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EXCESS THERMO ACOUSTICAL PARAMETERS OF BINARY LIQUID MIXTURES OF TRIMETHYLAMINE WITH FORMIC ACID AT DIFFERENT TEMPERATURES

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ABSTRACT

The densities, viscosities and ultrasonic velocities of the binary liquid mixtures of Trimethylamine with Formic acid have been measured at temperatures 298K, 303K and 308K over the entire range of mole fraction of Trimethylamine. From the experimental data various thermo acoustical parameters namely adiabatic compressibility (β), free length (Lf), free volume (Vf), internal pressure (π) and Gibb's free energy of activation have been evaluated. Excess values of the above parameters have also been calculated. The results are explained on the basis of molecular interactions present in these mixtures.

KEYWORDS: Acoustical properties, Ultrasonic velocity, Binary liquid mixture, Free length, Free volume.

INTRODUCTION

In recent years the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. Ultrasonic propagation parameters yield valuable information regarding the behaviour of liquid systems, because intramolecular and intermolecular association, dipolar interactions, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variations in the ultrasonic velocity. The acoustical and thermo dynamical parameters obtained in ultrasonic study show that the ion solvation is accompanied by the destruction or enhancement of the solvent structure [1,2].

Excess thermodynamic properties of liquid mixtures are of great interest to conveniently design industrial processes and also to provide useful information on the molecular interactions required for optimizing thermodynamic models [3]. When two or more liquids are mixed there occur some changes in physical and thermodynamic properties because of free volume change, change in energy and change in molecular orientations. Derived thermodynamic and acoustical parameters like internal pressure, free volume and acoustic impedance are of considerable interest in understanding the intermolecular orientations in binary liquid mixtures [4-6]. Excess thermomic properties of mixtures are useful in the study of molecular orientations and arrangements [7,8].

So in order to have a clear understanding of the intermolecular interactions between the component molecules, a thorough study on the binary liquid mixtures (Trimethylamine + Formic acid) using ultrasonic velocity data has been performed at temperatures 298K, 303K and 308K.

Material and Methods

In the present study the chemicals used were of analytical grade (E-Merck). Densities, viscosities and ultrasonic velocities were measured at 298K, 303K and 308K over a wide range of compositions. The densities of samples were measured using digital densitometer (Rudolph) with an accuracy of 0.0001. An Ostwald's viscometer was used for the viscosity measurements. An ultrasonic interferometer having the frequency 2 MHz was used for ultrasonic velocity measurements All the measurements were carried out using a water bath thermo statistically controlled to ±0.01 K. Acoustical parameters such as such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π) and Gibb's free energy of activation were calculated using standard equations.

THEORY AND CALCULATION OF ACOUSTICAL PARAMETERS

From the experimentally measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), various acoustic parameters are evaluated using standard equations mentioned below:

(i) Adiabatic compressibility:

$(\beta) = 1/U^2 \rho$ (1)

(ii) Intermolecular free length:

$(L_f) = K \beta^{1/2}$ (2)

Where K is temperature dependant constant

(iii) Molar volume:

$Vm= (X_1M_1+X_2M_2)/\rho$ (3)

Where, M_1 and M_2 are the molecular weights of the 1st and 2nd liquids.

(iv) Free volume:

$(V_f) = (M_{eff}U/ K \eta)^{3/2}$ (4)

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

(v) Internal Pressure

$(\pi) = bRT(K\eta/U)^{1/2} (\rho^{2/3}/M_{eff}^{7/6})$ (5)

Where, T is the absolute temperature, ρ is the density, and R is the gas constant.

(vi) Excess Gibb's free energy of activation:

$G^E = RT\{\ln(\eta Vm/\eta 2Vm2) – X1\ln(\eta 1Vm1/\eta 2Vm2)\}$ (6)

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality. The excess properties such as β^E, V_f^E, π^E and L_f^E have been calculated using the equation

$Y^E = Y_{EXPT} - \sum_{i=1}^{n} x_i y_i$ (7)

Where n = 2 for binary mixtures

RESULTS AND DISCUSSION

The experimental results of density, viscosity and ultrasonic velocity of pure liquids at temperatures 298K, 303K and 308K are given in Table 1. The measured values of density, viscosity and ultrasonic velocity of the binary liquid mixture of Trimethylamine with Formic acid over the entire composition range at three different temperatures are given in Table 2.

