



MOLECULAR INTERACTION STUDIES IN THE TERNARY LIQUID MIXTURE OF PYRIDINE + BENZENE + N, N-DIMETHYLFORMAMIDE BY ULTRASONIC VELOCITY MEASUREMENTS

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the ternary mixtures of benzene and N,N-dimethyl formamide with pyridine at 303, 308 and 313K. From the experimental data, adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), acoustic impedance (Z), relaxation time (τ), and Gibbs's free energy (ΔG^*) have been computed. The excess values of some of the above parameters were also evaluated and discussed in the light of molecular interactions in the mixture.

Keywords: molecular interactions, ultrasonic velocity, ternary liquid mixture, adiabatic compressibility, intermolecular free length.

1. INTRODUCTION

The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been successfully investigated by the ultrasonic method [1,3]. These interactions help in better understanding the nature of the solute and solvent i.e., whether the solute modifies or distorts the structure of the solvent. The measurement of ultrasonic speed enables the accurate determination of some useful acoustical and thermodynamic parameters and their excess functions, which are highly sensitive to molecular interactions in liquid mixtures [4,5].

Thermodynamic and transport properties of binary and ternary mixtures with different organic liquids have been studied by many authors [1,8]. Although a large number of investigations are carried in liquid mixtures having DMF (or) benzene as one of the components, it is found that no work has been made so far to measure the ultrasonic velocity in the ternary mixtures of benzene + N, N-DMF + pyridine. Pyridine (C_5H_5N) with nitrogen atom attached to one end of its structure is polar aprotic solvent [6] and negligibly basic [7]. It is used in wide variety of reactions, including electrophilic substitution, nucleophilic substitution, oxidation and reduction. N-N DMF is a versatile solvent, used in the separation of saturated and unsaturated hydrocarbons and serves as a solvent for many polymers. Benzene is a non-polar has slightly polar nature due to the delocalized electron cloud, which results in the solute-solvent molecular associates. Benzene exists as dimer. Therefore, in order to have a clear understanding of the intermolecular interactions between the component molecules, the author has performed a through study on the liquid mixtures using ultrasonic velocity data.

2. MATERIALS AND METHODS

The liquid mixtures of various concentrations in mole fraction were prepared by taking Analar grade

chemicals. In all systems, the mole fraction of the second component, benzene ($X_2 = 0.4$) was kept constant, while the mole fraction of the remaining two (X_1 and X_3) were varied from 0.1 to 0.6 so as to have the mixtures of different compositions. The ultrasonic velocity was measured by a single crystal interferometer with a high degree of accuracy operating at a frequency of 3MHz (model F-o5, with digital micrometer) at 303, 308 and 313K. The viscosity was measured by Ostwald's viscometer. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. Densities of the mixtures have been found by relative measurement method.

3. THEORY AND CALCULATIONS

Intermolecular free length (L_f), is calculated using the standard expression

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

Where K is a temperature dependent constant known as Jacobson constant and β is the adiabatic compressibility that can be calculated from the speed of sound (U) and the density of the medium (ρ) as

$$\beta = (u^2 \rho)^{-1} \quad (2)$$

The relation for free volume in terms of ultrasonic velocity and the viscosity (η) of liquid as

$$V_f = (M_{eff} U / k \eta)^{1/2} \quad (3)$$

Expression for the determination of internal pressure π_i by the use of free volume as

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

Where b stands for cubic packing which is assumed to be 2 for liquids and K is a dimensionless constant independent of temperature and nature of liquids and its



value is 4.281×10^9 , T is the absolute temperature and M_{eff} is the effective molecular weight.

The viscous relaxation time was obtained using the relation

$$\tau = (4/3) \beta \eta \quad (5)$$

Gibbs free energy is calculated from the relation

$$\Delta G = KT \ln(KT\tau/h) \quad (6)$$

Where τ is the viscous relaxation time, K the Boltzmann constant, T , the absolute temperature and h is the Planck constant.

In order to study the non-ideality of the liquid mixtures, namely excess parameters (A^E) of all the acoustic parameters were computed by

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (7)$$

Where $A_{\text{id}} = \sum^n A_i X_i$, A_i is any acoustical parameters and X_i the mole fraction of the liquid components of I ... The specific acoustic impedance is given by,

$$Z = U\rho \quad (8)$$

Where U and ρ are the velocity and density of liquid, respectively.

4. RESULTS AND DISCUSSIONS

The experimentally measured values of density, viscosity and ultrasonic velocity for the mixtures at 303, 308 and 313 K are presented in Table-1. Table-2 represents the values of adiabatic compressibility, intermolecular free length, free volume and internal pressure for the mixtures and their respective excess values are depicted in Table-3. Table-4 shows the computed values for acoustic impedance, relaxation time and Gibbs free energy for the mixtures at the three temperatures.

From the Tables-1, it was observed that the ultrasonic velocity of the ternary liquid mixtures decreases with increasing mole fraction of pyridine while the viscosity and density is found to increase with increasing the mole fraction. However the ultrasonic velocity, density and viscosity decrease in all cases as temperature is increased.

