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Static permittivity, refractive index, density and related properties of binary mixtures of pyridine and 1-propanol at different temperatures

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Static permittivity and permittivity at optical frequency of pyridine, 1-propanol and their binary mixtures at nine different concentrations have been measured at 303, 313 and 323 K temperatures. The investigation of binary mixtures showed a systematic change in permittivity with change in concentration of 1-propanol in the binary mixture. Measured properties of these mixtures were used to calculate Kirkwood correlation factor and excess permittivity. Determined parameters have been interpreted in terms of molecular interaction among the molecular species of the binary mixtures. Binary mixture data of static permittivity and refractive index are compared with the predicted values of static permittivity and refractive index using various mixing rules. Comparison of various mixing rules has been expressed in terms of root mean square deviation (RMSD).

Keywords: Kirkwood Correlation factor, Static permittivity, Permittivity, Optical frequency

1 Introduction

Dielectric studies of binary mixtures of pure polar liquids at static and optical frequencies can provide information about molecular structure and intermolecular interaction[1-4]. Measured values of dielectric permittivity can be used to calculate Kirkwood correlation factor and excess permittivity, which can give information about the structural properties of polar liquids[5]. Many researchers have attempted to get insight into the nature and degree of interactions that are present in polar liquid mixtures using excess properties[6-11].

Pyridine (C_5H_5N) is recognized as the non aqueous aprotic solvent having dielectric constant 12.40 at 25°C, dipole moment 2.22 D at 25°C, and boiling point[12] 115°C. Pyridine is used as a precursor to agrochemicals and pharmaceuticals and is also an important solvent and reagent. Pyridine has also been used as the major constituents of binary mixtures of required characteristics. Rana *et al*[13]. have studied the dielectric relaxation behaviour of pyridine and its mixture with benzonitrile in dilute solutions of benzene. Dielectric relaxation in binary mixtures of pyridine with some rigid polar molecules in dilute solutions of benzene has been studied by Vyas *et al*[14]. 1-Propanol (1-PrOH), on the other hand is associative liquid and useful in variety of industrial fields like oil industry, refrigeration, air conditioning and others. Dielectric parameters for pyridine-alcohol binary mixtures have been reported earlier by Chaudhari *et al*[15]. They observed a systematic change in the dielectric parameters with concentration and chain-length of alcohols. Molecular aspect of pyridine and 1-propanol is the motivation behind the present study for understanding the molecular interaction in their binary mixture. In the present paper, measured values of static permittivity and permittivity at optical frequency of pyridine, 1-propanol and their binary mixtures at different temperatures 303, 313 and 323 K are reported. The excess static permittivity and Kirkwood correlation factor have also been calculated from measured data. The excess properties provide valuable information for qualitatively analyzing the molecular interaction between molecules.

2 Experimental Details

1-Propanol (AR grade) and pyridine (AR grade) were commercially obtained from S D Fine-chem Limited (India) and used without further purification. Binary mixtures of 1-propanol and pyridine were prepared at nine concentrations by volume. Assuming ideal mixing behaviour the concentration was converted into the mol fraction[16].

The values of static permittivity of pure liquids, ε_o and of the binary mixtures, $\varepsilon_{\infty m}$ have been determined by using capacitive measurement method with a short compensation at 2 MHz. Agilent 4980 A precision LCR meter with a four terminal liquid dielectric test fixture (Agilent 16452A) was used for the capacitance measurement of the cell without and with sample. The measurement accuracy in ε_0 value is 0.3%. Dielectric permittivity at optical frequency, ε_∞ of pure liquids and $\varepsilon_{\infty m}$ of the binary mixtures was taken as square of the refractive index, n_D, which was measured with an Abbe refractometer at wavelength of sodium-D light. The maximum measurement error in ε_∞ value is ±0.02%. The density was measured using double arm pycknometer and a capillary bore with an internal diameter of 1mm. The densities are accurate to ± 0.1 kg m^{-3}.

3 Data Analysis

From the experimental values of static permittivity and permittivity at optical frequency, the excess static permittivity ($\varepsilon_0{}^E$) for binary mixtures was calculated using relation[17].

$$\varepsilon_0^E=(\varepsilon_0-\varepsilon_\infty)_m-\left[(\varepsilon_0-\varepsilon_\infty)_A X_A+(\varepsilon_0-\varepsilon_\infty)_B X_B\right] \quad \ldots(1)$$

where m, A and B are mixture, pyridine and 1-propanol, respectively.

