptane, indicating association in the molecules of the component liquids. It was observed that the variation in the free volume values show exactly the reverse trend as that of internal pressure.

In the present system, it is observed that free volume decreases and internal pressure increases. Further, the decrease in free volume and increase in internal pressure with increase in clearly show the increasing magnitude of interactions. This suggests that both solute- solute and solute solvent interaction exist in the system. If the temperature is increased, there is reduction in molecular interaction as they move away from each other. This reduces the cohesive force. Thus increase in free volume and decrease in internal pressure occurs with increase in temperature.

In the present case relaxation time, which is in the order of 10^{-12} s is due to structural relaxation process and in such situation it is suggested that the molecules get rearranged due to co-operative process. It is also observed that relaxation time increases with increase in molar concentration of 1-Butanol in n-Heptane, indicating high stability. Therefore relaxation time increases.

Gibb's free energy measures mobility of the medium. Higher the mobility of the medium, higher will be the entropy lower will be the free energy. It is observed that Gibb's free energy increases with increase in molar concentration of 1-Butanol in n-Heptane, indicating the mobility of the molecule is low i.e. highly ordered, due to outstanding salvation. Increasing value of Gibb's function suggests.

CONCLUSION

The non-linear variation of ultrasonic velocity and adiabatic compressibility with concentration in the liquid mixture is due formation of hydrogen bond or due to London desperation forces in the constituent molecules. The non –linear increase in internal pressure with concentration of binary liquid mixture indicates association in the molecules of the component liquid. The dipole-dipole interaction of pure 1-Butanol molecule is stronger than induced dipole –induced dipole interaction of pure n-Heptane molecule.

Conflicts of interest: The authors stated that no conflicts of interest.

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