

THE MOLECULAR INTERACTION STUDY OF PYRIDINE WITH LOWER ALCOHOLS AT 303K BY EXCESS ACOUSTIC AND THERMODYNAMIC PARAMETERS

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ABSTRACT

The densities, viscosities and ultrasound velocity of Pyridine with ethanol and n-propanol at 303K have been measured experimentally. The acoustic and thermodynamic parameters viz isentropic compressibility, intermolecular free length, specific acoustic impedance, molar & available volume, viscosity and their excess values have been computed at different composition of both components. The deviation of experimental from ideal values explained in terms of molecular interaction of binary non-aqueous system. The specific molecular interaction have been concluded in the above binary systems.

KEYWORDS: Binary Liquid, Ultrasound Velocity, Alcohol Molecule

INTRODUCTION

Recently, the acoustic and thermodynamic study¹⁻¹⁰ of binary liquid mixtures have got considerable importance in industry and engineering. The properties of liquid mixtures are very important as some of the polymers which are insoluble in pure solvent can be dissolved in solvent mixtures¹¹⁻¹³. Hence considerable attention has been paid to the study of polymer solutions in mixed solvents. Moreover, an additional support of acoustic study to the thermodynamic and transport studies has proved a powerful tool to deal with molecular interactions in binary liquid mixtures and developing theoretical models. Densitometric and viscometric studies¹⁴ of binary mixtures under present study have shown evidence of a weak molecular interaction between unlike molecules.

EXPERIMENTAL

Material and Methods

Pyridine (A.R., B.D.H.), propanol (A.R., B.D.H.), ethanol (A.R., B.D.H.), butanol (A.R., B.D.H.) were purified by the method mentioned elsewhere¹⁴. After triple distillation they were stored properly in bottles. The purity of these liquids were checked by density measurement and comparison with literature values¹⁵.

Ultrasonic velocity of pure liquids and binary liquid mixtures of different composition was measured using an ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) of frequency 2 Mhz with an accuracy of $\pm 0.037\%$ previously used by us (1-3). The measurement was carried out at 303K with the help of thermostat operating with an accuracy of $\pm 1\%$. The working of ultrasonic interferometer was checked for its accuracy by measuring ultrasonic velocity in liquids of known velocity enlisted in literature¹⁶.

The density was measured at 303K using specific gravity bottle by the standard procedure. The ultrasonic velocity was measured at 303K using a single crystal interferometer with a high degree of accuracy operating at a frequency of

2 Mhz. Binary liquid mixture of pyridine with ethanol, butanol and propanol of different composition were prepared by mixing known masses of pure liquids in air tight and narrow mouth ground glass stoppered bottles of minimize the leakage of volatile liquids.

RESULTS & DISCUSSIONS

The experimental measured density, viscosity and ultrasound velocity were used to compute the acoustic and thermodynamic parameters such as Isentropic Compressibility (β_s), Intermolecular Free Length (L_f), Molar Volume (V_m) and Available Volume (V_a) and their excess values by using standard derivation as following –

$$\beta_s = \frac{1}{v^2 \rho} \quad (1)$$

$$L_f = K \sqrt{\beta_s} \quad (2)$$

$$V_m = \frac{\bar{M}}{\rho} \quad (3)$$

$$V_a = V_T \{1 - V/V_\infty\} \quad (4)$$

The other symbols described as—

V = Ultrasound velocity, ρ = density of pure liquid and their binary mixtures

$$K = \text{Time dependent constant, } \bar{M} = \frac{M_1 X_1 + M_2 X_2}{M_1 + M_2} \beta$$

V_T = Ultrasound velocity, $V_\infty = 1600$ m/sec.

The excess values were calculated using the formula:

$$A^E = A_{\text{exp}} - A_{\text{add}}$$

Table 1: Experimental Values of Ultrasonic Velocity (V), Density (ρ), Viscosity (η) and Computed Acoustic Parameters viz. Isentropic Compressibility (β_s), Intermolecular Free Length (L_f), Molar Volume (V_m), Available Volume (V_a) for Pyridine in Ethanol and Butanol at 25°C

Mole Fraction of Pyridine	V (ms ⁻¹)	ρ^E (gm/ml.)	β_s^E (cm ² /Dyne. 10 ¹²)	L_f^E (Å°)	V_m^E (ml/Mole)	V_a^E (ml/Mole)	η^E
Pyridine + Ethanol							
0.0000	1120	0.8214	97.05	0.6157	56.00	16.80	1.1820
0.0719	1155	0.8316	90.14	0.5934	58.17	16.18	1.1617
0.1484	1190	0.8438	83.69	0.5718	60.34	15.46	1.1393
0.2300	1225	0.8568	77.77	0.5512	62.57	14.67	1.1154
0.3173	1260	0.8708	72.34	0.5316	64.89	13.79	1.0897
0.4108	1295	0.8857	67.32	0.5128	67.28	12.83	1.0622
0.5112	1330	0.9024	62.65	0.4947	69.72	11.77	1.0319
0.6193	1365	0.9204	58.31	0.4773	72.25	10.61	0.9992
0.7360	1400	0.9397	54.29	0.4605	74.88	9.36	0.9640

