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Study of Physical Properties of Binary Mixtures (N, N- DIMETHYLFORMAMIDE with 1-PROPANOL) at Atmospheric Pressure

A. N. Prajapati

Department of Applied Physics, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara (India)

Abstract: ***Ultrasonic speed (U), refractive index (n) and density (ρ) have been measured over the entire concentration range (0-0 1.0) for N,N-dimethylformamide (DMF) + 1-propanol (1-PrOH) at temperature 303.15 K and atmospheric pressure. Excess properties of experimentally measured and their evaluated quantities of binary mixtures have been calculated and discussed in terms of hetero interaction occurred between the participating molecules. The excess parameters are fitted with Redlich-Kister polynomial. Several theoretical mixing models for ultrasonic velocity (Nomoto, Impedance, Van dael and Vangeel, Rao's specific velocity and Junjie's) and refractive index (Lorentz-Lorenz (L-L), Weiner (W), Heller (H), Gladstone-Dale (G-D), Arago-Biot (A-B), Eykman (Eyk), Newton (Nw), Eyring-John (E-J) and Oster (Os)) for the binary mixture are applied and their validity have been tested for the same. A good agreement has been found between experimental and theoretical values of ultrasonic speed (U) and refractive index (n) for the binary mixtures.***

Keywords: Binary mixtures, Density, Hetero interaction, Mixing models, Refractive index, Ultrasonic velocity

1. Introduction

In recent years theoretical knowledge concerning the physicochemical properties of pure and binary mixtures are of great importance in basic and applied sciences. A number of empirical and semi-empirical theories already exists which provide mixing rules for theoretically predicting the ultrasonic velocity (u) and refractive index (n) of liquid mixtures with different components and concentrations. In addition to that experimental investigations of excess and deviation functions are also taken as interaction parameters to improve the results [1-3]. They are needful for design processes in chemical, pharmaceutical, petrochemical and to develop models. In basic and applied sciences hydrogen bonding in liquid systems has been intensively studied for long and it is still subject to a lively scientific debate. 1-PrOH is associative polar molecule used principally as a solvent in printing inks, paint, cosmetics, pesticides and insecticides. Amides have high polarity and strong solvating power; which makes them important solvents in chemical industry. N, N-Dimethylformamide (DMF) has been chosen for the present study because its properties have been the subject of considerable interest due to its relationship to peptides and proteins. Further it is an important solvent that finds applications in polymer science and pharmaceutical industry too. DMF is highly aprotic polar solvent with a large dipole moment and a relatively high dielectric constant [4]. Therefore, the solution chemistry of these compounds can be strongly influenced by inter and intra molecular H-bonding interactions, which consequently plays an important role in determining the physiochemical properties of these molecules. In the present paper, we report systematic concentration dependent ultrasonic, refractometric and volumetric study of binary mixtures of associative liquid 1-PrOH with non-associative liquid DMF at constant temperature 303.15K.

2. Experimental Details

N,N Dimethylformamide (DMF) of AR grade was obtained from Merck (India). 1-Propanol (1-PrOH) of AR Grade was procured from Sd-finechem (India). Using these polar liquids, binary mixture systems were prepared in hermetically sealed glass vials at 11 volume concentrations over the entire mixing range (0-1). Ultrasonic velocities (2 MHz) of binary mixtures are measured by Digital Ultrasonic Pulse-Echo Velocity meter (VI Microsystems, Chennai) with an accuracy of (±0.2 %). The refractive index (n) and density of binary mixtures are measured by Abbe's refractometer (at the wavelength of sodium–D light) and specific gravity bottle respectively. All measurements were carried out at atmospheric pressure and constant temperature (303.15 K). The temperature was controlled thermostatically (±0.1 ^{0}C) using constant temperature water bath. The experimental values of ultrasonic velocity (u), refractive index (n) and density (ρ) of individual compounds (DMF and 1-PrOH) presented in table 1 along with their literature values. Both are in quite good agreement.

Table 1: Comparison of experimental and literature values of pure compounds.