From the dielectric parameters, the information about the liquid structure as well as orientation of electric dipoles in polar liquids could be obtained using the Kirkwood correlation parameter[18] g.

$$\frac{4\pi N\mu^2\rho}{9kTM}g=\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \quad \ldots(2)$$

where ρ is the density of liquid, M the molecular weight, k the Boltzmann constant, N the Avogadro's number and μ is the dipole moment of polar molecule in gas phase. ε_∞ is taken as square of the refractive index. For the mixtures of two polar liquids, the effective averaged angular Kirkwood correlation factor (g^{eff}) of two different molecules is evaluated from the modified Kirkwood equation[19] for the binary mixture:

$$\frac{4\pi N}{9kT}\left[\frac{\mu_A{}^2\rho_A}{M_A}\varphi_A+\frac{\mu_B{}^2\rho_B}{M_B}\varphi_B\right]\times g^{eff}=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \ldots(3)$$

$$\frac{4\pi N}{9kT}\left[\frac{\mu_A{}^2\rho_A}{M_A}g_A\varphi_A+\frac{\mu_B{}^2\rho_B}{M_B}g_B\varphi_B\right]\times g^{f}=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \ldots(4)$$

4 Results and Discussion

Measured values of static permittivity and refractive index of pyridine and 1-propanol are presented in Table 1 along with their literature values and are found to be in good agreement.

The measured values ε_{0m} and $\varepsilon_{\infty m}$ for binary mixtures are presented in Table 2. Figure1 shows the

Table 2 — Experimental values of static permittivity and permittivity at optical frequency of mixtures of pyridine + 1-PrOH at 303, 313 and 323 K

Mol fraction of 1-PrOH	Static permittivity			Permittivity at optical frequency		
	303 K	313 K	323 K	303 K	313 K	323 K
0	12.87	12.24	11.05	2.2533	2.2416	2.2288
0.0833	13.58	12.88	11.69	2.2138	2.202	2.1848
0.1697	14.32	13.58	12.39	2.1877	2.1789	2.1612
0.2595	14.98	14.08	12.95	2.1521	2.1433	2.1258
0.3528	15.39	14.61	13.49	2.1255	2.1138	2.0857
0.4498	15.97	15.22	14.17	2.086	2.0785	2.0615
0.5508	16.57	15.84	14.84	2.0521	2.0423	2.0275
0.6561	17.16	16.45	15.52	2.0212	2.0073	1.9926
0.7658	17.98	17.22	16.26	1.9887	1.9774	1.9653
0.8803	18.8	18.04	17.06	1.9569	1.9457	1.9299
1	19.76	18.88	17.98	1.9182	1.9003	1.8967

Table 1 — Measured and literature values of static permittivity and refractive index of pyridine and 1-PrOH

Molecule	Temp. K	Present study		Literature values	
		Static permittivity	Permittivity at optical frequency	Static permittivity	Permittivity at optical frequency
Pyridine	303	12.87	2.25	13.55(20°C)[19] 12.0(25°C)[20]	2.30(20°C)[19]
	313	12.24	2.24	11.44(40°C)[19]	2.26(40°C)[19]
	323	11.05	2.23	—	—
1-PrOH	303	19.76	1.91	20.3(25°C)[21] 20.84(301K)[22]	1.91(25°C)[21] 1.93(301K)[22]
	313	18.88	1.9	19.38(313K)[23]	1.92(313K)[23]
	323	17.98	1.89	18.54(323K)[23]	1.90(323K)[23]

variation of static permittivity with variation in concentration of 1-PrOH at 303,313 and 323 K and Fig. 2 shows the variation of permittivity at optical frequency with variation in concentration of 1-PrOH at 303, 313 and 323 K.

Static permittivity is found to increase non-linearly with the concentration of 1-propanol. This indicates interaction between the components of the mixture. Mehrotra *et al*[24]. have reported that elevation of static permittivity with the concentration of the solute in a binary liquid mixture is due to the transition of spherical molecular aggregates to more correlated elongated aggregates, implying that when solute is added it modifies the packing density condition of the dipoles in the solvent. Rana *et al*[25]. have reported that non-linear variation of static permittivity with the concentration of one of the components in the mixture is an indication for the interaction between unlike molecules. Hence, it may be concluded that in this system hetero interaction exists.

4.1 Kirkwood correlation factor

Kirkwood correlation factor g is a parameter for obtaining information regarding orientation of electric dipoles in polar liquids[26]. The departure of g value from unity is a measure of degree of short range dipolar ordering due to H-bond interactions. For a liquid in which molecules tend to orient themselves with the parallel dipole alignments in the same direction results in g value greater than unity. When the polar liquid molecules prefer an ordering with anti parallel dipoles, the g value becomes smaller than unity and for non associating molecules, the g value is nearly unity. Table 3 presents the evaluated g^{eff} values of the investigated pyridine + 1-propanol mixtures.

The effective correlation factor g^{eff} of the binary mixtures are plotted against mole fraction of 1-propanol at different temperatures in Fig. 3. The value of g^{eff} for pyridine is close to unity, or less than unity, indicating antiparallel ordering of dipoles, whereas higher values of g^{eff} for 1-propanol indicate parallel alignment of the electric dipoles. The plots shows non linear variation over the entire concentration range at all the temperatures. This confirms the net increase in dipolar ordering due to H-bond complexation.

