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Optical Properties, Excess Volume Prediction from Refractive Index and Intermolecular Interactions in Dibutylamine + Isomeric Butanol

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The alkyl or alkanol amines are widely used as absorbent for CO_2 capture owing to interaction between amines and CO_2. In order to increase the CO_2 loading in amine based absorbents, blending of amine with alkanol may be one option. As thermophysical properties of of utmost importance in designing, in present work, the refractive index of dibutylamine (DBA) and isomeric butanol as well as their binary mixtures at 298.15 K to 308.15 K were measured. The Δn are found positive for DBA + isomeric butanol mixtures. The Δn values were correlated with Redlich-Kister polynomial. The refractive index data were also predicted by various correlations and results were expressed in terms of standard deviation. The Δn values were also employed to calculate the excess molar volume of the present binary mixtures. Further Δn data analysed in terms of intermolecular interaction among DBA (1) + isomeric butanol (2) mixtures.

Keywords: Isomeric butanol, Dibutylamine, Refractive Index, Molecular interactions, Mixing rules, Excess molar volume.

INTRODUCTION

The thermo-physical properties are of great significance in the chemical designing of engineering processes employed in various industries. Among various thermo-physical properties, the most important and frequently applied are the among these volume, surface tension, vapour pressure, density, viscosity, enthalpy, speed of sound and refractive index are frequently used [1-3]. The excess properties or deviation in these properties are important means to understand non-ideal behaviour due to intermolecular interactions [4-7]. Thermo-physical properties are sensitive to the size, shape, and polarity of the molecules as well as temperature, pressure and composition of mixtures. In various processes in different industries, organic liquids are frequently used. Many times, some properties or characteristics are compatible to that process and others are not. To make the liquid properties compatible and applied to the process, the liquids mixing were applied by the addition of different solvents like water, alcohols, amines, alkanol-amines, ethers, *etc*. This discussion suggests that the determination of thermo-physical of liquid mixtures applicable in various industries and processes is an area of keen interest for the researchers. The refractive indexes of pure liquids and mixtures have been reported since long time to understand the optical properties of the materials [8-16]. This property gives valuable information about the intermolecular interactions between the components of liquid mixtures. Refractive index is influenced by density and temperature of the medium. Therefore, determinations of the refractive index at different temperatures are required for the complete understanding of the properties and molecular interactions [17,18]. Accurate estimation of the refractive index can be correlated to the concentration, temperature and pressure of the liquid mixtures. Among various solvents (water, ether, alcohols, amines, *etc*.) used to alter the thermo-physical properties, alcohols are widely used solvents. Alcohols are associated molecules, which are assoc-iated with the presence of polar functional groups. The excess properties are highly influenced by the variability of carbon chain, geometry of the molecule and position of the functional group. In branching alcohols, the geometric area is highly occupied by the hydrophobic organic part, which affects the properties in liquid mixtures when they are added. Further alkyl amines and alkanolamines are the components which are used in various industries like post combustion carbon capture, pharmaceuticals, fertilizer, *etc*. [19-23]. For a long time, alcohols or amines were used in this process to alter these properties [24]. Amines are widely

applied in the production of agro-chemicals used for the crop protection. Alkanols were polar molecules and used in pharmaceutical industries in various synthesis processes. Therefore, determinations of various thermo-physical properties for binary mixtures containing amines and alkanols are useful for various industries.

Keeping these considerations, it is interesting to study the physical properties of binary liquid mixtures containing alkyl amines and alcohols. In the continuation of our earlier work on the excess properties of liquid mixtures, the present investigation reported the refractive indices data of dibutylamine (DBA) + isomeric butanol mixtures at 298.15 K to 308.15 K and fitted to Redlich-Kister polynomial equation. Further various mixing rules were applied to predict the experimental data. The deviation in refractive index (Δn) is used to analyze to interpret the molecular interaction between DBA and isomeric butanol molecules. The excess molar volumes were predicted from the measured n_D data of pure components and their binary mixtures by Nakata & Sakurai model [9,25].

EXPERIMENTAL

Dibutylamine (DBA) from Merck and butanol isomers (*n*-butanol, *sec*-butanol, isobutanol, *tert*-butanol) from CDH were purchased having purity >99%. All chemical were stored over molecular sieve (4Å) for more than one week before analysis. Purity of the samples was checked by the measurements of their density and refractive index. The density and refractive index were measured by Anton Paar-DSA 5000 and Abbemat-200, respectively. The uncertainty in the density and refractive index (n_D) was $\pm 10^{-3}$ kg m^{-3} data were measured with a refractometer (Abbemat-200) with temperature controlled within ±0.01 K having accuracy up to $\pm 1 \times 10^{-4}$. The binary mixtures were made using a balance of precision ±0.1 mg (OHAUS, AR224CN).