From the Table 2, it is observed that the density (ρ) and ultrasonic velocity (U) of binary liquid mixtures at each mole fraction decrease with increase of temperature. But only viscosity increases with increase of temperature. This is due to the fact that at high temperatures, formic acid may start evaporating, so the viscosity increases. From these values, various acoustical parameters like adiabatic compressibility, free length, free volume and internal pressure have been evaluated and are presented in Table 2. It is evident from Table 2 that the binary systems exhibit linear increase/decrease in ρ, η, U, β, L_f, V_m and π values with composition of Trimethylamine. This indicates the presence of strong interactions between the component molecules of the mixture. It is observed that the ultrasonic velocity and density decrease with increasing mole fraction of formic acid while the viscosity increases. This may be due to the association of a very strong dipole-induced dipole interaction between the component molecules. From Tables 2, it is observed that adiabatic compressibility, free length and free volume increase with increase in temperature and increase with increase in concentration of formic acid indicating the possibility of stronger interactions at higher concentration. Further, values of internal pressure decrease with increase in mole fraction of formic acid and temperature. The increase in adiabatic compressibility and intermolecular free length with increasing mole fraction of formic acid indicates significant interactions between Trimethylamine and formic acid molecules forming hydrogen bonding through dipole-dipole interaction.

Table 1. Density, viscosity and ultrasonic velocity for pure components Trimethylamine and Formic acid at 298K, 303K and 308K.

Component	Temp. T/K	ρ (Kg m^{-3})	η (10^{-3} Nsm^{-2})	U (ms^{-1})

Trimethyamine	298K	905.8	2.842	2238.3
	303K	901.3	2.789	2230.6
	308K	900.1	2.743	2225.3
Formic acid	298K	1187.2	2.484	1976.3
	303K	1179.8	2.715	1971.5
	308K	1175.0	3.108	1965.2

Table 2. Density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (L_f), molar volume (V_m) and internal pressure (π) for the binary mixtures of Trimethylamine+Formic acid at 298 K, 303K and 308K.

Mole fraction X1	ρ (Kgm^{-3})	η (10^{-3}Nsm^{-2})	U (ms^{-1})	β (10^{-10}m^{2}N^{-1})	L_f (A^o)	V_m (10^{-6} m^{3}mol^{-1})	π (10^6N/m^2)
			298K				
0	1187.2	2.4848	1976.3	2.1566	9.075	38.77	561.395
0.078	1163.9	3.6399	1957.3	2.2426	9.359	40.42	535.592
0.165	1130.4	3.4683	1905.6	2.4361	9.755	42.63	505.508
0.263	1107.4	3.3382	1864.6	2.5973	10.072	44.67	479.833
0.373	1083.1	3.2183	1822.6	2.7793	10.419	47.00	454.256
0.497	1059.6	3.1019	1785.3	2.9609	10.754	49.58	428.153
0.640	1040.1	3.0146	1740.3	3.1745	11.135	52.31	405.496
0.806	1014.3	2.9098	1689.3	3.4547	11.616	55.77	380.113
1	905.8	2.8421	2238.3	2.2035	9.173	65.25	274.466
			303K				
0	1179.8	2.7151	1971.5	2.1807	9.126	39.01	535.204
0.078	1157.4	3.2164	1950.3	2.2715	9.510	40.65	510.943
0.165	1125.6	3.0533	1899.3	2.4628	9.902	42.81	481.706
0.263	1102.0	2.9694	1859.5	2.6243	10.222	44.89	459.301
0.373	1078.1	2.8232	1817.3	2.8085	10.574	47.22	431.914
0.498	1055.3	2.7325	1779.6	2.9921	10.914	49.78	408.147
0.641	1036.8	2.6007	1734.6	3.2055	11.297	52.48	382.782
0.806	1011.3	2.5135	1680.6	3.5009	11.806	55.94	359.439
1	901.3	2.7891	2230.6	2.2299	9.228	65.58	255.257
			308K				
0	1175.0	3.1080	1965.2	2.2037	9.174	39.17	536.796
0.078	1153.0	3.1430	1945.3	2.2919	9.628	40.81	512.781
0.165	1120.6	2.9537	1890.3	2.4974	10.050	43.01	481.329
0.263	1097.9	2.8702	1851.6	2.6567	10.366	45.06	458.859
0.373	1074.5	2.7304	1810.3	2.8398	10.717	47.38	431.635
0.498	1052.3	2.6152	1772.6	3.0244	11.060	49.93	405.919
0.641	1033.7	2.5125	1729.6	3.2338	11.437	52.64	382.237

