

Study of concentration dependent Physico-chemical properties of 1-Propanol, Benzonitrile and their binary mixtures

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Abstract – In the present work static dielectric constant (ϵ_0), refractive index (n) and density (ρ) have been experimentally determined for binary liquid mixture of 1-Propanol (1-PrOH) with benzonitrile (BN) over the entire concentration range of mixture composition (0.0 \rightarrow 1.0) at constant temperature 303.15 K. Static dielectric constant (ϵ_0) and refractive index (n) for the binary mixture have been measured using high precision LCR meter (2 MHz) and Abbe's refractometer respectively. Molar refraction (R_m), atomic polarization (P_A), molecular radius (r) and polarizability (α) and internal pressure (P_{int}) for each the binary mixtures were calculated from the measured values of refractive indices and densities. Using the experimental data various excess parameters namely; excess static dielectric constant (ϵ_0)^E, excess refractive index (n)^E, excess density (ρ)^E, excess molecular radius (r)^E, excess atomic polarization (P_A)^E, excess internal pressure (P_{int})^E have been computed and discussed in terms of hetero-interaction (i.e. interaction between unlike molecules). These excess parameters were fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and standard deviations. In order to predict the static dielectric constant (ϵ_0) and refractive index (n) for binary mixtures several mixing rules were applied and their validity have been tested for the same.

Keywords: Alcohol, binary mixtures, density, internal pressure, static dielectric constant refractive index

I. Introduction

This Paper is a continuation of our earlier work related to the study of physico-chemical properties of binary mixtures [1]. In recent years, measurements of static dielectric constant, refractive index and density have been adequately employed in understanding the nature of molecular systems and physico-chemical behaviour in liquid mixtures. The nonrectilinear behaviour of above mentioned properties of liquid mixtures with changing mole or volume fractions is attributed to the difference in size of the molecules and strength of interactions [2]-[3]. In recent past alcohols have found various applications and commercial use in medical and other fields, for example 1-Propanol (1-PrOH) is very effective against a broad spectrum of microorganisms including bacteria, fungi and viruses such as HIV, hepatitis-B, and respirator syncytial viruses. Also 1-Propanol (1-PrOH) is in use as the safest antiseptic compound for topical use and is feedstock in the manufacture of insecticides [4]. Benzonitrile (BN) is one the important compound among the nitriles. Derivatives of benzonitrile are widely used in industry, pharmaceutical and medicinal fields. Because of its wide use and simple structure, a quite good number of

studies on benzonitrile (BN) were reported [5]-[6]. Therefore it seemed important to examine the physico-chemical study of 1-PrOH, BN and their binary mixtures over the entire concentration range at constant temperature 303 K.

II. Experimental Details

II.1. Materials

1-Propanol (1-PrOH) of AR Grade was procured from Sd-finechem, India. GR grade Benzonitrile (BN) was supplied by Spectrochem (India). All the chemicals were used without further purification. Using these polar liquids, binary mixture systems were prepared in hermetically sealed glass vials at 11 volume concentrations over the entire mixing range at 303.15 K. The mole fractions of the mixture constituents were determined using the formula:

$$X_B = \frac{(\Phi_B \times \rho_B / M_B)}{(\Phi_B \times \rho_B / M_B) + (\Phi_A \times \rho_A / M_A)} \quad (1)$$

where Φ is the volume fraction, ρ is the density, M is molecular mass, A and B are the components of the binary mixtures namely 1-Propanol (1-PrOH) and Benzonitrile (BN) respectively.

II.2. Measurements

The values of static dielectric constant of pure liquids ϵ_0 and of the binary mixtures ϵ_{0m} were determined by using capacitive measurement method with a short compensation at 2 MHz. A precision LCR meter (Agilent 4980) with a four terminal Liquid dielectric test fixture (Agilent 16542A) were used for the capacitance measurement of the cell without and with sample. The measurement accuracy of the static dielectric constant is $\pm 0.3\%$, which is estimated by the calibration of the cell with the standard liquids by using their literature values of static dielectric constant. The refractive index of the binary mixtures are measured at a wavelength of Sodium-D light using an Abbe Refractometer. The refractometer is initially calibrated by HPLC grade Chemicals (acetone and methanol) and then used to perform refractive index measurement at temperatures 303.15 K. The temperature of the refractometer is controlled by circulation of water and measured with a thermometer located near the sample holder assembly. Refractive index data are accurate to 0.0001 units. Density of pure liquids and their binary mixtures are measured by using specific gravity bottle having bulb volume of 10 cm^3 and capillary with the internal diameter 1 mm. The experimental values of refractive index and density of individual compound namely 1-PrOH and BN along with their literature values are presented in Table I.