The densities (ρ) and refractive indices (n_D) of pure compounds and their binary mixtures are given in Tables 1 and 2, respectively.

TABLE-1
MEASURED DENSITIES (ρ) AND REFRACTIVE INDICES (n_D) OF THE PURE COMPOUNDS

Compound	ρ (g cm^{-3})		n_D	
	Experimental	Literature	Experimental	Literature
Dibutylamine				
298.15 K	0.755650	0.755480 [26]	1.4159	1.41690 [27]
308.15 K	0.747440	0.747270 [26]	1.4109	1.41180 [27]
318.15 K	0.739185		1.4058	1.40650 [27]
n-Butanol				
298.15 K	0.805918	0.805907 [28]	1.3970	1.39728 [29]
		0.805890 [28]		
		0.805806 [30]		
308.15 K	0.798201	0.798290 [31]	1.3929	1.39324 [29]
		0.798250 [32]		
		0.798101 [30]		
318.15 K	0.790333	0.790212 [29]	1.3887	1.38911 [29]
		0.790180 [33]		
sec-Butanol		0.790248 [30]		
298.15 K	0.802750	0.802847 [34]	1.3949	1.39520 [35]
		0.802420 [36]		1.39500 [37]
		0.802938 [30]		
308.15 K	0.794245	0.794363 [34]	1.3903	
		0.794210 [38]		
		0.794435 [30]		
318.15 K	0.785348	0.785210 [31]	1.3856	
		0.785546 [30]		
Isobutanol				
298.15 K	0.798146	0.798200 [39]	1.3928	1.39390 [40]
		0.798200 [41]		
308.15 K	0.790296	0.790629 [29]	1.3886	
		0.790260 [42]		
318.15 K	0.782227	0.781982 [29]	1.3844	
tert-Butanol				
298.15 K	0.780511	0.780720 [29]	1.3846	1.38488 [29]
		0.780680 [43]		
308.15 K	0.770347	0.770212 [29]	1.3795	1.37985 [29]
		0.770240 [41]		1.37947 [12]
		0.770296 [30]		
318.15 K	0.760157	0.759502 [29]	1.3742	1.37402 [29]
		0.759870 [44]		1.37384 [12]

TABLE-2
REFRACTIVE INDEX (n_D) AND DEVIATION IN REFRACTIVE INDEX (Δn)

