

Acoustic Investigation of the Self-Association of Aniline in 1-Hexanol-Hexane Mixtures At 303k

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Abstract: The study of ultrasonic velocities (u), densities (ρ), viscosities (η), were carried out for Aniline+1-Hexanol+Hexane at 303k. These ternary system was comprise of a polar, non-polar molecules and calculated thermo dynamical properties such as adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), and excess values predicted to the system. The results were combined with excess adiabatic compressibility reported previously to obtain ideal isothermal compressibility (K_T^{id}), ideal isobaric expansibility (α_p^{id}) and ideal molar heat capacitance (σ^{id}) derivatives of excess adiabatic compressibility (β^E). these discusses the nature and strength of molecular intermolecular interaction in the system.

Keywords: Sound Velocity, Density, Molecular Interaction, Excess values.

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I. Introduction

A previous in the study of liquid mixture, it was comprehended that the extent to which real liquid mixtures deviate from ideality is best expressed through the use of thermodynamics excess function (1-2). Excess properties of liquid mixtures reveal the existence of molecular interaction (3-4), In many petrochemical industrialized application, liquid mixtures rather than single component liquid system, are used in processing and product formulation (4-5). The present ultrasonic investigation deals with density, viscosity, velocity computation of adiabatic compressibility and its excess values at 303k in the ternary system of Aniline+1-Hexanol+Hexane

II. Experimental details

The liquid combinations of various concentrations in mole fraction were prepared by taking AR grade chemicals, which were decontaminate by standard methods (6). 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_a), 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 (7).

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

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

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

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

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

$$A_{id} = \sum x_i A_i \tag{6}$$

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 (8).

III. Theoretical Background

From the measured data, adiabatic compressibility (β) and its excess values (β^E) were calculated using the following standard expression (9)

$$\beta = 1/\rho U^2 \tag{1}$$

$$\beta^E = \beta_{exp} - \beta^{id} \tag{1.1}$$

The ideal adiabatic compressibility $\beta \left(-\frac{1}{V^{id}} \frac{\partial V^{id}}{\partial \rho} \right)$, is calculated from the usual thermodynamic relation (10) 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

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

The consideration of ideal mixing laws of thermodynamic Gibbs an properties (11) demands that the isothermal compressibility, thermal expansibility and the heat capacitance should be expressed in terms of ideal volume fraction ϕ_i and hence,

$$K_T^{id} = \sum \phi_i K_{T,i} \tag{1.3}$$

$$\alpha_p^{id} = \sum \phi_i \alpha_{p,i} \tag{1.4}$$

$$\sigma^{id} = \sum \phi_i \sigma_i \tag{1.5}$$

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

$$\sigma = C_{p,m} / V_m \tag{1.6}$$

and the ideal volume fraction as

$$\phi_i = (X_i V_i) / \sum (X_i V_i) \tag{1.7}$$

The respective standard values of isothermal compressibility, isobaric expansibility and heat capacity for the components are taken from literature (12-14).

IV. Results and Discussion

The observed values of the system of Aniline+1-Hexanol+Hexane 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 the systems.

Table-1. Values of density (ρ), viscosity (η), and ultrasonic velocity (U) of Aniline+1-Hexanol+ Hexane at 303k

Mole Fraction		ρ $\times \text{kgm}^{-3}$	η $\times 10^3 \text{Nsm}^{-2}$	U ms^{-1}
X_1	X_3			
0.0000	0.7000	725.3	0.973	1321.3
0.0777	0.2307	775.2	0.994	1351.2
0.2467	0.2460	855.3	1.214	1408.8
0.3558	0.2145	887.3	1.345	1439.0
0.4657	0.2304	929.0	1.742	1502.3
0.5362	0.2291	952.6	1.943	1538.1
0.6197	0.2306	996.4	2.265	1622.2
0.7000	0.0000	1008.6	2.432	1642.3

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 (15-16), 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, increase in viscosity (17) is expected. All the observed values vary linearly and this indicates the existence of interaction in the medium. This is in line with the observation made in some ternary system

Table-2. Values of adiabatic compressibility (β_a), free length (L_f), free volume (V_f) and internal pressure (π_i) of Aniline+1-Hexanol+Hexane at 303k