Compound	u_{expt} (m/s)	u_{lit} (m/s)	ρ_{expt} (gm/cc)	ρ_{lit} (gm/cc)	n_{expt}	n_{lit}
DMF	1422.17	1446.40 [a]	0.9425	0.9419 [a]	1.4210	1.4267 [b]
1-PrOH	1178.08	1189.00 [c]	0.7966	0.7955 [c]	1.3780	1.3810 [c]

*a-Ref. 7, b-Ref. 8, c-Ref. 9

3. Results and Discussion

From the measured values of ultrasonic velocity (u) and density (ρ) of binary mixtures some acoustical parameters namely adiabatic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (Z) and interaction parameter (X) are calculated using standard equations reported in literature [3,5]. Ultrasonic velocity (u), refractive index (n), density (ρ), adiabatic (β_s), intermolecular free length (L_f), acoustic impedance (Z) and interaction parameter (X) are tabulated in table 2.

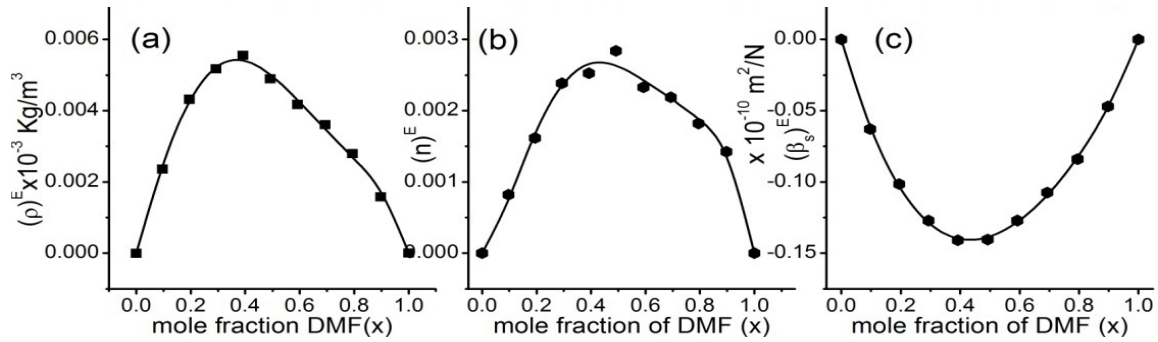
Table 2: Values of ultrasonic velocity (u), refractive index (n), density (ρ), adiabatic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (Z) and interaction parameter (X) of against mole fraction of DMF in (1-POH+DMF) mixtures at 303.15 K.

x	u (m/s)	n	ρ x 10^{-3} (Kg/m^3)	βs x 10^{-10} (m^{2}N^{-1})	L_fx10^{11} (m)	Z x 10^{-6} (Kgm^{-2}s^{-1})	X
0.0000	1176.08	1.3780	0.7966	9.0762	6.2530	0.9368	0.0000
0.0972	1204.23	1.3830	0.8131	8.4807	6.0444	0.9792	0.0249
0.1950	1230.08	1.3880	0.8293	7.9689	5.8592	1.0202	0.0428
0.2934	1256.06	1.3930	0.8446	7.5050	5.6861	1.0608	0.0572
0.3924	1281.75	1.3974	0.8594	7.0828	5.5238	1.1015	0.0672
0.4921	1306.75	1.4020	0.8733	6.7061	5.3749	1.1411	0.0717
0.5924	1330.39	1.4058	0.8872	6.3685	5.2379	1.1803	0.0692
0.6933	1353.91	1.4100	0.9013	6.0525	5.1063	1.2203	0.0615
0.7949	1378.28	1.4140	0.9153	5.7510	4.9774	1.2616	0.0495
0.8971	1400.80	1.4180	0.9291	5.4854	4.8612	1.3014	0.0287
1.0000	1422.17	1.4210	0.9425	5.2460	4.7539	1.3404	0.0000

A perusal of table 2 indicate that the values of ultrasonic velocity (u), refractive index (n) and density (ρ) of binary mixtures increase as the concentration of DMF increase in the mixtures. Adiabatic compressibility (β_s) and intermolecular free length (L_f) decreases as the concentration of DMF increases in the mixture while opposite trend is observed for the acoustic impedance (Z). A plausible explanation may be proposed, addition of DMF molecules in 1-PrOH causes the dissociation self associated H-bonded structure of 1-PrOH and subsequently formation of new H-bond between proton accepter oxygen atom of (C = O) group of DMF and hydrogen atom of (-OH) hydroxyl group of 1-PrOH molecules. This dissociation and formation of new bond leads decrease in adiabatic compressibility (β_s) and intermolecular free length (L_f) as the concentration of DMF molecules increase in the binary mixtures. In order to investigate nature and strength of the hetero interaction between the molecular species of the binary liquid mixtures, it is necessary to discuss the same in terms of excess parameters rather than actual values. In the present study excess values of density (ρ), refractive index (n), adiabatic compressibility (β_s), intermolecular free length (L_f) and acoustic impedance (Z) are determined and fitted with Redlich-Kister polynomial [1,2]. The values of their coefficients (a_0, a_1, a_2, a_3) along with correlation coefficient (r) are presented in table 3.

