Study of Acoustic and Thermodynamic Properties of Pyrrolidine With Alcohols

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Abstract- *Study of acoustic and thermodynamic properties of Pyrrolidine with alcohols with a view to determination of molecular interaction with various acoustic and thermodynamic parameters.*

The ultrasound velocity, density and viscosity measurement have been utilized to compute several parameters such as specific acoustic impedance, isentropic compressibility, intermolecular free length, molar volume, available volume, Rao's Constant. Wada's constant, shear's relaxation time and their excess values. Ultrasound velocity is determined by interferometric technique and used the ultrasonic interferometer. Density is determined by calibrated double walled bi-capillary pycknometer. Viscosity is determined by viscometer.

Keywords- Acoustic, Interferometer, Parameters, Thermodynamic.

I. INTRODUCTION

Measurement of the sound velocity offers a convenient method for determining certain thermodynamic properties of liquids not easily obtained by other means. Thermodynamic functions have been extensively used to investigate the properties of liquids and liquid mixtures (1-3). Such a type of study has been found to yield information regarding the intermolecular process and the structure of liquid state. Recent studies (4-8) show the utility of other thermodynamic parameters to predict the nature of molecular interactions.

This paper deals with our investigation of the acoustic and thermodynamic properties of binary liquid mixtures and in continuation of our previous studies (9-10). In the present investigation, the isentropic compressibility, intermolecular free length, molar volume, available volume and excess properties in the binary liquid mixtures namely Pyrrolidine with methanol, ethanol and propanol have been computed from the experimental velocity, density and viscosity data. In addition, the Shear's relation time, Rao's constant and Wada's constant have also been computed and results are discussed in terms of intermolecular interaction between the components of liquid mixtures.

II. EXPERIMENTAL DETAILS

Ultrasound velocities were measured using single crystal ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) of frequency 2 MHZ (accuracy + 0.03%). The working of ultrasonic interferometer was checked for its accuracy by measuring ultrasonic velocities in different liquids for which these were available in literature.

Table 1 : Pyrrolidine + Methanol at 35^0C

Mole Fraction of Pyrrolidine	Isentropic Compressi-bility (excess) $cm^2/dyne.10^{12}$	Molar Volume (excess) ml/mole	Available Volume (excess) ml/mole	Viscosity (excess) C.P.	Intermol Free-length (excess) A	Shear Relaxation Time (τ_s)	Rao's constant (R)	Wada's constant (B)
0.0000	0.00	0.00	0.00	0.0000	0.0000	0.55	9.73	48.87
0.0423	0.83	-0.46	-0.46	-0.0058	0.0035	0.56	9.37	47.14
0.0905	1.61	-0.86	-0.86	-0.0072	0.0067	0.58	8.99	45.26
0.1457	2.31	-1.21	-1.21	-0.0086	0.0095	0.59	8.56	43.22
0.2097	2.89	-1.48	-1.48	-0.0090	0.0118	0.61	8.10	40.96
0.2846	3.31	-1.66	-1.66	-0.0085	0.0134	0.63	7.59	38.44
0.3738	3.48	-1.74	-1.74	-0.0072	0.0141	0.66	7.01	35.57
0.4814	3.31	-1.67	-1.67	-0.0056	0.0133	0.68	6.35	32.25
0.6141	2.62	-1.41	-1.41	-0.0040	0.0106	0.71	5.56	28.31
0.7817	1.18	-0.90	-0.90	-0.0025	0.0051	0.75	4.61	25.53
1.000	0.00	0.00	0.00	0.0000	0.0000	0.81	3.42	17.46

Densities of the mixtures have been determined by using calibrated double walled bi-capillary pycknometer. The viscosities have been determined by using by calibrated suspended label canon ubbehalaude type viscometer. The source of errors and precautions taken has also been mentioned. The temperature was maintained by circulating water around liquid cell from thermostat. Pyrrolidine (A.R./B.D.H.) methanol, ethanol and propanol (A.R./B.D.H.) were redistilled by standard methods.

The various thermodynamic and acoustic parameters viz. isentropic compressibility ($ß_s$), intermolecular free length (L_f), molar volume (V_m), available volume (V_a). Rao's constant (r), Wada's constant (B), Shear's relaxation time (τ) have been evaluated by using the following relations :