Table 1: Contd.,

0.8625	1435	0.9607	50.55	0.4444	77.60	8.00	0.9258
1.0000	1460	0.9846	47.65	0.4314	80.34	7.03	0.8836
Pyridine + Butanol							
0.0000	1302	0.8848	66.67	0.5103	83.78	15.60	2.9288
0.1038	1319	0.8934	64.34	0.5013	83.56	14.67	2.7184
0.2068	1336	0.9033	62.02	0.4922	83.20	13.73	2.5082
0.3089	1353	0.9132	59.82	0.4834	82.85	12.79	2.2999
0.4101	1370	0.9230	57.72	0.4748	82.52	11.86	2.0932
0.5105	1387	0.9327	55.73	0.4666	82.19	10.94	1.8883
0.6100	1402	0.9430	53.93	0.4590	81.83	10.11	1.6844
0.7087	1417	0.9531	52.27	0.4519	81.47	9.33	1.4821
0.8066	1433	0.9632	50.59	0.4445	81.12	8.49	1.2815
0.9037	1447	0.9732	49.10	0.4379	80.79	7.74	1.0825
1.0000	1460	0.9846	47.65	0.4314	80.34	7.03	0.8836

Table 2: Experimental Values of Ultrasonic Velocity (V), Density (ρ), Viscosity (η) and Computed Acoustic Parameters viz. Isentropic Compressibility (β_s), Intermolecular Free Length (L_f), Molar Volume (V_m), Available Volume (V_a) for Pyridine in Ethanol and Butanol at 30°C

Mole Fraction of Pyridine	V (ms ⁻¹)	ρ^E (gm/ml.)	β_s^E (cm ² /Dyne. 10 ¹²)	L_f^E (Å°)	V_m^E (ml/ Mole)	V_a^E (ml/ Mole)	η^E
Pyridine + Ethanol							
0.0000	1105	0.7836	104.52	0.6451	58.70	18.16	1.1765
0.0719	1142	0.7929	96.75	0.6207	61.01	17.48	1.1530
0.1484	1175	0.8048	90.00	0.5986	63.26	16.80	1.1267
0.2300	1207	0.8175	83.95	0.5781	65.58	16.10	1.0986
0.3173	1238	0.8311	78.53	0.5592	67.98	15.39	1.0685
0.4108	1270	0.8457	73.31	0.5403	70.47	14.53	1.0363
0.5112	1303	0.8620	68.33	0.5216	72.99	13.55	1.0009
0.6193	1336	0.8795	63.70	0.5036	75.61	12.48	0.9627
0.7360	1369	0.8984	59.39	0.4863	78.32	11.31	0.9216
0.8625	1402	0.9188	55.37	0.4695	81.14	10.04	0.8770
1.0000	1410	0.9428	53.35	0.4609	83.90	9.96	0.8274
Pyridine + Butanol							
0.0000	1290	0.8024	74.89	0.5461	92.39	17.90	2.8514
0.1038	1308	0.8146	71.75	0.5345	91.64	16.72	2.6438
0.2068	1326	0.8287	68.63	0.5227	90.69	15.53	2.4358
0.3089	1344	0.8428	65.69	0.5114	89.78	14.37	2.2296
0.4101	1362	0.8567	62.93	0.5005	88.91	13.23	2.0251
0.5105	1380	0.8705	60.32	0.4901	88.08	12.11	1.8224
0.6100	1398	0.8847	57.83	0.4799	87.21	11.01	1.6205
0.7087	1406	0.8989	56.25	0.4733	86.39	10.46	1.4203
0.8066	1412	0.9130	54.98	0.4679	85.59	10.08	1.2218
0.9037	1414	0.9269	53.94	0.4634	84.82	9.85	1.0249
1.0000	1410	0.9428	53.35	0.4609	83.90	9.96	0.8274