TABLE I.
 Comparison of experimental values of refractive index (n), density (ρ) and static dielectric constant (ϵ_0) with literature values of pure component at 303.15 K.

Pure → liquids	1-PrOH		BN	
	Expt.	Lit.	Expt.	Lit.
n	1.3788	1.3754 [8]	1.5230	1.5234 [5]
ϵ_0	19.50	19.78 [7]	24.46	25.10 [5]
ρ	0.7951	0.7900 [8]	0.9952	0.9976 [5]

From the Table I, it is clear that the experimental values of refractive index (n), static dielectric constant (ϵ_0) and density (ρ) of individual component namely 1-PrOH and BN found in the present investigation are in good agreement with the literature values.

III. Results and Discussion

The refractive index n of a material is defined as the ratio c/v , where v is the speed of light in the material and c the speed of light in vacuum. This dimensionless optical property is very sensitive to changes in the

molecular association of pure liquids, solutions and mixtures. From the measured values of refractive indices molar refraction (R_m) is calculated using the relation,

$$R_m = \left(\frac{n^2 - 1}{n^2 - 1} \right) V_m \quad (2)$$

The molar volume of binary mixtures are determine by

$$V_m = \frac{(x_A M_A + x_B M_B)}{\rho} \quad (3)$$

where M is the molecular mass, suffix A & B have their usual meaning and ρ is the density of the solution.

The atomic polarization (P_A) is determined using the relation

$$P_A = 1.05n^2 \quad (4)$$

Polarizability (α) is related to the refractive index of molecule by the Lorentz-Lorentz relation as

$$\left(\frac{n^2 - 1}{n^2 - 1} \right) = \left(\frac{4}{3} \right) \pi n^2 \alpha \quad (5)$$

where $n^2 = (N/V_m)$, N is Avogadro's constant and V_m is the molar volume.

Besides these parameters the molecular radii (r) is one of the important parameter of pure liquids and liquid mixtures, which reflects their structural features. Liquids in their mixtures behave differently than they behave individually. Relative strength of hetero-molecular interaction is different in different mixtures. In recent years, several attempts have been made to predict theoretically the values of molecular radii of liquid and liquid mixtures. Bhatt et al used several empirical relations based on acoustic methods to calculate the molecular radii of pure liquids [9]. In the present paper, we have calculated molecular radii (r) of pure liquids and their binary mixtures using refractive index data [1].

$$r = \left[\frac{3}{4\pi N} V_m \frac{n^2 - 1}{n^2 + 2} \right]^{1/3} \quad (6)$$

The internal pressure P_{int} can be obtained by using the Buchler-Hirschfelder Curties equation of state [10], by applying the following relation

$$P_{int} = \frac{2^{1/6} RT}{2^{1/6} V_m - 2rN^{1/3} V_m^{2/3}} \quad (7)$$

Molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α), molecular radii (r) and internal pressure (P_{int}) have been determined from the experimentally measured values of refractive index

X_A	n	ρ	ϵ_0	V_m	R_m	P_A	r	α	P_{int}
0.0000	1.5230	0.9952	24.46	103.62	31.65	2.44	2.32	12.55	95.22
0.1322	1.5111	0.9744	23.76	99.99	29.96	2.40	2.28	11.88	96.86
0.2552	1.4978	0.9544	23.06	96.55	28.29	2.36	2.24	11.22	98.25
0.3701	1.4857	0.9351	22.39	93.25	26.76	2.32	2.20	10.61	99.80
0.4775	1.4712	0.9166	21.59	90.10	25.19	2.27	2.15	9.99	100.96
0.5782	1.4534	0.8902	21.22	87.91	23.78	2.22	2.11	9.43	100.59
0.6728	1.4398	0.8717	20.64	85.10	22.42	2.18	2.07	8.89	101.67
0.7618	1.4234	0.8518	19.91	82.60	21.05	2.13	2.03	8.35	102.03
0.8458	1.4059	0.8321	19.75	80.21	19.70	2.08	1.98	7.81	102.12
0.9250	1.3932	0.8119	19.60	78.01	18.63	2.04	1.95	7.39	102.85
1.0000	1.3788	0.7951	19.50	75.60	17.46	2.00	1.91	6.93	103.64

A close perusal of Table II, indicate that refractive index (n) and density (ρ) of each binary mixtures increases as the concentration of BN increases, because refractive index (n) and density (ρ) of BN is higher than that of 1-PrOH. Molar refraction is a measure of volume occupied with an atom or molecule and depends on the refractive index. It is noticed that the molar refraction (R_m) of the studied binary mixtures increases as the molar volume and refractive index. These reflect in increase in atomic polarization (P_A), polarizability (α) and molecular radii (r), except internal pressure (P_{int}) of binary mixtures. The internal pressure (P_{int}), is defined as the energy required to vaporize a unit volume of a substance.