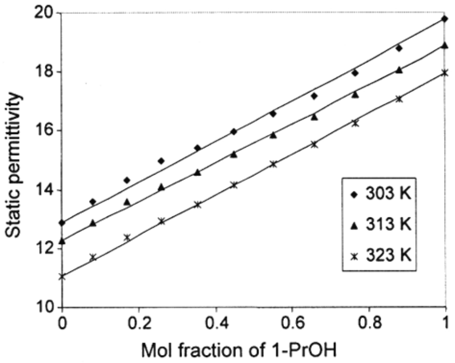

Fig. 1 — Variation of static permittivity with variation in mol fraction of 1-PrOH (Solid line indicate weighted values of static permittivity)

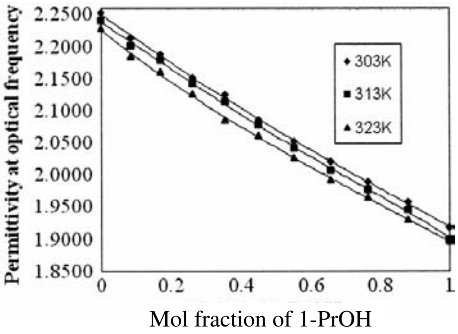

Fig. 2 — Variation of permittivity at optical frequency ε_0 with variation in mol fraction of 1-PrOH

Table 3 — Experimental values of Kirkwood correlation factor (g^{eff}) and corrective correlation factor (g^{f}) of pyridine + 1-propanol at 303, 313 and 323 K

Mol fraction of 1-PrOH	Kirkwood correlation factor (g^{eff})			Corrective correlation factor (g^{f})		
	303 K	313 K	323 K	303 K	313 K	323 K
0	1.00	0.76	0.55	1.00	1.00	1.00
0.0833	1.12	0.86	0.63	1.01	1.00	0.99
0.1697	1.26	0.97	0.72	1.01	1.00	0.99
0.2595	1.40	1.09	0.82	1.01	0.99	0.99
0.3528	1.53	1.22	0.94	0.99	0.98	0.97
0.4498	1.71	1.39	1.10	0.99	0.98	0.98
0.5508	1.92	1.60	1.29	0.98	0.98	0.98
0.6561	2.15	1.84	1.53	0.97	0.98	0.98
0.7658	2.45	2.14	1.86	0.98	0.98	0.98
0.8803	2.82	2.56	2.30	0.98	0.99	0.99
1	3.30	3.05	2.89	1.00	1.00	1.00

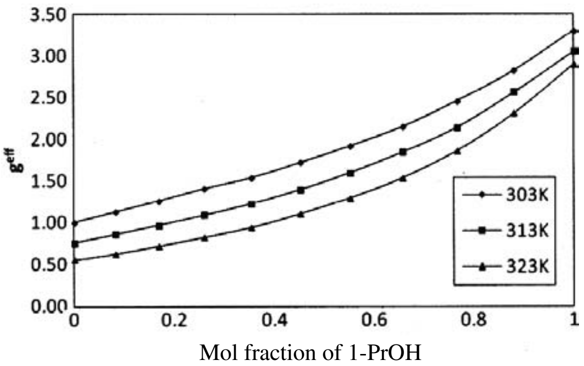

Fig. 3 — Variation of Kirkwood correlation factor (g^{eff}) with variation in mol fraction of 1-PrOH

4.2 Excess static permittivity

From the excess static permittivity values of the liquid binary mixtures, following information can be extracted.

(1) $\varepsilon_0^E = 0$ indicates that the mixture constitutes do not interact or there is no change in the net dipole alignments and thus polar liquids have ideal mixing behaviour. (2) $\varepsilon_0^E < 0$ indicates that one of the mixture constitutes act as structure breaker for other constituent H-bonded structure with orientation of some of the neighbouring dipoles in opposite direction (anti-parallel). Hence, there is decrease in total number of parallel aligned effective dipoles that contributes to the mixture dielectric polarization. (3) $\varepsilon_0^E > 0$ indicates that the constituent of the binary mixture interact in such a way that act as H-bonded structure makers with parallel dipolar alignments in the same direction, which results in increase in total number of parallel align effective dipoles that contributes to the mixture dielectric polarization. (4) The magnitude of ε_0^E values is the evidence of the strength of unlike molecular H-bond interactions. i.e. the higher the values, the stronger the H-bond molecular connectivity and vice versa.

Plot of excess permittivity versus mol fraction of 1-PrOH is shown in Fig. 4. The excess permittivity values show mixed behaviour with change in concentrations of 1-PrOH in the mixture. Excess permittivity is found to be positive in pyridine rich region, this indicates that both unlike molecules interact in such a way that the dipolar alignment is parallel and the effective dipole moment increases. While in the 1-PrOH rich region, the excess permittivity is negative, and this indicates that the mixture constituents interact so as to reduce total effective dipoles. The behaviour of structural changes with change in concentration of 1-PrOH is similar at all the three temperatures with a slight change in their magnitudes.