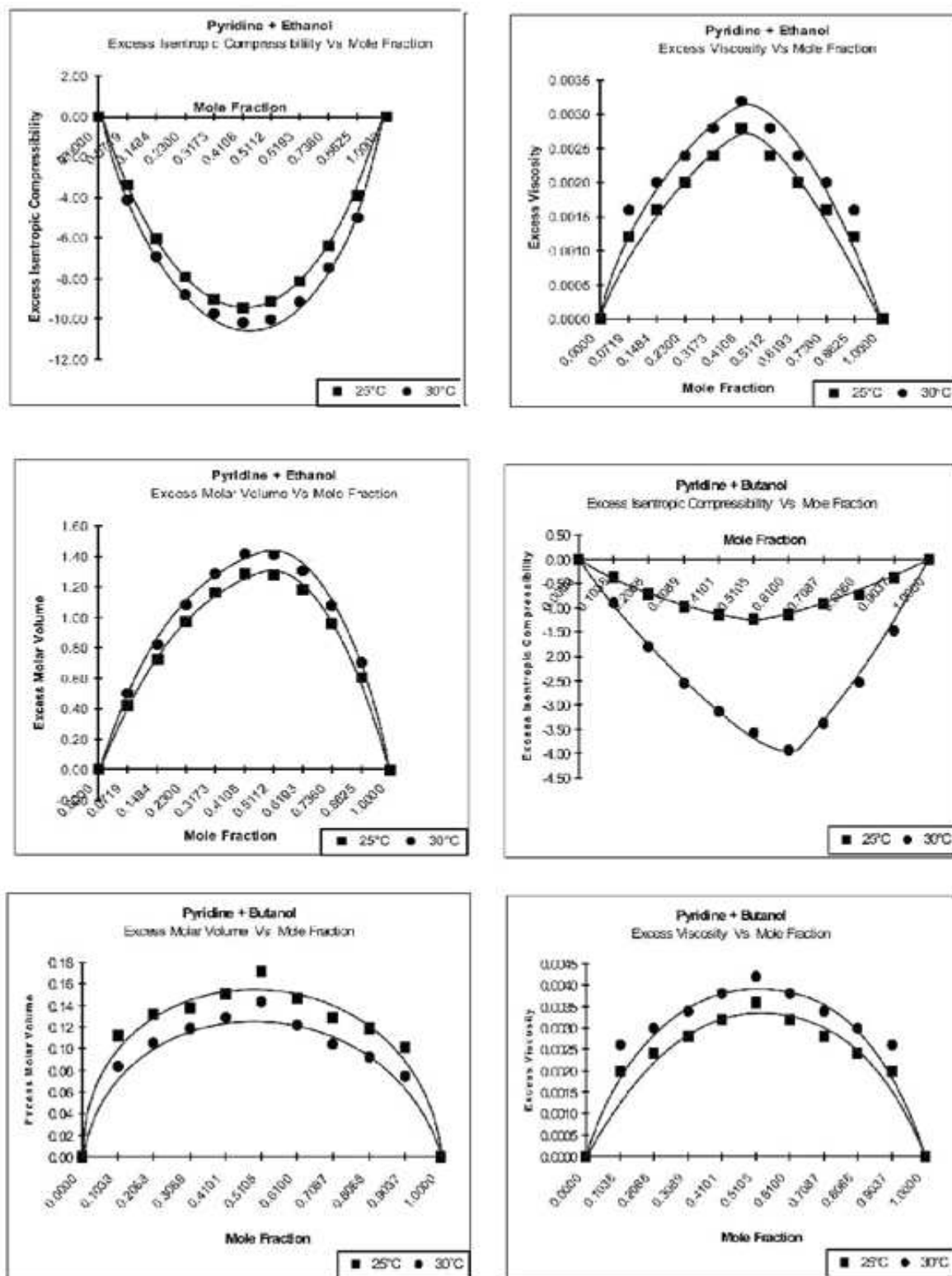


Figure 1

Table 1 & 2 shows the value of ultrasonic velocity (V), density (ρ) and excess isentropic compressibility (β_s^E), excess intermolecular free length (L^E), excess molar volume (V_m^E) and excess available volume (V_a^E). The excess values of viscosity (η^E) are also given on the tables. The values of different parameter with there excess values for pyridine + ethanol

and pyridine + n-propanol at 303K. It is observed that on increasing mole fraction of pyridine is decreases the ultrasound velocity in both liquid mixture systems as shown in table 1 & 2. The isentropic compressibility decrease on increasing mole fraction of pyridine in both binary liquid mixture. The other computed, parameters like specific acoustic impedance, intermolecular free length, molar and available volume sear's relaxation time (τ_s) have shown on the table 1 and 2. The excess values of intermolecular free length, molar and available volume and viscosity were plotted on the figure. The change of variation of β_s^E is negative while η^E is positive which indicate the specific interaction¹⁷ between the pyridine and alcohol molecule. The positive trend of variation of V_m^E being less deviation Suppose the strong interaction between the pyridine and alcohol. The pyridine is unsaturated heterocyclic compound while alcohols are polar and associating in nature so there is possibility of strong interaction between the pyridine and alcohol. The ethanol is more polar than butanol hence extent of interaction is more in pyridine + ethanol than pyridine + butanol. This is verified by more extent excess values of β_s^E and η^E as show in tables 1 and 2.

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