Many researchers have suggested that molecules with similar internal pressures would interact with each other [10]-[11]. Comparison of the values for the pure components reveals that the internal pressure (P_{int}) of 1-PrOH (103.48 MPa) is very close to the internal pressure (P_{int}) of BN (95.22 MPa). This suggests hetero interaction is possible in the molecular species.

The excess functions give an idea about the extent to which the given liquid mixtures deviate from ideality. Therefore these excess properties are fundamentally important in understanding the intermolecular interactions and nature of molecular campaigning in hetero molecules. In the present study we have calculated excess refractive index, (n)^E, excess molecular radii (r)^E, excess molar refraction (R_m)^E, excess atomic polarization (P_A)^E, excess internal pressure (P_{int})^E and excess static dielectric constant (ϵ_0)^E of the binary mixtures are evaluated. The evaluated values of (n)^E, (V_m)^E, (r)^E, (P_A)^E, (P_{int})^E and (ϵ_0)^E were fitted to Redlich-Kister polynomial [12].

$$A^E = (x_A x_B) \sum_i a_i (x_A - x_B)^i \quad (8)$$

The values of coefficients, a_i ($i = 0,1,2,3$) evaluated by the method of least-squares, with all points weighted equally, together with the corresponding standard deviation, σ calculated by using the relation.

(n) and density (ρ) of pure components and their binary mixtures are presented in Table II.

$$\sigma = \left[\frac{\sum (A_{exp}^E - A_{cal}^E)^2}{m - k} \right]^{1/2} \quad (9)$$

Where, m is the number of experimental data points and k is the number of a_i coefficients considered. The values of coefficients, a_i and corresponding standard deviation (σ) against deviation functions are presented in Table III.

TABLE III.
 Values of adjustable parameters (a_i) evaluated from least square fit method for the excess functions with standard error.

A^E	a_0	a_1	a_2	a_3	σ
(n) ^E	0.06528	0.01071	-0.02361	-0.00009	0.00102
(r) ^E	0.11141	-0.00218	0.02009	-0.00024	0.00307
(R_m) ^E	1.39997	-0.12345	-0.393064	-0.680605	0.04113
(P_A) ^E	0.16512	0.03817	-0.05283	-0.00001	0.00275
(P_{int}) ^E	6.75618	2.89485	-11.51349	0.01514	0.18839
(ϵ_0) ^E	-1.61134	2.53379	-1.37367	-0.00582	0.10281

Deviation of excess functions against mole fraction of first component (1-PrOH) is shown in Figure 1.

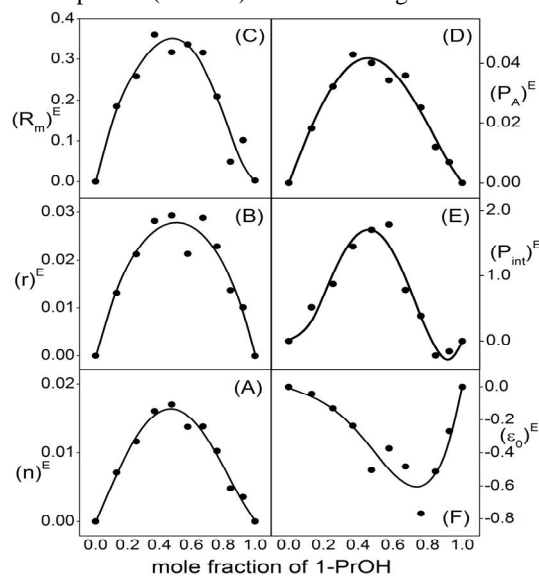


Fig.1. Variation of (n)^E, (V_m)^E, (r)^E, (P_A)^E, (P_{int})^E and (ϵ_0)^E against mole fraction of 1-PrOH. Solid circle (●) and solid line shows experimental points and Redlich-Kister fitting respectively. It is clear from Figures 1(A-F) that (n)^E, (r)^E, (R_m)^E, (P_A)^E and (P_{int})^E values are positive, while (ϵ_0)^E values show reverse trend over the whole composition range. Deviation in excess refractive index (n)^E against concentration can be interpreted as a measure of

intermolecular interactions [2]. $(R_m)^E$ represents the electronic perturbation due to orbital mixing of two components and gives information regarding the strength of interaction in mixture and is sensitive function of wavelength, temperature and mixture composition. The positive deviation of $(R_m)^E$ and $(P_A)^E$ suggests the dipole-dipole and donor-acceptor interaction between unlike molecules. It is known that 1-PrOH is associative in nature and associated through hydrogen-bond in pure state. The mixing of non associative liquid BN with 1-PrOH tends to break the associates present in the 1-PrOH molecules.

