

Excess Adiabatic Compressibility, Viscosity, Density Study For The Binary System Of Aniline+1-Pentanol, 1-Hexanol,1-Heptanol At 303k

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Abstract: Adiabatic compressibility(β) and free length (L_f) and free volume(V_f), internal pressure(π_i) have been determined from the measurement of ultrasonic sound velocity(U) and densities (ρ) viscosity (η) for the binary mixtures. The separate efficiency of aniline in the binary Aniline+1-pentanol,1-hexanol,1-heptanol have been analyzed in ultrasonic techniques at 303k. The excess adiabatic compressibility has predicted of ideal heat isothermal compressibility (K_T^{id}) and ideal isobaric expansibility (α_p^{id}) and molar heat capacitance(σ) have been interpreted in terms of possible molecular interaction between the molecules.

Keywords: Binary mixture, Molecular interaction, Sound velocity, polar molecules, Excess adiabatic compressibility.

I. Introduction

Grouping of solvents into classes is often based on the nature of the inter-molecular forces because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. After the introduction of the concept of ionization power of solvents effect on the rate equilibrium processes [1-2] because of the close connection between liquid structure and macroscopic properties, determination of density, viscosity and ultrasonic speeds is a valuable to learn the liquid state [3-4].

The study of molecular interaction application are used many industrial process such as petrochemical, pharmaceutical and cosmetics have greatly stimulated the need for extensive information in this various properties. Beside this Aniline is a very useful solvent used in dyeing industries [5-6]. Viscosity and density of these binary liquid mixtures are used to understand molecular interaction between the components of the mixture to develop new theoretical models and also for engineering application [7-8].

In this paper we extend our studies to the binary mixtures formed from Aniline represented (A), 1-pentanol (B), 1-Hexanol (C), 1-Heptanol (D). Above the all solvent have proton donor and proton acceptor groups leading to self association in pure state and mutual association in combined state through significant degree of H-bonding [9-10]. Thus determination of density, viscosity, speeds of sound helps in understand both excess adiabatic compressibility in this type of binary mixtures containing polar compounds.

II. Experimental Details

The liquid combinations of various concentrations in mole fraction were prepared by taking AR grade chemicals, which were decontaminated by standard methods [11]. The ultrasonic velocity (U) in liquid mixtures have been deliberated using an ultrasonic interferometer (Mittal type, Model F-80) working at 2 MHz frequency with an accuracy of $\pm 0.1 \text{ ms}^{-1}$. The density (ρ) and viscosity (η) are deliberated using a pycnometer and an Ostwald's viscometer respectively with an accuracy of 3 parts in 10^5 for density and 0.001 Nsm^{-2} for viscosity.

Using the deliberated data, the acoustical restrictions such as adiabatic compressibility (β), free length (L_f), free volume (V_f), and internal pressure (π_i) and their excess restrictions have been enumerated using the following standard expressions [12].

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

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

$$V_f = \left[\frac{M_{eff} U}{\eta k} \right]^{\frac{3}{2}} \quad (3)$$

$$\pi_i = bRT \left[\frac{k\eta}{U} \right]^{\frac{1}{2}} \left[\frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}} \right] \quad (4)$$

$$A^E = A_{exp} - A_{id} \quad (5)$$

$$A_{id} = \sum x_i A_i \quad (6)$$

where, K_T is the temperature dependent constant having a value 201.1209×10^{-8} in MKS system, k is a constant equal to 4.28×10^9 in MKS system, unconventional of temperature for all liquids, b is the cubical packing fraction taken as 2 for all the liquids, R is the universal gas constant, T is the innovative temperature, $M_{eff} = \sum x_i m_i$ where, x is the mole fraction and m is the molecular weight of i^{th} component and A^E stands for excess property of any given parameter, A_{exp} is the innovative value and A_{id} is the ideal value [13].

III. Formulae Used

From the measured data, adiabatic compressibility (β) and its excess values (β^E) were calculated using the following standard expression [14]

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

$$\beta^E = \beta_{exp} - \beta^{id} \quad (1.1)$$

The ideal adiabatic compressibility β ($= -(1/V^{id}_m) / \partial V^{id}_m / \partial \rho$), is calculated from the usual thermodynamic relation [15] having the ideal isothermal compressibility K_T^{id} , ideal isobaric expansibility α_p^{id} , and the ideal molar heat capacitance σ and the experimental temperature T as

$$\beta^{id} = K_T^{id} - T(\alpha_p^{id})^2 / \sigma^{id} \quad (1.2)$$

The consideration of ideal mixing laws of thermodynamic Gibbs an properties [16] demands that the isothermal compressibility, thermal expansibility and the heat capacitance should be expressed in terms of ideal volume fraction φ_i and hence,