Table 3: Values of coefficients of R. K. polynomial with correlation constant for excess parameters ($(n)^E$, $(\rho)^E$, $(\beta_s)^E$, $(L_f)^E$, $(Z)^E$).

parameter	$(\rho)^E$	$(n)^E$	$(z)^E$	$(\beta_s)^E$	$(L_f)^E$
a_0	0.0198	0.0105	0.0214	-1.9166	-0.5529
a_1	-0.0126	-0.0031	-0.0150	0.5312	0.1373
a_2	0.0053	0.0020	0.0143	-0.2517	-0.0765
a_3	0.0107	0.0108	0.0206	-0.0471	-0.0363
r	0.9986	0.9954	0.9909	0.9990	0.9996



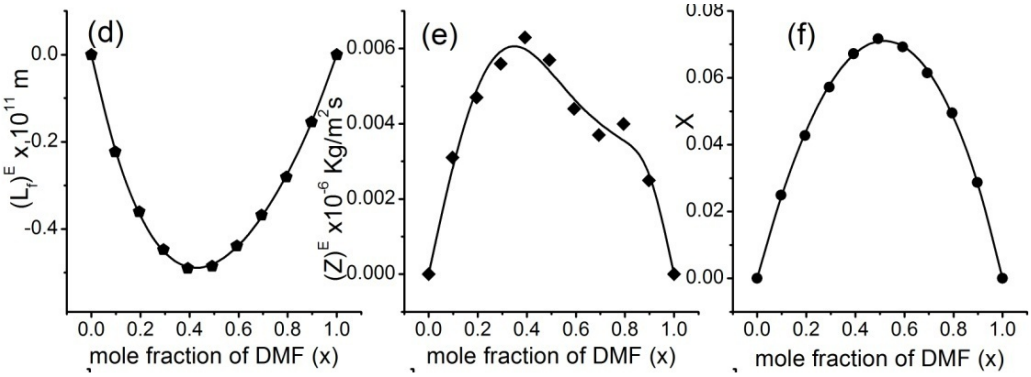


Figure 1: Variation of excess parameters against mole fraction of DMF in binary mixtures. (Solid shape-(expt. Points) and smooth line-(R. K. Fitting))

Figure 1.(a-f) show the deviation of excess parameters ($(n)^E$, $(\rho)^E$, $(\beta_s)^E$, $(L_f)^E$ and $(Z)^E$) from their linear behavior against mole fraction of DMF in binary mixtures. The sign (positive/negative) and magnitude depend on the strength of hetero interaction between the molecular species in the mixtures. The excess refractive index $(n)^E$ and excess density $(\rho)^E$ (Fig. 1(a) & (b)) show similar trend (positive deviation) against mole fraction of DMF, which suggest the specific interaction between participating molecules [1]. Looking the behavior of excess acoustic parameters; $(\beta_s)^E$ and $(L_f)^E$ show identical whereas $(Z)^E$ show opposite trend. Several authors have reported that the negative deviation of $(\beta_s)^E$ and $(L_f)^E$ indicate chemical/specific interaction which include charge transfer, hydrogen bond formation and other complex forming interactions [6,7]. Swain et al suggested from their studies, that values of $(\beta_s)^E$ and $(L_f)^E$ become increasingly negative with increase in the strength of interaction between the components of binary mixtures [6]. The positive deviation of excess acoustic impedance $(Z)^E$ suggests strong molecular interaction in the binary mixtures (Fig. 1(e)). In the present study (Fig. 1(f)), maximum positive values for interaction parameter (X) is observed at equimolar concentration of DMF (x = 0.5) indicate strong molecular interaction.

Table 4: Comparison of experimentally and theoretically estimated values ultrasonic velocity against mole fraction DMF in (1-PrOH-DMF) mixtures with average percentage deviation (APD).