The negative deviation of $(\epsilon_0)^E$ indicates that both molecular species (1-PrOH & BN) interact so as to reduce the total effective dipoles due to orientation of some of the neighboring dipoles in opposite direction in the system. This results in intermolecular interaction between the molecular constituents [13].

The positive deviation in $(P_m)^E$ indicate attractive forces are greater than the repulsive interactions while the small negative deviation in 1-PrOH rich region (Figure. 1(E)) indicates loosing cohesion of BN molecules in the system implying weak intermolecular interactions. Similar results have also been reported by Bhatia et al in their study [14].

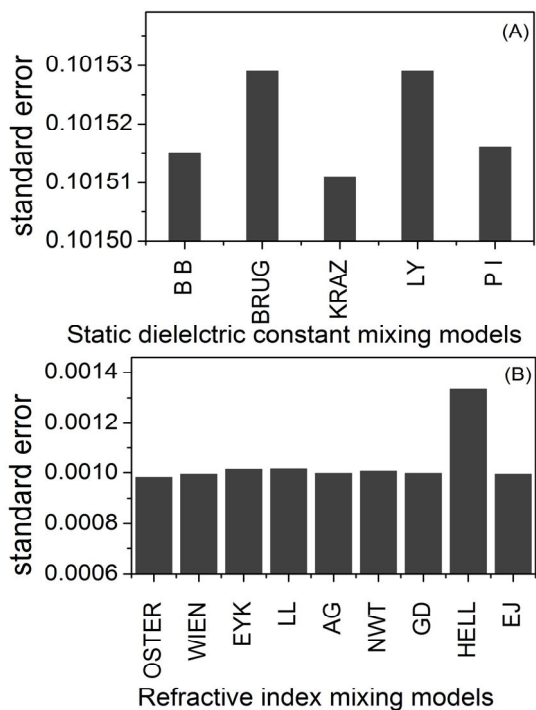


Fig. 2. Comparison of various mixing models with experimental data (static dielectric constant & refractive index).

For many practical purposes it is necessary to predict the nonideality of the binary liquid mixtures from physical parameters of the pure components using adequate models. Static dielectric constant (ϵ_0) and Refractive index (n) of liquid mixtures are predicted from the

density, together with the refractive index (n), static dielectric constant (ϵ_0) and density (ρ) of pure components, by using various mixing rules available in the literature [1]-[15].

In the present work, we tested five different static dielectric constant mixing models and nine eight different refractive index mixing models, viz; Böttcher-Bordewijk (B B), Bruggeman (BRUG), Kraszewski (KRAZ), Looyenga (LY), Peon-Iglesias (P I), Oster (OSTER), Weiner (WEIN), Eykman (EYK), Lorentz-Lorentz (LL), Arago-Biot (AG), Newton(NWT), Gladstone-Dale (GD), Heller(HELL) and Eyring-John (EJ) to calculate static dielectric constant (ϵ_0) and refractive index (n) of the present system. The comparison of various mixing models is shown in Figure 2. From the figure 2, it is clear that among all static dielectric mixing models KRAZ model presents the best fit result (minimum standard error) and the predictive model BRUG and LY are the worst for the present system. Intermediate results are obtained by the PI and BB models. Similarly for the refractive index mixing models except the HELL model all other are well within the limit.

IV. Conclusion

In this paper refractive index (n), static dielectric constant (ϵ_0) and density (ρ) are measured over the entire range of mixture composition of 1-PrOH with BN at 303.15 K. A good agreement has been found between the experimental and the literature values of refractive index (n), static dielectric constant (ϵ_0) and density of 1-PrOH and BN. Out of these measured data molar volume (V_m), molar refraction (R_m), atomic polarization (P_A), polarizability (α), molecular radii (r) and internal pressure (P_{int}) have been determined. $(n)^E$, $(r)^E$, $(R_m)^E$, $(P_A)^E$, $(P_{int})^E$ and $(\epsilon_0)^E$ values have been computed and the results of deviation/excess functions have been fitted to the Redlich-Kister equation. $(n)^E$, $(r)^E$, $(R_m)^E$, $(P_A)^E$ and $(P_{int})^E$ values are positive, while $(\epsilon_0)^E$ values show reverse trend over the whole composition range confirm that weak intermolecular interactions or the structure breaking effect of 1-PrOH on the addition of BN dominate over the H-bond interactions of the type C-N...H-O between 1-PrOH and BN molecules. The refractive index (n) and static dielectric constant (ϵ_0) of binary mixtures are correlated theoretically from pure component data by using the various mixing models.

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