$$K_T^{id} = \sum \varphi_i K_{T,i} \quad (1.3)$$

$$\alpha_p^{id} = \sum \varphi_i \alpha_{p,i} \quad (1.4)$$

$$\sigma^{id} = \sum \varphi_i \sigma_i \quad (1.5)$$

As the molar volume V_m and the molar isobaric heat capacity $C_{p,m}$ are mole fraction additive, the heat capacitance or the heat capacity per unit volume for the components can be done as

$$\sigma = C_{p,m} / V_m \quad (1.6)$$

and the ideal volume fraction as

$$\varphi_i = (X_i V_i) / (\sum X_i V_i) \quad (1.7)$$

The respective standard values of isothermal compressibility, isobaric expansibility and heat capacity for the components are taken from literature [17,18,19].

IV. Result And Discussion

The observed values of the system of aniline+1-pentanol, 1-hexanol, 1-heptanol are presented in Table 1. The values of the density (ρ), viscosity (η), and ultrasonic sound (U) shown an increasing trend with increase in mole fraction of aniline in all the systems.

Table 1: Values of density (ρ), viscosity (η), and ultrasonic velocity (U) Of aniline (A) +1-pentanol (B),1-hexanol (C),1-heptanol (D) at 303k

Mole fraction of A	$\rho \text{ kgm}^{-3}$			$\eta \times 10^3 \text{ Nsm}^{-2}$			$U \text{ ms}^{-1}$		
	B	C	D	B	C	D	B	C	D
0.0000	939.2	945.2	945.2	3.5916	5.8342	7.3187	1253.0	1261.3	1222.0
0.0995	945.2	945.3	957.8	3.8490	4.5567	1.3293	1347.0	1285.0	1301.2
0.1997	951.5	951.5	964.4	3.4924	4.0137	1.4965	1358.1	1344.5	1332.5
0.3000	957.8	957.8	970.4	3.2357	3.4281	1.6306	1401.0	1353.0	1366.1
0.3997	964.0	964.1	976.4	3.0982	3.6795	1.6587	1429.3	1357.8	1383.1
0.5000	970.4	970.6	983.0	2.8707	3.4732	2.1541	1494.4	1384.5	1410.0
0.6000	976.7	976.7	989.3	2.6218	3.0677	2.6557	1510.0	1442.0	1422.6
0.7002	983.0	983.3	995.6	2.3335	2.8003	2.8545	1554.2	1473.3	1465.0
0.8000	989.3	989.4	1001.9	2.1679	2.5472	3.2385	1594.6	1532.4	1493.5
0.9002	995.6	995.7	1008.2	1.5150	2.2907	3.5719	1612.0	1559.0	1566.2
1.0000	1001.9	1001.2	1014.5	2.9612	2.9612	2.9612	1614.3	1614.3	1614.3

As ρ increases, the number of particles in a given region is increased and this leads to quick transfer of sound energy and thus velocity also increases [20]. As aniline having a high boiling point, the energy between molecules of aniline is so high that the molecular bonds of aniline cannot be ruptured, whereas for 1-hexanol, it is not so. The increasing mole fraction aniline supports rupturing of components and hence, decrease in viscosity [21] is expected. All the observed values vary non-linearly and this indicates the existence of interaction in the medium. This is in line with the observation made in some binary systems [22].

Table 2: Values of adiabatic compressibility(β), free length(L_f), free volume(V_f) and internal pressure(π_i) of aniline(A)+1-pentanol(B),1-Hexanol(C),1-Heptanol(D) at 303k.

Mole fraction of A	$\beta \times 10^{10} \text{ pa}^{-1}$			$L_f \times 10^{11} \text{ m}$			$V_f \times 10^7 \text{ m}^3 \text{ mol}^{-1}$			$\pi_i \times 10^8 \text{ pa}$		
	B	C	D	B	C	D	B	C	D	B	C	D
0.0000	6.7810	6.6500	7.0846	5.2372	5.1864	5.3532	0.1926	0.1172	9.6516	9.0782	9.7498	9.5609
0.0995	5.8307	6.4070	6.1662	4.8564	5.0907	4.9942	0.1950	0.1723	1.3291	9.1155	8.6224	4.0786
0.1997	5.6978	5.8137	5.8398	4.8007	4.8493	4.8602	0.2304	0.2200	1.1185	8.6332	8.0349	4.3989
0.3000	5.3190	5.7031	5.5224	4.6384	4.8030	4.7262	0.2730	0.2726	0.9896	8.1616	7.5135	4.6650
0.3997	5.0773	5.6324	5.3519	4.5318	4.7731	4.6527	0.3028	0.2474	0.9513	7.8888	7.7727	4.8161
0.5000	4.6142	5.3758	5.1167	4.3202	4.6631	4.5493	0.3660	0.2742	0.6403	7.4117	7.7031	5.6000
0.6000	4.4903	4.9236	4.9944	4.2618	4.4627	4.4948	0.4295	0.3462	0.4584	7.0295	7.2034	6.3794
0.7002	4.2112	4.6864	4.6797	4.1272	4.3538	4.3507	0.5383	0.4041	0.4154	6.4840	6.0392	6.3245
0.8000	3.9751	4.3043	4.4744	4.0098	4.1726	4.2542	0.6296	0.4878	0.3416	6.1574	6.5666	7.3245
0.9002	3.8651	4.1323	4.0433	3.9540	4.0883	4.0441	1.1048	0.5787	0.3059	5.1085	6.2670	7.8246
1.0000	3.8641	3.8298	3.6455	3.8641	3.9359	3.8400	0.4199	0.4085	0.2730	7.0558	7.1109	8.2187