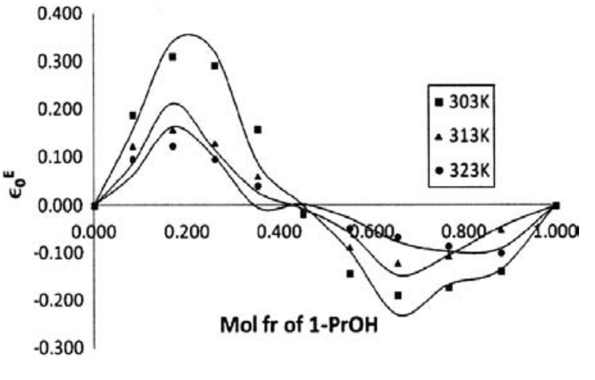

Fig. 4 — Variation of excess relative permittivity with variation in mol fraction of 1-PrOH and solid line shows experimental points of Redlich-Kister fitting, respectively

The evaluated values of excess static permittivity were fitted to Redlich-Kister polynomial[27] (Table 4)

$$A^E = (X_A X_B)\sum_{i=0}^{n} a_i[(X_A - X_B)]^i \qquad \ldots(5)$$

4.3 Bruggeman factor

The information related to the solute-solvent interaction is given by the Bruggeman factor. According to the Bruggeman, ε_{0m}, ε_{0A} and ε_{0B} may be related to the volume fraction of the solute (1-PrOH) by the following formula[28], assuming ideal mixing behaviour:

$$f_B = \frac{(\varepsilon_{0m} - \varepsilon_{0A})}{(\varepsilon_{0B} - \varepsilon_{0A})}\left(\frac{\varepsilon_{0B}}{\varepsilon_{0m}}\right)^{1/3} = 1 - \phi \qquad \ldots(6)$$

Yielding a linear relationship between Bruggeman factor f_B and volume fraction of solute. The Bruggeman plots for pyridine +1-PrOH mixtures are shown in Fig. 5. The value of f_B is not a linear function of volume fraction (Fig. 5). To fit the experimental data, Eq. (6) has been modified as follows[29]:

$$f_B = 1 - [a - (a-1)\phi]\phi \qquad \ldots(7)$$

where '*a*' is a numerical fitting parameter. The values of '*a*' for pyridine + 1-PrOH mixtures along with standard error and correction coefficients are presented in Table 5. For pyridine + 1-PrOH mixtures *a* > 1. This suggests that the effective volume fraction of 1-PrOH in pyridine has decreased which indicates stronger molecular interaction in this system.

4.4 Molar refraction, polarization and polarizability

The molar refraction *R* was obtained from the formula[30]:

$$R = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)V_m \qquad \ldots(8)$$

Table 4 — Values of coefficients of Redlich-Kister polynomial a_i with standard deviation σ and fitness coefficient δ

Temperature	a_0	a_1	a_2	a_3	a_4	σ	δ
303 K	-0.3566	2.6128	3.6499	-0.2623	-3.6191	0.0447	0.9828
313 K	-0.2259	1.3759	1.1011	-0.2382	0.1714	0.0349	0.9643
323 K	-0.1346	0.7018	0.9918	1.1095	-1.0929	0.0311	0.9543

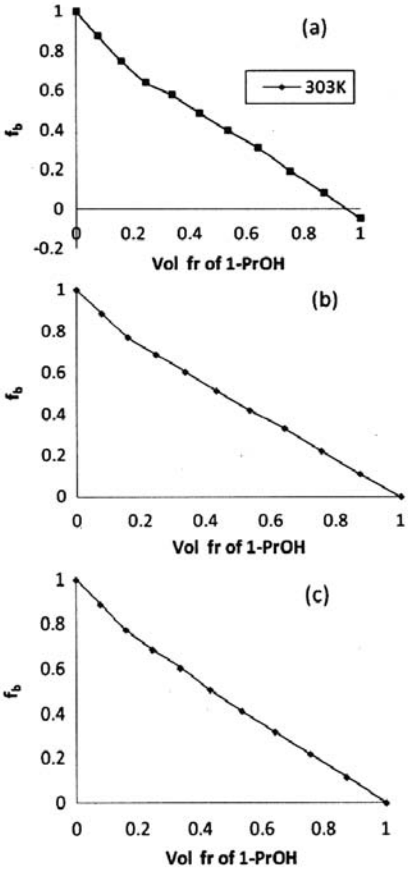

Fig. 5 — Bruggeman plots for pyridine + 1-PrOH at temperature 303, 313 and 323 K

Table 5 — Values of fitting parameter '*a*' for Bruggeman factor for pyridine + 1-PrOH binary mixture at 303, 313 and 323 K

Temperature in K	Fitting parameter '*a*'	Standard Error	Correction coefficient
303	1.2907	0.02802	0.9964
313	1.1559	0.01755	0.9985
323	1.1773	0.01398	0.9990

where n_D is the refractive index of the liquid sample and $V_m=(M/d)$ is the molar volume, where M is the molecular weight and d is the density of the liquid mixture.

The right hand side of the Eq. (8) is equal to the summation of both the atomic polarization (P_a) and electronic polarization (P_E) which is the total polarization (P_T).