Mole Fraction		β $\times 10^{10} \text{Pa}^{-1}$	L_f $\times 10^{11} \text{m}$	V_f $\times 10^7 \text{m}^3 \text{mol}^{-1}$	π_i $\times 10^8 \text{Pa}$
X_1	X_3				
0.0000	0.7000	7.8973	5.6519	1.4285	3.9849
0.0777	0.2307	7.0655	5.3459	1.4564	4.1061
0.2467	0.2460	5.8909	4.8814	1.1728	4.6695
0.3558	0.2145	5.4426	4.6920	1.0504	4.9383
0.4657	0.2304	4.7316	4.3748	0.7705	5.6121
0.5362	0.2291	4.4401	4.2379	0.6799	5.9410
0.6197	0.2306	3.8137	5.9276	0.6008	6.3043
0.7000	0.0000	3.6760	5.8560	0.5697	6.3675

The calculated values of β_a , L_f , V_f , and π_i for the present system are given **Table .2**. As expected β_a and V_f are continuously decreasing with increasing mole fraction of aniline [18]. The inspection of these trends reveals a unanimous higher β_a (and V_f) which reveals that the present system can provide some compactness, and the observed trend of L_f -confirms the existence of strong dipolar type interaction is evident.

The V_f and π_i values are behaving mutually opposite to each other. Decreasing V_f and increasing π_i values with increasing mole fraction of aniline is noticed, as observed in other liquid system [19]. Further, the gradual increase in π_i indicates that the adhesive forces between the components are much more enhanced than the cohesive forces within the component. All the observation fully supports the existence of dipolar type interaction, especially at higher mole fraction aniline. To confirm the existence of interaction in system, it's to calculate the excess values of the parameter considered in the work.

The excess parameters have been calculated and are illustrated in **figures 1-4**. The values for ternary mixture are β_a^E and L_f^E shows a continuous increase in magnitude and confirms that the strong interaction are enhanced as aniline mole fraction is increased. The trends of V_f^E and π_i^E are initial trends negative and exhibit a dip at 0.3 mole fraction of aniline. Further, a more or less symmetrical variation is noticed on either side of the dip in both V_f^E and π_i^E values[20]. The observation support that all the added aniline are in the cluster formation with hexane+1-hexanol binary complexes at this mole fraction.

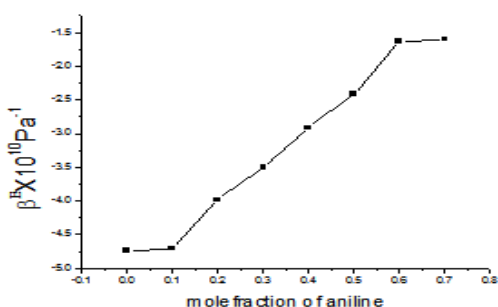


Fig-2: Mole fraction vs Excess Adiabatic Compressibility

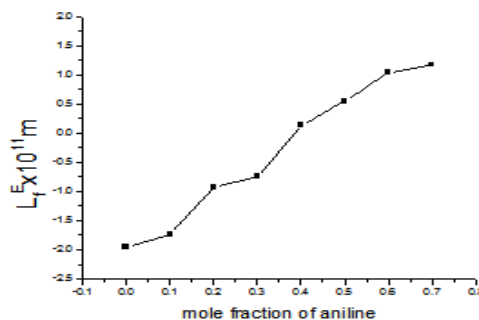


Fig-2: Mole fraction vs Excess Free Length.

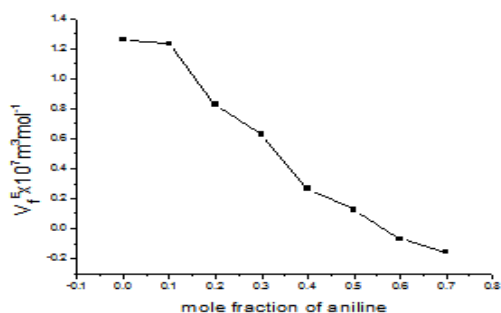


Fig-3: Mole fraction vs Excess Free volume

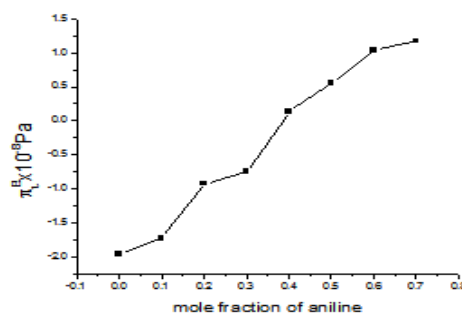


Fig-4: Mole fraction vs Excess Internal Pressure.

V. Conclusions

- i) The presence of specific strong dipolar interaction is in the ternary system.
- ii) A weak dispersive interaction in small magnitude exists at lower mole fraction.
- iii) All the component molecules get completely engaged in the interaction process.

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