

Ultrasonic study of molecular interaction in binary liquid mixture containing α -picolin in ethanol at 301.15 K and 305.15K

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ABSTRACT

The ultrasonic velocity (u), density (ρ) and viscosity (η) have been measured in binary liquid mixtures containing α -picolin in Ethanol at 301.15 K and 305.15 K. From these data some of acoustical parameters such as adiabatic compressibility (β_a), free length (L_f), free volume (V_f) and internal pressure (π_i) have been computed using the standard relations. The excess values of these parameters are also evaluated over the whole concentration range. The result is interpreted in terms of molecular interaction such as dipole-dipole interaction through hydrogen bonding between components of mixtures. The dependence of excess properties of mixture compositions were compared and discuss in terms of the intermolecular free length and other factors affecting the solvation and self-association effect. The excess values of these indicate dipole-induced dipole interaction complexity in the binary liquid mixture.

Keywords: molecular interaction, Ultrasonic velocity, adiabatic compressibility, inter-molecular free length, internal pressure.

INTRODUCTION

The ultrasonic investigations of pure liquids and liquid mixtures consisting polar & non-polar components are considerable importance in analyzing intermolecular interaction between component molecules[1-3]. These studies find several applications in industries. Such studies as variations in concentration and temperature are useful in giving insight in to structure and various bonding of associated molecular complexes [4-6] and other related molecular processes. Ultrasonic velocity and related thermodynamic parameters helps us for characterizing thermodynamic and physico-chemical aspects of binary liquid mixtures such as molecular association and dissociation [7-8]. Thermodynamics studies of binary liquid mixtures have attracted much attention of scientists. These physico-chemical analyses are used to handle the mixtures of hydrocarbons, alcohols, aldehydes, ketones etc. The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values [9-12]. These excess values of ultrasonic velocity, adiabatic compressibility, molar volume and viscosity in binary liquid mixture are useful in understanding the solute-solvent interactions.

The study of molecular association in binary liquid mixture having alcohol as one of component is of particular interest since alcohols are strongly self associated liquids having three dimensional network of hydrogen bonding and can be associate with any other group having some degree of polar attraction [13-16]. The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentration and temperature through molecular interactions [17-20]. In order to have clear understanding of intermolecular interaction between component molecules of an attempt has been made to study the ultrasonic behaviors of α -picoline in ethanol at different temperature.

MATERIALS AND METHODS

The chemicals α -picoline and ethanol used were of analytical grade and obtain from Merck chemicals private Ltd. (Purity 99.5%). The densities of pure components and binary mixtures were measured by hydrostatic sinker method with an accuracy 1 part in 10^5 . Special attention was given to avoid the vaporization of solution. Comparing their density with literature values checked the purity of chemicals. The mixtures of various concentrations in mole fraction were prepared. The ultrasonic velocities in pure liquids and their mixtures have been measured by pulse echo-overlap technique (PEO) using ultrasonic time intervalometer (UTI-101) supplied by M/s Innovative Instruments Ltd. Hyderabad at a central frequency of 10 MHz with accuracy ± 0.01 m/s. The viscosity of pure and mixture is measured by an Ostwald's Viscometer with accuracy ± 0.001 Nm⁻²s. The temperature of pure liquids and their mixtures is maintained constant with the help of thermostat U-10 with an accuracy of ± 0.01 K.

Theory:

The adiabatic compressibility (β_a) has been calculated from sound velocity (u) and the density (ρ) of the medium using the relation

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

The intermolecular free length (L_f) has been determined by the equation.

$$L_f = K_T \sqrt{\beta} \quad (2)$$

Where K_T is a Jacobsen's constant.

The free volume (V_f) in terms of ultrasonic, velocity (u) and the viscosity (η) of a liquid is

$$V_f = \left(\frac{M_{eff} u}{k \eta} \right)^{3/2} \quad (3)$$

Where M_{eff} is the effective molecular weight given as

$$M_{eff} = \sum m_i x_i \quad (4)$$

In above equation ' m_i ' & ' x_i ' are the molecular weights and mole fraction of individual constituents respectively and ' k ' is a temperature dependent constant equal to 4.28×10^9 for all liquids in MKS system.

The Rao constant (R) is related to molecular weight (M) and density (ρ) is by

$$R = \left(\frac{M}{\rho} \right) u^{1/3} = V_m u^{1/3} \quad (5)$$

Where ' V_m ' is molar volume which obey the rule of additivity.

$$V_m = x_1 V_1 + x_2 V_2 \quad (6)$$

On the basis of statistical thermodynamics suryanarayan derived an expression for internal pressure (π_i) given as

$$\pi_i = bRT \left(\frac{K\eta}{u} \right)^{1/2} \left(\frac{\rho^{3/2}}{M_{eff}^{7/6}} \right) \quad (7)$$

Where ' b ' is a constant, ' K ' is an absolute temperature in K, ' η ' is Viscosity in Nsm⁻², ' u ' is the ultrasonic velocity in m/s and ' M_{eff} ' is effective molecular weight.

An excess value of ultrasonic related parameters has been calculated by using the relations.

$$\beta^E = \beta_{\text{exp t}} - \sum x_i B_i \quad (8)$$

$$V^E = V_{\text{exp t}} - \sum x_i V_i \quad (9)$$

$$\eta^E = \eta_{\text{exp t}} - \sum x_i \eta_i \quad (10)$$

Where V^E , β_a^E and η^E are the excess values of molar volume, adiabatic compressibility and viscosity respectively.

Gruenberg and Nissan give the relationship as

$$\ln \left(\frac{\eta}{\eta_0} \right) = x_i \ln \left(\frac{\eta}{\eta_0} \right) + x_1 x_2 d \quad (11)$$

Where ' η_d ' some constant of viscosity and ' d ' is a constant proportional to the interchange energy.