The atomic polarization P_a was calculated from equation[31]:

$$P_a = 1.05 n_D^2 \qquad \ldots(9)$$

The polarizability α was calculated using the Lorentz-Lorenz formula[32],

$$\alpha = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\left(\frac{3V_m}{3\pi N}\right) \qquad \ldots(10)$$

Considering spherical forms of the solvated molecules[33], the solvated radii of the solvents were calculated using the equation,

$$V = \left(\frac{4}{3}\pi\right) r^3 \qquad \ldots(11)$$

Table 6 presents volume fraction (φ_1 and φ_2), the measured refractive indices, densities, molar volume (V), molar refraction (R), polarizability (α), solvated radii (r), atomic polarization (P_a) and electronic polarization (P_E) for pyridine + 1-PrOH at 303, 313 and 323 K temperatures. Polarizability values for pyridine and 1-propanol at 30°C are 9.5 and 6.9 Å^3, respectively.

This clearly suggests that in pure pyridine London dispersion forces are dominant. Whereas in case of 1-propanol intermolecular forces due to hydrogen bonding and dipole-dipole interaction, forces are more dominant then the London dispersion forces. London dispersion forces exist between all molecules and are determined by the polarizability of the molecules. Polarizability depends on the total number of electrons and the volume over which they are spread. The greater the number of electrons and greater the volume over which they are spread, the greater the polarizability and greater the London dispersion forces. More dominance of the London dispersion forces in pyridine than 1-propanol is also evidenced by the higher value of boiling point of the former compound than the later compound (BP of pyridine is 115.2°C and of 1-propanol is 97-98°C). Polarizability values decrease with increases in the concentration of 1-propanol in the mixture. Polarizability values of all the mixture concentration increase with increase in temperature. This is due to increase in the molar volume with increase in temperature. Figure 6 shows the relation between the molar refraction (R) and volume fraction of 1-PrOH at 303, 313 and 323 K temperatures. Since molar refraction R is proportional to polarizability, the molar refraction in the optical region is related to the strength of the dispersion forces. The higher the permanent electric dipole moment of molecules, the more dominant are the

Table 6 — Volume fractions (φ_1, φ_2), refractive indices (n_D),densities (d), molar volume (V), molar refraction (R), polarizability (α), solvated radii (r), atomic polarization (P_a) and electronic polarization (P_E) of pyridine and 1-PrOH at 303,313 and 323K temperatures

φ_1	φ_2	n_D	d g/cc	V cm^3/mol	R cm^3/mol	α*10^{-23} cm/mol ecule	r A^0	P_a	P_E
Temp.= 303 K									
0.000	1.000	1.5011	0.9638	82.079	24.186	0.95	2.67	2.37	21.82
0.078	0.922	1.4879	0.9566	81.443	23.461	0.93	2.66	2.32	21.14
0.160	0.840	1.4791	0.9488	80.785	22.913	0.90	2.66	2.30	20.62
0.247	0.753	1.4670	0.9329	80.105	22.227	0.88	2.65	2.26	19.97
0.337	0.663	1.4579	0.9227	79.400	21.661	0.86	2.64	2.23	19.43
0.433	0.567	1.4443	0.9059	78.671	20.910	0.83	2.63	2.19	18.72
0.534	0.466	1.4325	0.8978	77.915	20.229	0.80	2.62	2.15	18.07
0.640	0.360	1.4217	0.8772	77.130	19.588	0.78	2.62	2.12	17.47
0.753	0.247	1.4102	0.8659	76.317	18.917	0.75	2.61	2.09	16.83
0.873	0.127	1.3989	0.8396	75.472	18.252	0.72	2.60	2.05	16.20
1.000	0.000	1.3850	0.8058	74.594	17.481	0.69	2.59	2.01	15.47
Temp. = 313 K									
0.000	1.000	1.4972	0.9477	83.463	24.431	0.97	2.68	2.35	22.08
0.079	0.921	1.4839	0.9409	82.482	23.594	0.94	2.67	2.31	21.28
0.161	0.839	1.4761	0.9277	81.964	23.122	0.92	2.67	2.29	20.83
0.248	0.752	1.4640	0.9061	82.103	22.656	0.90	2.67	2.25	20.41
0.339	0.661	1.4539	0.8931	81.361	22.029	0.87	2.66	2.22	19.81
0.435	0.565	1.4417	0.8763	80.835	21.376	0.85	2.66	2.18	19.19
0.536	0.464	1.4291	0.8642	79.754	20.565	0.82	2.64	2.14	18.42
0.642	0.358	1.4168	0.8464	79.043	19.869	0.79	2.64	2.11	17.76
0.755	0.245	1.4062	0.8315	77.883	19.139	0.76	2.62	2.08	17.06
0.874	0.126	1.3949	0.8137	76.808	18.410	0.73	2.61	2.04	16.37
1.000	0.000	1.3785	0.7977	75.343	17.391	0.69	2.60	2.00	15.40
Temp. = 323 K									
0.000	1.000	1.4929	0.9373	84.391	24.522	0.97	2.69	2.34	22.18
0.078	0.922	1.4781	0.9336	83.130	23.536	0.93	2.68	2.29	21.24
0.161	0.839	1.4701	0.9161	83.011	23.164	0.92	2.68	2.27	20.90
0.247	0.753	1.4580	0.8943	83.202	22.703	0.90	2.68	2.23	20.47
0.338	0.662	1.4442	0.8726	83.288	22.132	0.88	2.68	2.19	19.94
0.434	0.566	1.4358	0.8600	82.392	21.534	0.85	2.67	2.16	19.37
0.535	0.465	1.4239	0.8551	80.623	20.569	0.82	2.65	2.13	18.44
0.641	0.359	1.4116	0.8316	80.467	20.005	0.79	2.65	2.09	17.91
0.754	0.246	1.4019	0.8161	79.367	19.321	0.77	2.64	2.06	17.26
0.873	0.127	1.3892	0.8025	77.886	18.430	0.73	2.62	2.03	16.40
1.000	0.000	1.3772	0.7837	76.691	17.648	0.70	2.61	1.99	15.66