0.806	1009.2	2.3808	1675.3	3.5305	11.950	56.06	355.664
1	900.1	2.7432	2225.3	2.2435	9.256	65.67	251.839

Table 3. Excess adiabatic compressibility (β^E), excess free length (L_f^E) and excess free volume (V_f^E) of Trimethylamine and Formic acid at temperatures 298K, 303K and 308K.

(X_1)	β^E ($10^{-10}m^2N^{-1}$)	L_f^E (10^{-10} m)	V_f^E ($10^{-6}m^3mol^{-1}$)	π^E (10^6Nm^{-2})	G^E (J/mol)
		298K			
0	0.0000	0.0000	0.0000	0.00	0.00
0.0783	0.0769	1.7361	-0.4315	-33.30	8.54
0.1655	0.2625	5.6029	-0.8775	-84.08	-1.21
0.2630	0.4169	8.6809	-1.4146	-60.92	-2.77
0.3730	0.5932	12.0423	-2.0410	-120.73	-3.35
0.4978	0.7696	15.2682	-2.7294	96.02	-3.90
0.6409	0.9786	18.9362	-3.6391	27.98	-3.07
0.8063	1.2548	23.5834	-4.6596	50.08	-2.15
1	0.0000	0.0000	0.0000	0.00	0.00
		303K			
0	0.0000	0.0000	0.0000	0.00	0.00
0.0783	0.0811	1.8381	-0.6190	-23.34	1.58
0.1655	0.2643	5.6705	-1.2277	-71.75	-6.19
0.2630	0.4188	8.7653	-2.0828	-22.69	1.88
0.3730	0.5969	12.1772	-2.8382	11.23	-7.98
0.4978	0.7750	15.4472	-3.8615	12.31	1.23
0.6409	0.9837	19.1239	-4.8896	26.98	-1.46
0.8063	1.2749	24.0420	-6.3401	49.96	1.96
1	0.0000	0.0000	0.0000	0.00	0.00
		308K			
0	0.0000	0.0000	0.0000	0.00	0.00
0.0783	0.0804	1.8049	-0.7237	-16.97	2.70
0.1655	0.2792	5.9545	-1.3667	-83.15	-1.09
0.2630	0.4328	9.0276	-2.3299	-29.85	2.01

0.3730	0.6110	12.4475	-3.2125	11.21	4.05
0.4978	0.7912	15.7695	-4.2699	10.98	9.08
0.6409	0.9967	19.4130	-5.5556	28.06	2.00
0.8063	1.2901	24.4040	-6.9502	48.64	1.83
1	0.0000	0.0000	0.0000	0.00	0.00

In order to substantiate the presence of interaction (either adhesive or cohesive forces) between the molecules, it is essential to study excess parameters like excess free volume (V_f^E),excess internal pressure (π^E) etc., as these parameters are found to be more sensitive towards intermolecular interactions in the liquid mixtures [9]. The values of excess acoustic and thermodynamic parameters are given in Tables 3. The excess properties of the mixtures are influenced by the following three main types of contribution, (a) physical: due to non-specific Vander Walls type forces (b) chemical: due to hydrogen bonding , dipole-dipole and donor-acceptor interaction between unlike molecules and (c) structural: due to fitting of smaller molecules into the voids created by the bigger molecules [10]. The first effect leads to contraction in volume and hence leads to negative contribution towards π^E. The excess values of adiabatic compressibility, β^E of Trimethylamine + Formic acid are shown in Table 3 and are observed to be positive for all concentrations. The positive values of β^E for the system suggest the presence of weak interaction between unlike molecules. The size of component molecules almost not equal, it is seen that their molecules do not pack well into each other's structures. This results in expansion of volume and hence positive β^E. The positive values of L_f^E assist in deciding upon the concentration range in which maximum association in between the reacting components may be possible. The negative values of excess free volume V_f^E , excess internal pressure π^E and excess Gibb's free energy G^E clearly indicate the presence of strong hydrogen bonding interactions between unlike molecules. Increase in temperature causes variation in the excess thermodynamic properties as the local structure of liquids are destroyed, thus affecting the intermolecular free length and kinetic energy so the value of excess free volume (V_f^E), excess internal pressure (π^E) varies with temperature (Table 3). Similar temperature dependence results are reported earlier by several researchers [11-13].