1. $$\beta_s = \frac{1}{u^2 . \rho}$$

2. $$L_F = K\sqrt{\beta s}$$

3. $V_m = \frac{M}{\rho}$

4. $V_a = V_m \left(1 - \frac{V}{V_\infty}\right)$

5. $B = \left(\frac{M}{\rho}\right) \beta_s^{-1/7}$

6. $\tau_S = \frac{4}{3} . \eta . \beta_s$

7. $A^E = A_{real} - A_{ideal}$

Table 2 : Pyrrolidine + Ethanol at 35^0C

Mole Fraction of Pyrrolidine	Isentropic Compressibility (excess) $cm^2/dyne. 10^{12}$	Molar Volume (excess) ml/mole	Available Volume (excess) ml/mole	Viscosity (excess) C.P.	Intermol Free-length (excess) A	Shear Relaxation Time (τ_s) 10^9	Rao's constant (R)	Wada's constant (B)
0.0000	0.00	0.00	0.00	0.0000	0.0000	0.55	9.73	48.87
0.0423	0.83	-0.46	-0.46	-0.0058	0.0035	0.56	9.37	47.14
0.0905	1.61	-0.86	-0.86	-0.0072	0.0067	0.58	8.99	45.26
0.1457	2.31	-1.21	-1.21	-0.0086	0.0095	0.59	8.56	43.22
0.2097	2.89	-1.48	-1.48	-0.0090	0.0118	0.61	8.10	40.96
0.2846	3.31	-1.66	-1.66	-0.0085	0.0134	0.63	7.59	38.44
0.3738	3.48	-1.74	-1.74	-0.0072	0.0141	0.66	7.01	35.57
0.4814	3.31	-1.67	-1.67	-0.0056	0.0133	0.68	6.35	32.25
0.6141	2.62	-1.41	-1.41	-0.0040	0.0106	0.71	5.56	28.31
0.7817	1.18	-0.90	-0.90	-0.0025	0.0051	0.75	4.61	25.53
1.000	0.00	0.00	0.00	0.0000	0.0000	0.81	3.42	17.46

Table 3 : Pyrrolidine + Propanol at 35^0C

Mole Fraction of Pyrrolidine	Isentropic Compressibility (excess) $cm^2/dyne. 10^{12}$	Molar Volume (excess) ml/mole	Available Volume (excess) ml/mole	Viscosity (excess) C.P.	Intermol Free-length (excess) A	Shear Relaxation Time (τ_s) 10^9	Rao's constant (R)	Wada's constant (B)
0.0000	0.00	0.00	0.00	0.0000	0.0000	0.50	11.67	58.46
0.0354	1.14	-0.61	-0.61	-0.0046	0.0046	0.52	11.25	56.46
0.0762	2.25	-1.15	-1.15	-0.0070	0.00090	0.53	10.80	54.29
0.1239	3.30	-1.62	-1.62	-0.0085	0.0130	0.55	10.30	51.90
0.1804	4.25	-2.00	-2.00	-0.0097	0.0167	0.58	9.75	49.22
0.2482	5.04	-2.27	-2.27	-0.0106	0.0197	0.60	9.14	46.18
0.3312	5.58	-2.39	-2.39	-0.0116	0.0215	0.63	8.42	42.65
0.4351	5.72	-2.31	-2.31	-0.0125	0.0218	0.66	7.58	38.45
0.5690	5.23	-1.95	-1.95	-0.0128	0.0196	0.70	6.54	33.26
0.7482	3.71	-1.17	-1.17	-0.0110	0.0137	0.74	5.22	26.61
1.000	0.00	0.00	0.00	0.0000	0.0000	0.81	3.42	17.46

III. RESULT AND DISCUSSION

In the above three binary system of Pyrrolidine with methanol, ethanol and propanol, we have experimentally determined ultrasound velocity, density and viscosity at temperature, 35^0C. Above facts are used to compute different thermodynamic and acoustic parameters like acoustic impedance, isentropic compressibility, intermolecular free length. Molar and available volume, their excess values. Some another important parameters like Rao's constant. Wada constant and Shear's relaxation time are also computed.

The excess values of β_S^E, L_f^E, V_a^E, η^E have also been calculated.

It is clear from the tables that excess isentropic compressibilities of Pyrrolidine with methanol, ethanol and propanol are positive while excess values of viscosities are negative. The trend of positive excess compressibilities and negative excess viscosities indicate the dispersion forces are dominant as observed by Islam and Ibrahim (11). Positive values of isentropic compressibility (β_S^E) and negative values of η^E decide the weak interaction between the liquid molecules due to dispersion forces. In these interactions dispersion forces are present in every case and in addition to this, there could be dipole-dipole and dipole-induced dipole interactions. The best example of this type of interaction is showed in Vander Waals interaction. This type of interaction arises between the polar and non-polar liquids of the mixtures. The polar molecules having high dipole moment induced polarity in the non-polar molecules by disturbing their electron system. So there must be temporary interaction arise between the dipole and induced dipole molecule.

The positive value of L_f^E indicates that no complex formation between solvent molecules. The tabulated excess values of molar volume and available volume are also observed in supporting trends. The excess molar and available volume are also tabulated against mole fraction show the negative trend of variation. It is reported negative as by Nikam *et.al.* (13). They determined molar volume of aniline with higher alcohols.

The Shear's relaxation time is a better and more informative parameter than isentropic compressibility at incorporates the shear viscosity effects also. The Shear's relaxation times of the binary liquid mixtures varied significantly with variation of solvent composition and as in pure solvents, their order magnitude was 10^{-10}. The variation of (τ_s) with solvent composition in binary mixtures gave similar information as was obtained from other parameters. The Rao's and Wada's constant are found to be independent of temperature but vary linearly with change in solvent composition. Variation in *R* and *B* values with solvent composition suggest the existence of dipole-dipole type of interaction between solvent molecules.

The temperature depends upon the study of binary systems has revealed that with the increasing of temperature, the density, ultrasound velocity and viscosity decrease. However, isentropic compressibility increases and other parameters such as, molar volume show a definite trend. The temperature variation is also reflected in the tables that more deviation is in decreasing order of temperatures.

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