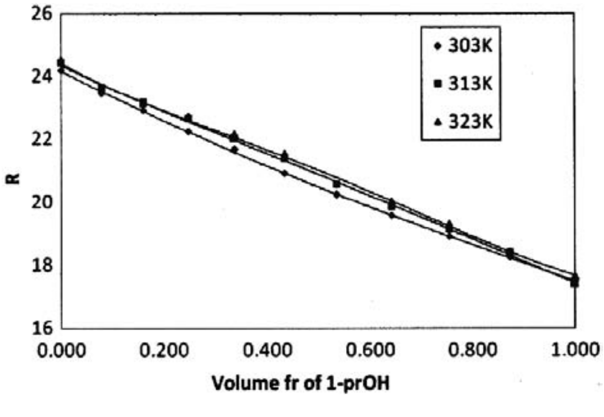

Fig .6 — Variation of molar refraction (R) with variation in volume fraction of 1-PrOH

orientational effects. Since we measured the refractive indexes in the optical region, the polarizability should not include orientational effects. Therefore, the molar refraction should not depend on temperature T over a small temperature range.

4.5 Estimation models of permittivity

4.5.1 Static permittivity

In present work, measured experimental permittivity data of the pyridine + 1-PrOH binary mixtures were compared to those estimated by five mixing rules which were proposed by:

Looyenga[34]

$$\varepsilon = [\varepsilon_A^{1/3} + \varphi_A(\varepsilon_B^{1/3} - \varepsilon_A^{1/3})]^3 \qquad \ldots(12)$$

Kraszewski *et al*[35].

$$\varepsilon^{1/2} = \varphi_A \varepsilon_A{}^{1/2} + \varphi_B \varepsilon_B{}^{1/2} \qquad \ldots(13)$$

Iglesias-Peon[36]

$$\varepsilon = \varphi_A \varepsilon_A + \varphi_B \varepsilon_B \left[1 - \frac{2}{3} \ln \left(\frac{1 + \varphi_A \left(\frac{\varepsilon_A}{\varepsilon_B} - 1 \right)}{\left(\frac{\varepsilon_A}{\varepsilon_B} \right)^{\varphi_A}} \right) \right] \qquad \ldots(14)$$

Lichtenecker-Rother[37]

$$\varepsilon = \varepsilon_A{}^{\varphi A} \varepsilon_B{}^{\varphi B} \qquad \ldots(15)$$

Bottcher[38]

$$\frac{3\varepsilon_A}{2\varepsilon + \varepsilon_A} \varphi_A + \frac{3\varepsilon_B}{2\varepsilon + \varepsilon_B} \varphi_B = 1 \qquad \ldots(16)$$

where φ_A and φ_B are volume fractions of the components of mixture.

The comparison between experimental and calculated data of relative permittivity for liquid mixtures of pyridine and 1-PrOH using the predictive models at 303, 313 and 323 K temperatures is listed in Table 7. For the binary mixtures, the prediction ability of these theoretical models is almost similar.

From the Table 7, it can be seen that the Kraszewski and Rother model offers the best result while intermediate results are obtained by Igleasis and Bottcher models. The Standard deviation or Root Mean Square Deviation (RMSD) of these models as compared to our experimental results are also given in Table 9. This deviation is calculated using following equation:

$$\text{RMSD} = \left[\frac{1}{m \sum \left(\varepsilon_{\exp} - \varepsilon_{cal} \right)^2} \right]^{1/2} \qquad \ldots(17)$$

where *m* is the number of data points. $\varepsilon_{\exp}$ and ε_{cal} are experimental and calculated values of relative permittivity, respectively.

Table 7 — Comparison of the experimental relative permittivities from those estimated by the mixing rules proposed by Looyenga (Lg), Bottcher (B),Iglesias (Ig), Lichtenecker–Rother (L-R) and Kraszewski (Kz) for binary mixture of pyridine and 1-propanol at temperatures from 303, 313 and 323 K