Table-1. Density (ρ), viscosity (η) and velocity (U) of Pyridine + Benzene+ N, N-DMF.

Mole fraction		$\rho \text{ Kg m}^{-3}$			$\eta \times 10^3 \text{ N s m}^{-2}$			$U \text{ m s}^{-1}$		
X_1	X_3	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.0000	0.6000	912.232	907.538	904.832	0.6814	0.6395	0.6047	1386.90	1369.5	1350.3
0.1000	0.5000	916.715	913.079	908.084	0.6870	0.6457	0.6097	1382.18	1365.3	1347.45
0.1999	0.4001	917.419	915.806	909.403	0.7012	0.6607	0.6194	1378.8	1362.3	1342.65
0.2999	0.3001	919.176	917.654	910.722	0.7120	0.6705	0.6336	1373.5	1358.7	1339.35
0.4000	0.2000	924.363	919.501	913.184	0.7205	0.6753	0.6356	1369.25	1352.10	1332.60
0.5001	0.0999	927.263	922.843	915.645	0.7235	0.6805	0.6380	1366.28	1347.75	1327.80
0.6000	0.0000	930.779	926.273	917.755	0.7275	0.6832	0.6432	1355.25	1339.50	1319.10

Table-2. Adiabatic compressibility (β), Free length (L_f), Free volume (V_f) of Pyridine + Benzene+ N, N-DMF.

Mole fraction		$\beta \times 10^{10} \text{ Pa}^{-1}$			$L_f \times 10^{10} \text{ m}$			$V_f \times 10^7 \text{ m}^3 \text{ mol}^{-1}$			$\pi_i \times 10^6 \text{ Pa}$		
X_1	X_3	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.0000	0.6000	5.6991	5.8750	6.0614	0.47633	0.4875	0.4998	2.1337	2.3028	2.4519	445.52	439.99	437.00
0.1000	0.5000	5.7100	5.8754	6.0653	0.4768	0.4875	0.5000	2.1221	2.2864	2.4431	445.42	440.49	436.27
0.1999	0.4001	5.7336	5.8837	6.0999	0.4778	0.4878	0.5014	2.0748	2.2279	2.4015	446.65	442.85	436.89
0.2999	0.3001	5.7665	5.9030	6.1211	0.4791	0.4886	0.5023	2.0401	2.1963	2.3400	447.40	443.24	438.82
0.4000	0.2000	5.7719	5.9488	6.1666	0.4794	0.4905	0.5041	2.0176	2.1824	2.3385	448.41	442.48	437.43
0.5001	0.0999	5.7772	5.9656	6.1945	0.4796	0.4912	0.5053	2.0222	2.1720	2.3396	446.70	441.98	435.90
0.6000	0.0000	5.8494	6.0170	6.2620	0.4826	0.4933	0.5080	2.0042	2.1640	2.3151	446.90	441.36	435.88

Further the adiabatic compressibility shows an inverse behavior compared to the ultrasonic velocity in the

mixtures with increase in concentration as shown in Table-2. It is primarily the compressibility that changes with the



structure and this lead to the change in ultrasonic velocity [8]. The addition of interacting molecules breaks up the molecular clustering of the other, releasing several dipoles for the interactions. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes, take place due to the existence of electrostatic field. Thus structural arrangement of molecules results in increasing adiabatic compressibility there by showing progressively intermolecular interactions. Similar results in some liquid mixtures were also reported by Bhatti and Singh [9].

Intermolecular free length is found to be a predominating factor, which depends upon the adiabatic

compressibility and shows a similar behavior as that of compressibility. On the basis of sound propagation in liquid, the increase in free length results a decrease in the velocity [10,11].

From the Table, it was observed that as the concentration of primary amine increases, free volume decreases. Internal pressure increases with the increase in concentration. However, with rise in temperature, increase in free volume and decrease in internal pressure are noticed. This suggests the close packing of the molecules inside the shield.

Table-3. Excess Values of Adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) And Internal Pressure (π_i^E) of Pyridine + Benzene+ N, N-DMF.

Mole fraction		$\beta^E \times 10^{10} \text{ Pa}^{-1}$			$L_f^E \times 10^{10} \text{ m}$			$V_f^E \times 10^7 \text{ m}^3 \text{ mol}^{-1}$			$\pi_i^E \times 10^{-6} \text{ Pa}$		
X_1	X_3	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.0000	0.6000	-0.1923	-0.1836	-0.2484	-0.0065	-0.0060	-0.0084	0.1143	-0.1251	-0.1397	-13.637	-14.002	-0.466
0.1000	0.5000	-0.1928	-0.1962	-0.2584	-0.0065	-0.0066	-0.0088	0.0992	0.0107	-0.1456	-12.041	-11.997	-0.068
0.1999	0.4001	-0.1807	-0.2008	-0.2377	-0.0060	-0.0069	-0.0080	0.0484	0.0469	-0.1843	-91.168	-81.220	1.6800
0.2999	0.3001	-0.1592	-0.1945	-0.2305	-0.0052	-0.0066	-0.0077	0.0102	0.0136	-0.2429	-66.718	-62.170	4.738
0.4000	0.2000	-0.1653	-0.1617	-0.1989	-0.0054	-0.0053	-0.0065	-0.0157	-0.0019	-0.2415	-39.668	-54.620	4.476
0.5001	0.0999	-0.1714	-0.1579	-0.1849	-0.0057	-0.0051	-0.0059	-0.0146	-0.0014	-0.2375	-39.81	-44.470	4.074
0.6000	0.0000	-0.1106	-0.1195	-0.1314	-0.00336	-0.0036	-0.0038	-0.0361	-0.0023	-0.2591	-20.868	-35.520	5.182