The calculated values of adiabatic compressibility(β), intermolecular free length(L_f), free volume(V_f) and internal pressure(π_i) are given in **Table 2**. All these parameters invariably show a decreasing trend with increase in mole fraction of aniline except V_f in 1-heptanol system. In 1-hexanol system, unlike the other systems, V_f shows an increasing trend and all the other parameters, i.e., β , L_f , and π_i shows a decreasing trend with increase in mole fraction of aniline irrespective of the alcohol type.

The compactness of the system with increase in mole fraction of aniline is indicated by reduced β values and the same is favored by the decreasing trend of L_f . Such trend was noticed in some similar liquid systems [23]. A continuous decrease in β or L_f is a clear evidence for the existence of strong interactions. Such strong interaction may be due to charge transfer, dipole-dipole, dipole-induced dipole, etc.

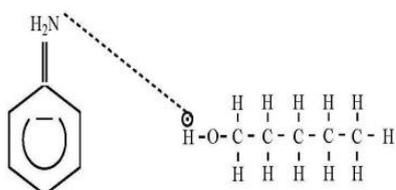


Fig-1

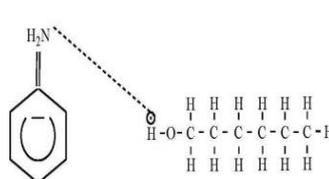


Fig-2

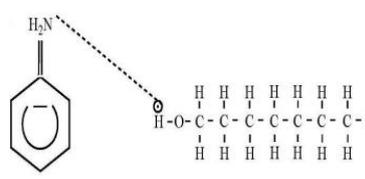


Fig-3

Shows **Fig-1,2,3**, Aniline as a polar solvent, is certainly to some extent associated by dipole-dipole interaction, and is of particular interest because of the absence of any significant structural effects due to lack of hydrogen bonds, therefore it may work as on aromatic, with amino groups is comparatively a strong electron donor. The H atoms in the NH₂ group can also play the role of electron acceptors centers, and high dielectric constant with large dipole moment. so it can interact easily other molecules[24].

All the three alcohols are having one hydroxyl group with increasing number of methyl groups. The hydrophilic hydroxyl groups in all three alcohols can interact with the amino group of aniline, and thus dipole-dipole, dipole-induced dipole type interaction are evident in all three systems [25].

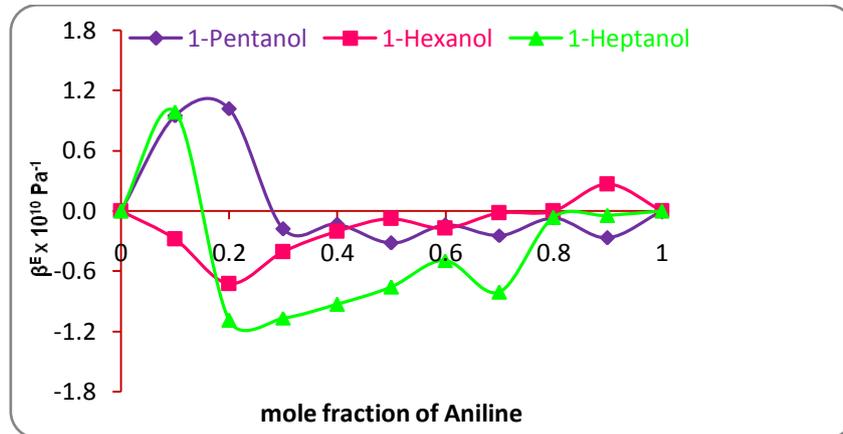


Fig-4. Mole fraction vs excess adiabatic compressibility at 303 k.