φ_2	Exp.	Lg	Kz	Ig	L-R	B
			Temp.= 303 K			
0.000	12.87	12.86	12.87	12.87	12.87	12.87
0.078	13.58	13.48	13.50	13.50	13.44	13.49
0.160	14.32	14.24	14.26	14.23	14.25	14.26
0.247	14.98	14.89	14.93	14.89	14.92	14.86
0.337	15.39	15.42	15.44	15.48	15.34	15.46
0.433	15.97	16.02	16.04	16.02	16.03	16.01
0.534	16.57	16.62	16.62	16.63	16.58	16.64
0.640	17.16	17.22	17.24	17.24	17.21	17.20
0.753	17.98	18.10	18.10	18.12	18.06	18.08
0.873	18.8	18.84	18.86	18.88	18.90	18.82
1.000	19.76	19.70	19.76	19.76	19.76	19.76
			Temp. = 313 K			
0.000	12.24	12.21	12.24	12.24	12.24	12.24
0.079	12.88	12.79	12.84	12.85	12.79	12.76
0.161	13.58	13.54	13.52	13.47	13.45	13.49
0.248	14.08	14.00	14.09	14.10	13.99	14.02
0.339	14.61	14.64	14.63	14.64	14.57	14.67
0.435	15.22	15.29	15.26	15.32	15.22	15.33
0.536	15.84	15.92	15.92	16.01	15.91	15.90
0.642	16.45	16.54	16.49	16.51	16.50	16.58
0.755	17.22	17.30	17.32	17.27	17.25	17.28
0.874	18.04	18.10	18.16	18.12	18.09	18.14
1.000	18.88	18.83	18.88	18.88	18.88	18.88
			Temp. = 323 K			
0.000	11.05	11.02	11.05	11.05	11.05	11.05
0.078	11.69	11.62	11.68	11.70	11.64	11.66
0.161	12.39	12.32	12.32	12.35	12.32	12.34
0.247	12.95	12.87	12.96	12.99	12.79	12.89
0.338	13.49	13.51	13.61	13.63	13.42	13.55
0.434	14.17	14.20	14.24	14.31	14.09	14.23
0.535	14.84	14.95	14.89	14.96	14.85	14.91
0.641	15.52	15.57	15.56	15.58	15.55	15.59
0.754	16.26	16.32	16.30	16.28	16.33	16.34
0.873	17.06	17.17	17.12	17.11	17.10	17.13
1.000	17.98	17.93	17.98	17.98	17.98	17.98

The predictions of the mixing rules mentioned above are substantially equivalent. As RMSD values indicate, relative permittivity values for mixtures are predicted with high accuracy for all the mixtures under consideration. The best predictions are observed for the Kraszewski, while the RMSD values predicted by Looyenga, Rother, Igleasis and Bottcher relations are relatively higher.

4.5.2 Refractive index

Measured experimental refractive index values of the pyridine + 1-PrOH binary mixtures were compared to those estimated by five mixing rules which are shown in Table 8 were proposed by:

Eyring-John (E-J)[39]

$$n = n_A \varphi_A^2 + n_B \varphi_B^2 + 2(n_A n_B)^{1/2} \qquad \ldots(18)$$

Table 8 — Comparison of the experimental refractive index values with those from estimated by the mixing rules proposed by Eyring-John (E-J), Gladstone-Dale (G-D), Newton (Nw), Arago-Biot (A-B), Heller (H) and Lorentz-Lorenz (L-L) for binary mixture of pyridine and 1-propanol at temperatures 303, 313 and 323 K

φ_2	Exp.	E-J	G-D	Nw	A-B	H	L-L
			Temp.=303 K				
0.000	1.501	1.501	1.501	1.501	1.501	1.501	1.501
0.078	1.488	1.489	1.492	1.490	1.489	1.489	1.490
0.160	1.479	1.477	1.483	1.478	1.477	1.477	1.478
0.247	1.467	1.465	1.472	1.467	1.466	1.465	1.467
0.337	1.458	1.453	1.462	1.455	1.454	1.453	1.458
0.433	1.444	1.441	1.451	1.443	1.442	1.441	1.442
0.534	1.433	1.429	1.439	1.430	1.429	1.428	1.432
0.640	1.422	1.417	1.427	1.418	1.418	1.417	1.422
0.753	1.410	1.405	1.414	1.406	1.405	1.404	1.410
0.873	1.399	1.394	1.400	1.395	1.394	1.393	1.398
1.000	1.385	1.385	1.385	1.385	1.385	1.384	1.385
			Temp.=313 K				
0.000	1.497	1.497	1.497	1.497	1.497	1.497	1.497
0.079	1.484	1.485	1.485	1.486	1.485	1.485	1.483
0.161	1.476	1.473	1.473	1.474	1.473	1.473	1.476
0.248	1.464	1.460	1.461	1.462	1.461	1.461	1.463
0.339	1.454	1.448	1.449	1.450	1.449	1.448	1.452
0.435	1.442	1.436	1.436	1.438	1.436	1.436	1.443
0.536	1.429	1.423	1.424	1.425	1.424	1.423	1.429
0.642	1.417	1.411	1.412	1.413	1.412	1.411	1.417
0.755	1.406	1.399	1.399	1.400	1.399	1.398	1.406
0.874	1.395	1.388	1.388	1.388	1.388	1.387	1.392
1.000	1.379	1.378	1.378	1.378	1.378	1.377	1.378
			Temp.=323 K				
0.000	1.493	1.493	1.493	1.493	1.493	1.493	1.493
0.078	1.478	1.481	1.481	1.482	1.481	1.481	1.481
0.161	1.470	1.469	1.469	1.470	1.469	1.469	1.468
0.247	1.458	1.457	1.458	1.459	1.458	1.457	1.455
0.338	1.444	1.445	1.445	1.447	1.445	1.445	1.441
0.434	1.436	1.433	1.434	1.435	1.434	1.433	1.433
0.535	1.424	1.421	1.421	1.422	1.421	1.420	1.421
0.641	1.412	1.409	1.410	1.411	1.410	1.409	1.408
0.754	1.402	1.397	1.397	1.398	1.397	1.396	1.396
0.873	1.389	1.386	1.386	1.387	1.386	1.385	1.384
1.000	1.377	1.377	1.377	1.377	1.377	1.376	1.376