Figures 1-5 represent the graphical variation in excess values of adiabatic compressibility, free length, free volume, internal pressure and Gibb's free energy of activation with mole fraction of Trimethylamine at different temperatures.

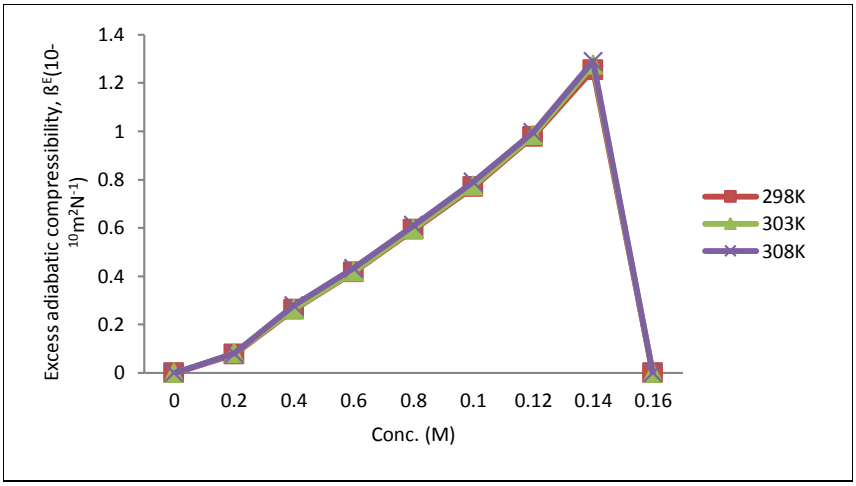

Figure 1: Variation of excess adiabatic compressibility with mole fraction of Trimethylamine at different temperatures

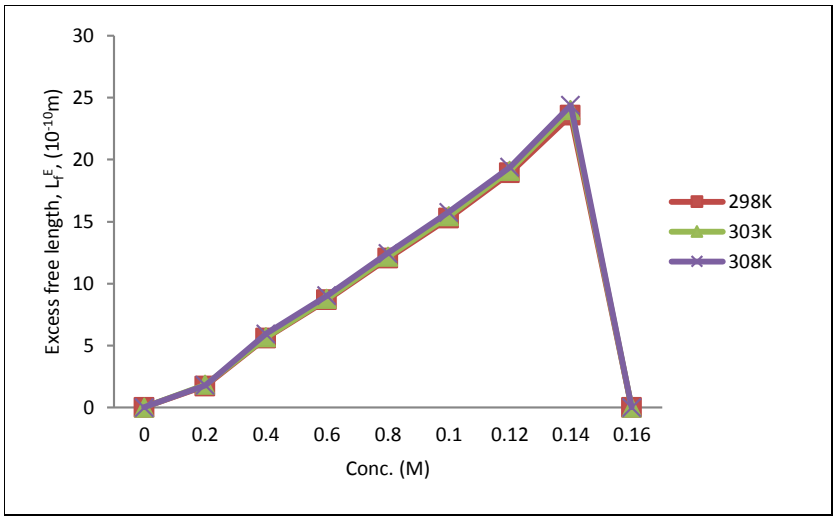

Figure 2: Variation of excess free length with mole fraction of Trimethylamine at different temperatures.