DISCUSSION

Ultrasonic velocity (u), density (ρ), viscosity (η), adiabatic compressibility (β_a) and other related excess thermodynamic parameters B_{ap}^E , V^E , η^E and Gruenberg and Nissan parameter ' d ' are evaluated for the binary mixture α -picoline in ethanol over the whole concentration range at two temperatures 301.15K and 305.15 K and presented in Table - I and Table -II respectively.

Table I. - Ultrasonic velocity (u), densities (ρ), viscosities (η), molar volume (V), intermolecular free length (L_f), internal pressure (π_i) and grunberg parameter (d) as a function of mole concentration (x) of α -picoline in ethanol at 301.15K.

x	u ms ⁻¹	$\rho \times 10^{-3}$ kgm ⁻³	$\eta \times 10^{-3}$ Nm ⁻² s	$\beta_a \times 10^{-10}$ m ² n ⁻¹	$V \times 10^{-3}$ m ³	$L_f \times 10^{-10}$ m	$\pi_i \times 10^{-5}$ Pas	d
0	1138.6	0.7875	0.9659	9.795	58.53	0.6472	2.9483	0
0.1	1144.6	0.7924	0.9298	9.6327	64.11	0.6415	2.5867	-0.1464
0.2	1160.9	0.8071	0.9057	9.1591	68.51	0.6258	2.3201	-0.0154
0.3	1174.3	0.8283	0.8945	8.7549	72.68	0.6119	2.1161	-0.0185
0.4	1208.9	0.8375	0.8867	8.1702	77.5	0.5911	1.9161	0.029
0.5	1242.9	0.8493	0.8729	7.6219	81.96	0.5709	1.7443	0.0761
0.6	1248.1	0.8783	0.8556	7.5585	87.5	0.5685	1.1628	0.0259
0.7	1271.1	0.8847	0.8326	6.9959	89.31	0.5469	1.4931	0.0261
0.8	1292	0.899	0.8226	6.6636	93.13	0.5338	1.3908	0.0549
0.9	1339.2	0.9197	0.7916	6.0626	96.14	0.5092	1.2765	-0.1022
1	1398.3	0.9358	0.7705	5.4653	99.51	0.4834	1.1737	0

Table II. - Ultrasonic velocity (u), densities (ρ), viscosities (η), molar volume (V), intermolecular free length (L_f), internal pressure (π_i) and grunberg parameter (d) as a function of mole concentration (x) of α -picoline in ethanol at 305.15K

x	u ms ⁻¹	$\rho \times 10^{-3}$ kgm ⁻³	$\eta \times 10^{-3}$ Nm ⁻² s	$\beta_a \times 10^{-10}$ m ² n ⁻¹	$V \times 10^{-3}$ m ³	$L_f \times 10^{-10}$ m	$\pi_i \times 10^{-5}$ Pas	d
0	1120.8	0.7848	0.8901	10.147	58.74	0.6635	2.8581	0
0.1	1119.4	0.7914	0.8634	10.084	64.97	0.6614	2.5518	-0.2662
0.2	1126.9	0.8057	0.8312	9.7944	68.97	0.6519	2.2762	0.0628
0.3	1159.7	0.8151	0.8106	9.1221	73.86	0.6291	1.0321	-0.0026
0.4	1195.2	0.8362	0.7929	8.3716	77.62	0.6027	1.8446	-0.0684
0.5	1227.3	0.8461	0.7698	7.8465	82.27	0.5834	1.6661	-0.0557
0.6	1230.8	0.8759	0.7493	7.5365	84.84	0.5718	1.5564	-0.028
0.7	1258.5	0.8819	0.7239	7.1593	89.6	0.5573	1.4147	-0.0745
0.8	1281.8	0.7252	0.7252	6.7935	93.45	0.5429	1.3254	-0.0652
0.9	1317.8	0.9072	0.7102	6.3474	97.47	0.5248	1.2239	-0.067
1	1382.9	0.9317	0.7121	5.6123	99.95	0.4934	1.2583	0

In the binary liquid system under investigation, the variation of ultrasonic velocity (u) and excess adiabatic compressibility (β_a) indicate existence of molecular interaction between solvent and solute. The excess adiabatic compressibility B_a^E is positive over whole concentration range and it becomes minimum at a concentration (0.5) of α -picoline in ethanol at observed temperatures. This indicates that the intermolecular interaction at this optimum at this concentration and it may leads to formation weak hydrogen bonded complex in binary liquid mixture. The same effects are also observed in excess volume (V^E) and excess viscosity (η^E). The Gruenberg and Nissan parameter (d) which indicate the extent of molecular interaction⁶ in the liquid mixture also shows same variations over the whole

concentration range. This conclusion is further supported by thermodynamic studies [4-10] on a similar system by IR and NMR [21-22]. It is observed that beyond this optimum concentration, addition of solute (α -picoline) in a solvent (ethanol) tries to break this weak complex structure and tends towards the values of pure components. The presence of hydroxyl group and shortness of chain of the carbon in ethanol is responsible to participate in hydrogen bonding leads to the association with the molecules of α -picoline. It is evident that in the case of α -picoline, the normal inductive effect of methyl group has interaction with ethanol is also observed. [4.6].

CONCLUSION

The acoustic data of ultrasonic velocity (u), density (ρ), viscosity (η) and Related thermodynamic parameters with their excess values of α -picoline in ethanol over the whole concentration range may suggest the existence of a strong molecular interaction in binary liquid mixture. The negative values of some thermo-acoustic parameters like excess compressibility indicate a strong intermolecular interaction in the constitute molecules due to presence of hydroxyl group of binary liquid mixture and it may leads to the formation of weak complex in the liquid mixture at particular concentration.

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