Gladstone – Dale (G-D)[40]

$$n-1=(n_A-1)\varphi_A+(n_B-1)\varphi_B \qquad \ldots(19)$$

Newton (Nw)[41]

$$n^2-1=(n_A^2-1)\varphi_A+(n_B^2-1)\varphi_B \qquad \ldots(20)$$

Arago-Biot (A-B)[42]

$$n=n_A\varphi_A+n_B\varphi_B \qquad \ldots(21)$$

Table 9 — Values of RMSD against various mixing rules

Mixing rule	RMSD 303 K	313 K	323 K
	Refractive index		
E-J	0.0035	0.0049	0.0025
G-D	0.0031	0.0045	0.0023
Nw	0.0025	0.0039	0.0020
A-B	0.0032	0.0046	0.0023
H	0.0038	0.0053	0.0029
L-L	0.0010	0.0012	0.0033
	Static permittivity		
Lg	0.0695	0.0675	0.0669
Kz	0.0653	0.0598	0.0561
Ig	0.0792	0.0767	0.0760
L-R	0.0694	0.0641	0.0673
B	0.0702	0.0698	0.0712

Heller (H)[43]

$$\frac{(n-n_A)}{n_A}=\frac{3}{2}\times\frac{\left(\left(\frac{n_B}{n_A}\right)^2-1\right)}{\left(\left(\frac{n_B}{n_A}\right)^2+2\right)}\varphi_B \qquad \ldots(22)$$

Lorentz-Lorenz (L-L)[44]

$$\frac{n^2-1}{n^2+1}=\varphi_A\left(\frac{n_A^2-1}{n_A^2+2}\right)+\varphi_B\left(\frac{n_B^2-1}{n_B^2+2}\right) \qquad \ldots(23)$$

where n, n_A, n_B, φ_A, φ_B represent refractive index of mixture, pyridine and 1-PrOH, volume fraction of pyridine and volume fraction of 1-PrOH, respectively.

$$\text{R.M.S.D.}=\left(\frac{1}{m\Sigma(n_{\text{exp}}-n_{\text{cal}})^2}\right)^{1/2} \qquad \ldots(24)$$

where m is the number of experimental data points.

The Root Mean Square Deviation (RMSD) values for the Erying-Johns (E-J), Gladstone–Dale (G-D), Newton (Nw), Arago–Biot (A-B), H (Heller) and Lorentz-Lorenz (L-L) are presented in Table 9. As RMSD values indicate, refractive index for mixtures are predicted with high accuracy for all the mixtures under consideration. A close similarity is observed between the A-B and G-D relations. The RMSD values for G-D and A-B relations are found to be identical when volume additivity is assumed. The best predictions are observed for the L-L followed by Nw while the RMSD values predicted by E-J, G-D, A-B, and H relations are relatively higher. Since the liquid mixtures of different nature and significantly different molecular sizes are considered, a particular relation provides good agreement at one place and deviates at others. This study indicates that all the theoretical mixing rules are interrelated in a simple quantitative manner and perform well within the limits of experimental error. The applicability of these semi-empirical relations for predicting refractive indices has also been emphasized by others[37-39].

5 Conclusions

This paper reports experimental data for static permittivity, refractive index, density and related properties of binary mixtures of pyridine and 1-propanol at 303, 313 and 323 K temperatures. The investigation of binary mixtures showed a systematic change in static permittivity and permittivity at optical frequency with change in concentration of pyridine in 1-propanol. Excess permittivity is found to be positive in pyridine rich region, this indicates that both unlike molecules interact in such a way that the dipolar alignment is parallel and the effective dipole moment increases. While in the 1-PrOH rich region the excess permittivity is negative, this indicates that the mixture constitutes interact so as to reduce total effective dipoles. The value of g^{eff} for pyridine is close to unity, or less than unity, indicating anti-parallel ordering of dipoles, whereas higher values of g^{eff} for 1-propanol indicate parallel alignment of the electric dipoles. Binary mixture data of static permittivity and refractive index are compared with the predicted values using various mixing rules. For static permittivity the best predictions are observed for the Kraszewski, while the RMSD values predicted by Looyenga, Rother, Igleasis and Bottcher relations are relatively higher. For refractive index the best predictions are observed for the L-L followed by Nw while the RMSD values predicted by E-J, G-D, A-B, and H relations are relatively higher.

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