X	u_{expt} (m/s)	u_{NM}	$u_{vandeal}$	u_{rao}	u_Z	u_{zunjie}
0.0000	1176.08	1176.08	1176.08	1176.08	1176.08	1176.08
0.0972	1204.23	1198.92	1189.49	1198.64	1203.88	1190.80
0.1950	1230.08	1222.13	1204.59	1221.63	1230.89	1207.07
0.2934	1256.06	1245.73	1221.59	1245.06	1257.15	1225.06
0.3924	1281.75	1269.72	1240.72	1268.95	1282.68	1244.97
0.4921	1306.75	1294.11	1262.27	1293.28	1307.51	1267.04
0.5924	1330.39	1318.90	1286.59	1318.09	1331.68	1291.54
0.6933	1353.91	1344.09	1314.11	1343.37	1355.20	1318.83
0.7949	1378.28	1369.69	1345.39	1369.14	1378.11	1349.33
0.8971	1400.80	1395.72	1381.11	1395.40	1400.42	1383.55
1.0000	1422.17	1422.17	1422.17	1422.17	1422.17	1422.17
APD	-----	0.5808	2.0609	0.6188	-0.0370	1.8369

Table 5: Comparison of experimentally and theoretically estimated values refractive index (n) against mole fraction DMF in (1-PrOH-DMF) mixtures with average percentage deviation (APD)

x	n	Nw	G-D	L-L	EYK	A-G	H	W
0.0000	1.3780	1.3780	1.3780	1.3780	1.3780	1.3780	1.3778	1.3780
0.0972	1.3830	1.3823	1.3823	1.3833	1.3823	1.3823	1.3821	1.3823
0.1950	1.3880	1.3867	1.3866	1.3884	1.3865	1.3866	1.3864	1.3865
0.2934	1.3930	1.3910	1.3909	1.3930	1.3908	1.3909	1.3907	1.3908
0.3924	1.3974	1.3953	1.3952	1.3974	1.3951	1.3952	1.3950	1.3951
0.4921	1.4020	1.3996	1.3995	1.4013	1.3994	1.3995	1.3994	1.3994
0.5924	1.4058	1.4039	1.4038	1.4052	1.4037	1.4038	1.4037	1.4037
0.6933	1.4100	1.4082	1.4081	1.4093	1.4080	1.4081	1.4080	1.4080
0.7949	1.4140	1.4125	1.4124	1.4133	1.4123	1.4124	1.4123	1.4123
0.8971	1.4180	1.4167	1.4167	1.4172	1.4167	1.4167	1.4167	1.4167
1.0000	1.4210	1.4210	1.4210	1.4210	1.4210	1.4210	1.4210	1.4210
APD ---	0.0966	0.1037	0.0179	0.1059	0.1057	0.1111	0.1058	

Theoretical values of ultrasonic velocity (u) with average percentage deviations (APD) for Nomoto's Relation (u_{NM}), Vandeal Vangael Ideal Mixing Relation ($u_{vandeal}$), Impedance Dependence Relation (u_Z), Rao's specific velocity method (u_{rao}) and Junjie's relation (u_{junjie}) determined from the standard relations reported in literatures [3]. The experimental values of ultrasonic velocity (u) for the binary mixtures along with theoretical values and percentage deviations are listed in table 4. Similarly, Theoretical mixing relations (Lorentz–Lorenz (L-L), Gladstone–Dale (G-D), Arago–Biot (A-B), Wiener (W), Heller (H), Newton (Nw) and Eykman (Eyk)) for refractive index (n) and average percentage deviations (APD) are evaluated from the standard relations reported in literatures [1,2]. Experimentally measured refractive index (n) and theoretically determined mixing relations with average percentage deviations are presented in table 5. It can be seen from Tables 4 and 5 that the theoretical values of ultrasonic velocity (u) and refractive index (n) computed by various theories show deviation from experimental values. From the table 3 and 4 considering the APD values, for ultrasonic velocity (u) [$APD_{(uz)}$ < $APD_{(uNM)}$ < $APD_{(urao)}$ < $APD_{(uzunjie)}$ < $APD_{(uvandeal)}$] and refractive index (n) [$APD_{(L-L)}$ < $APD_{(Nw)}$ < $APD_{(G-D)}$ < $APD_{(A-G)}$ < $APD_{(w)}$ < $APD_{(EYK}$ < $APD_{(H)}$] impedance dependence relation (u_z) and Lorentz – Lorentz relation show quite good agreement with the experimental values respectively. While Vandeal Vangael Ideal Mixing Relation ($u_{vandeal}$) and Heller (H) deviates from the experimental results. Alternatively these deviations confirm the hetero molecular interactions between molecular species in the mixtures.

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