Table-4. Acoustic impedance (Z) Relaxation time (τ) and Gibb's free energy (ΔG^*) of Pyridine + Benzene + N, N-DMF.

Mole fraction		$Z \times 10^{-6} \text{ Kg m}^{-2} \text{ s}^{-1}$			$\tau \times 10^{12} \text{ s}$			$\Delta G^* \times 10^{20} \text{ KJ mol}^{-1}$		
X_1	X_3	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.0000	0.6000	1.2652	1.2429	1.2218	0.5178	0.5009	0.4887	0.3984	0.3986	0.4017
0.1000	0.5000	1.2670	1.2466	1.2240	0.5230	0.5052	0.4930	0.4021	0.4023	0.4051
0.1999	0.4001	1.2649	1.2476	1.2210	0.5360	0.5183	0.5037	0.4113	0.4115	0.4134
0.2999	0.3001	1.2625	1.2468	1.2270	0.5474	0.5277	0.5171	0.4191	0.4183	0.4235
0.4000	0.2000	1.2759	1.2432	1.2210	0.5544	0.5356	0.5225	0.4238	0.4239	0.4275
0.5001	0.0999	1.2669	1.2437	1.2211	0.5573	0.5412	0.5269	0.4258	0.4279	0.4307
0.6000	0.0000	1.2614	1.2407	1.2110	0.5673	0.5481	0.5370	0.4324	0.4327	0.4380

In order to understand more about the nature of interaction between the components of liquid mixtures, it is necessary to discuss the same in terms of excess parameters rather than actual values. They can yield an idea about the non linearity of the system as association or other type of interactions [9]. It can be seen from Table-3, that the excess compressibility is negative over the entire range of mole fraction for the systems. Sridevi *et al.* [12] suggested that the negative excess compressibility has

been due to closed packed molecules with positive excess values due to weak interaction between the unlike molecules. Similar conclusions were also arrived by Islam and Quadri [13]. The excess properties were found to decrease with increasing temperature.

The values of excess inter molecular free length follows the same trend as that of β^E . The values of excess inter molecular free length (L_f^E) are negative. The negative deviation of excess free volume is an indication of the existence of strong interaction between the components



[14]. The negative excess internal pressure π^E over the entire range of mole fraction of the system also supports the presence of interaction.

It is inferred from the Table-4 that the relaxation time τ decreases for system and increases with increase in mole fraction and the same decrease with rise in temperature. The relaxation time, which is in the order of 10^{-12} sec, is due to structural relaxation process [15] and in such situation it is suggested that the molecules gets rearranged due to co-operative process [16].

Pure Pyridine and DMF exists in monomer form in benzene solutions. The linear variation of the relaxation time in the whole concentration range may be taken as the absence of every solute-solute molecular association in the binary mixture. On the other hand, the non linear variation of the relaxation time with the mole fraction of one of the constituent is interpreted as possible solute-solute molecular association the binary mixtures. At $X_1 = X_3 = 0.3$ mole fraction there are pyridine and DMF molecules nearly equal in ratio, so solute-solute molecular association is proposed. Further increasing the temperature in the binary mixture at 303, 308 and 313K shows the presence of solute-solute molecular associations. Increasing the mole fraction of pyridine in the mixture indicates the presence of solute-solvent association. The polar molecule may associate with the non-polar solvent molecules. It is proposed that the molecular association rise because of the interaction of the positive fractional charge at the sight of carbon atoms in DMF and π -delocalized electron cloud in the benzene ring of the benzene molecule [17].

The observed values from the Tables-4, shows that the Gibbs's free energy (ΔG^*) increases with increase in concentration. Moreover the Gibbs's free energy increases with rise in temperature indicating the need for longer time for the co-operative process or the rearrangement of molecules in the mixtures [18].

The acoustic impedance decreases with increasing mole fraction of pyridine and the same decreases with rise in temperature. This decrease in specific acoustic impedance indicates significant interaction between the component molecules[19].

CONCLUSIONS

The solute- solute molecular association arise due to dipole-dipole inter action and the polar nature of different molecular entities in the mixture. The solute-solvent association arise due to slightly polar solute and polar nature of the solvent. In this system, solute – solute molecular association is proposed for nearly equal in ratio of pyridine and DMF. Further increase in pyridine shows solute-solvent association of pure pyridine in benzene solution. It is proposed that the molecular association arise because of interaction of the fractional charge at the site of carbon atom in DMF and π – delocalized electron cloud in the benzene ring of the benzene molecule.

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