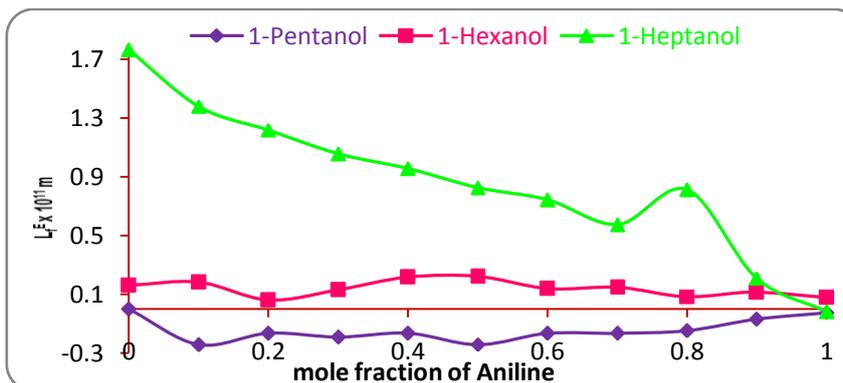


Fig-5. Mole fraction vs excess free length at 303k.

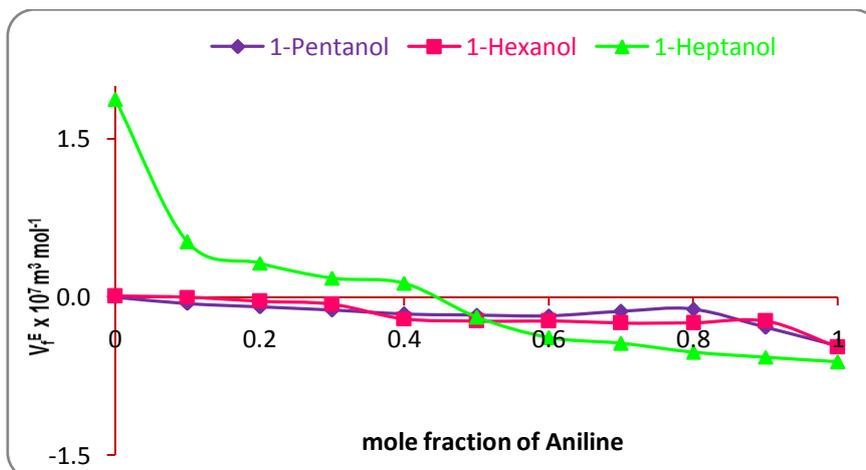


Fig-6. Mole fraction vs excess free volume at 303k.

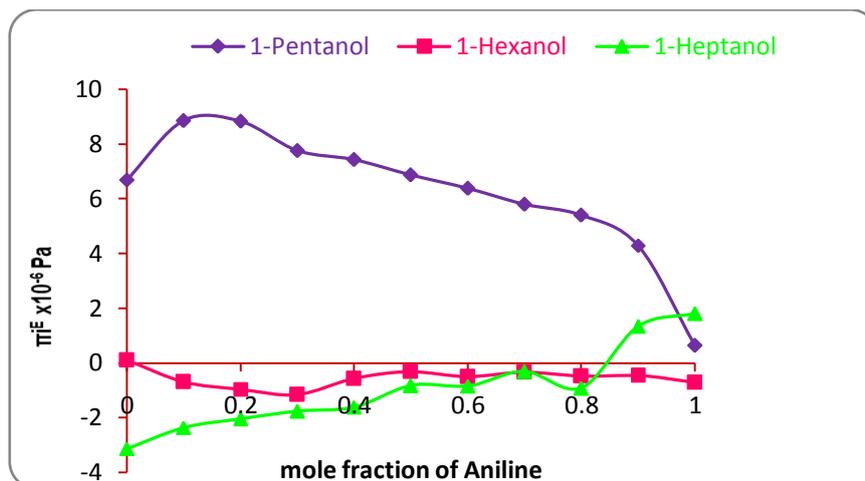


Fig-7. Mole fraction vs excess internal pressure at 303k.

The excess parameter values are depicted in **figs 4-7**. The perusal of these figures indicates that β^E and V_f^E in the mixture are initially positive and goes to negative, which confirms the existence of strong interactions. L_f^E and π_i^E initially negative and goes to positive, but L_f^E shows decreasing trend with increasing trend of aniline, whereas π_i^E values are highly fluctuating. The positive but decreasing V_f^E suggests that the dipole-dipole interaction need not to be a fully attractive type [26]. The existence of polar like interaction is also reflected in the π_i^E values.

In the 1-heptanol system, V_f^E are observed to be positive and fluctuating. Whereas π_i^E values are negative and have haphazard variations. These fluctuations in then considered binary mixture reflect the possibility of new induced dipoles. Thus dipole-dipole and induced dipole types are confirmed in the system.

V. Conclusion

1. Intermolecular interaction is confirmed in all the systems.
2. Existing interaction are strong in magnitude of alcohol chain length.
3. In addition to the unanimous existence of dipole-dipole interaction, and dipole-induced dipole types are additionally present in the 1-heptanol system.

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