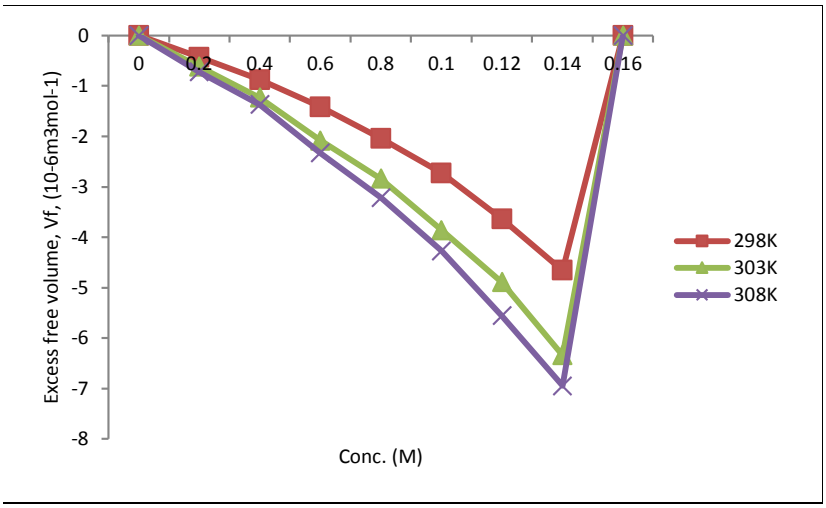

Figure 3: Variation of excess free volume with mole fraction of Trimethylamine at different temperatures.

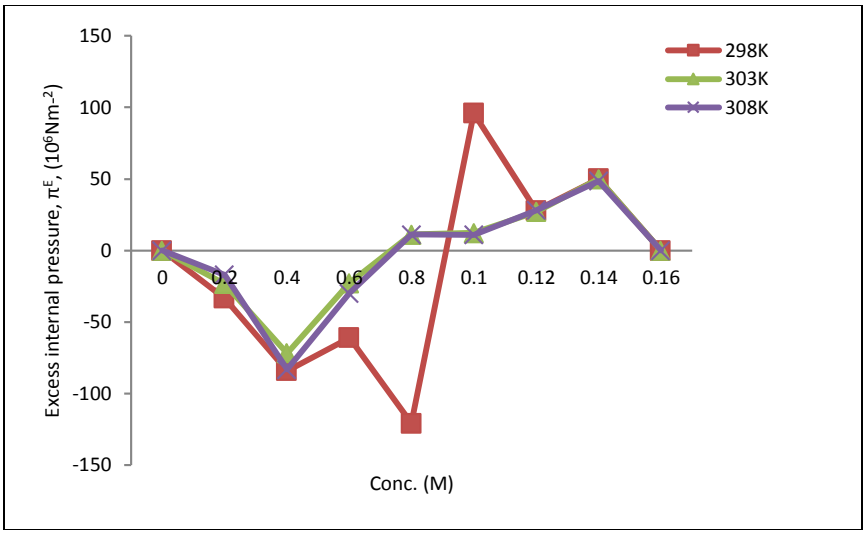

Figure 4: Variation of excess internal pressure with mole fraction of Trimethylamine at different Temperatures.

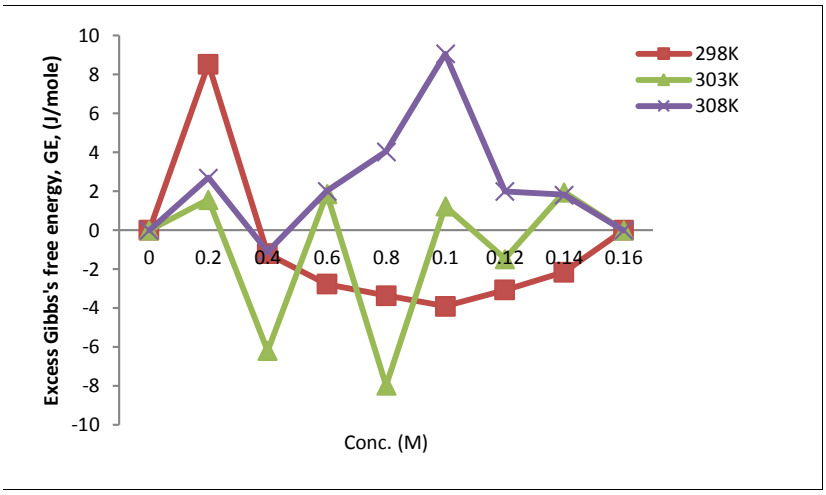

Figure 5: Variation of excess Gibb's free energy of activation with mole fraction of Trimethylamine at different temperatures.

CONCLUSION

The acoustic data of ultrasonic velocity (U), density (ρ) and viscosity (η) and related thermodynamic parameters with their excess values of Trimethylamine and Formic acid system over the whole concentration range suggest the existence of strong molecular interaction s between unlike molecules in binary liquid mixture.

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