x_1	298.15 K		308.15 K		318.15 K		x_1	298.15 K		308.15 K		318.15 K	
	n_D	Δn	n_D	Δn	n_D	Δn		n_D	Δn	n_D	Δn	n_D	Δn
DBA (1) + *n*-butanol (2)							DBA (1) + *sec*-butanol (2)						
0	1.3961	0.0000	1.3920	0.0000	1.3879	0.0000	0.0000	1.3952	0.0000	1.3908	0.0000	1.3864	0.0000
0.0635	1.3994	0.0020	1.3952	0.0020	1.3910	0.0020	0.0594	1.3979	0.0015	1.3933	0.0013	1.3888	0.0012
0.1073	1.4015	0.0033	1.3972	0.0032	1.3929	0.0031	0.0839	1.3989	0.0020	1.3943	0.0018	1.3898	0.0017
0.1494	1.4033	0.0043	1.3990	0.0042	1.3946	0.0041	0.1282	1.4008	0.0030	1.3961	0.0027	1.3915	0.0026
0.2108	1.4057	0.0055	1.4013	0.0053	1.3967	0.0050	0.1858	1.4030	0.0040	1.3983	0.0038	1.3937	0.0036
0.2648	1.4075	0.0062	1.4030	0.0060	1.3986	0.0059	0.2618	1.4055	0.0050	1.4008	0.0047	1.3962	0.0045
0.3259	1.4093	0.0068	1.4047	0.0066	1.4002	0.0065	0.3612	1.4082	0.0056	1.4035	0.0054	1.3988	0.0052
0.3973	1.4111	0.0071	1.4064	0.0069	1.4018	0.0068	0.4306	1.4097	0.0056	1.4049	0.0054	1.4002	0.0052
0.4697	1.4124	0.0070	1.4078	0.0069	1.4030	0.0067	0.5042	1.4109	0.0054	1.4062	0.0052	1.4014	0.0049
0.5484	1.4136	0.0066	1.4089	0.0065	1.4040	0.0063	0.5658	1.4118	0.0050	1.4070	0.0048	1.4022	0.0045
0.6286	1.4144	0.0059	1.4098	0.0059	1.4048	0.0056	0.6215	1.4125	0.0046	1.4076	0.0043	1.4028	0.0040
0.7575	1.4154	0.0043	1.4105	0.0042	1.4056	0.0042	0.6856	1.4132	0.0040	1.4084	0.0037	1.4035	0.0034
0.8182	1.4157	0.0034	1.4109	0.0034	1.4058	0.0033	0.7458	1.4139	0.0034	1.4090	0.0031	1.4041	0.0028
0.8572	1.4159	0.0028	1.4110	0.0028	1.4059	0.0027	0.7940	1.4143	0.0028	1.4094	0.0026	1.4045	0.0022
0.8972	1.4159	0.0020	1.4110	0.0020	1.4061	0.0021	0.8584	1.4149	0.0021	1.4101	0.0019	1.4051	0.0016
0.9230	1.4159	0.0015	1.4110	0.0016	1.4060	0.0016	0.9138	1.4153	0.0014	1.4105	0.0013	1.4057	0.0010
1.0000	1.4159	0.0000	1.4109	0.0000	1.4058	0.0000	1.0000	1.4157	0.0000	1.4110	0.0000	1.4064	0.0000
DBA (1) + isobutanol (2)							DBA (1) + *tert*-butanol (2)						
0.0000	1.3928	0.0000	1.3886	0.0000	1.3844	0.0000	0.0000	1.3847	0.0000	1.3796	0.0000	1.3745	0.0000
0.0659	1.3968	0.0025	1.3925	0.0024	1.3882	0.0023	0.0672	1.3884	0.0016	1.3832	0.0014	1.3779	0.0013
0.0962	1.3984	0.0034	1.3940	0.0033	1.3897	0.0032	0.0989	1.3900	0.0022	1.3847	0.0020	1.3795	0.0018
0.1558	1.4011	0.0047	1.3967	0.0047	1.3923	0.0046	0.1393	1.3920	0.0030	1.3867	0.0027	1.3814	0.0025
0.1967	1.4028	0.0054	1.3983	0.0053	1.3938	0.0052	0.1939	1.3945	0.0037	1.3893	0.0036	1.3840	0.0034
0.2681	1.4053	0.0063	1.4007	0.0061	1.3961	0.0060	0.2674	1.3976	0.0045	1.3923	0.0043	1.3871	0.0041
0.3132	1.4067	0.0067	1.4021	0.0065	1.3974	0.0063	0.3319	1.3998	0.0048	1.3947	0.0046	1.3895	0.0044
0.3956	1.4089	0.0070	1.4042	0.0068	1.3995	0.0066	0.4050	1.4021	0.0048	1.3970	0.0046	1.3918	0.0044
0.4699	1.4106	0.0069	1.4058	0.0067	1.4010	0.0066	0.4915	1.4047	0.0046	1.3995	0.0044	1.3944	0.0042
0.5552	1.4121	0.0065	1.4073	0.0063	1.4025	0.0062	0.5791	1.4070	0.0042	1.4018	0.0040	1.3968	0.0038
0.6322	1.4132	0.0058	1.4084	0.0057	1.4035	0.0056	0.6466	1.4085	0.0036	1.4034	0.0035	1.3984	0.0033
0.7567	1.4144	0.0041	1.4095	0.0040	1.4047	0.0041	0.6907	1.4095	0.0032	1.4044	0.0031	1.3994	0.0029
0.8163	1.4148	0.0031	1.4098	0.0030	1.4050	0.0031	0.7760	1.4112	0.0023	1.4061	0.0022	1.4013	0.0020
0.8647	1.4150	0.0022	1.4101	0.0023	1.4051	0.0022	0.8387	1.4126	0.0017	1.4076	0.0016	1.4027	0.0015
0.8978	1.4151	0.0016	1.4103	0.0017	1.4053	0.0016	0.8867	1.4136	0.0012	1.4086	0.0011	1.4038	0.0010
0.9162	1.4152	0.0013	1.4104	0.0014	1.4053	0.0013	0.9129	1.4140	0.0009	1.4091	0.0008	1.4044	0.0008
1.0000	1.4159	0.0000	1.4109	0.0000	1.4058	0.0000	0.9471	1.4148	0.0006	1.4099	0.0005	1.4052	0.0005
							1.0000	1.4159	0.0000	1.4110	0.0000	1.4064	0.0000

RESULTS AND DISCUSSION

The deviations in refractive index (Δn) were calculated from the measured refractive index data for binary DBA (1) + isomeric butanol (2) mixtures using eqn. 1:

$$\Delta n = n_D - \sum_{i=1}^{2} x_i n_{Di} \quad (1)$$

In eqn. 1, n_{Di} and n_D are the refractive index of pure components and their binary mixture, respectively. The n_D and Δn for the binary mixtures in entire range of mole fractions are given in Table-2. The Δn values were also fitted Redlich-Kister equation:

$$\Delta n = x_1(1-x_1)\left[\sum_{n=1}^{4} A^{(j)}(2x_1-1)^{(j-1)}\right] \quad (2)$$

where $A^{(j)}$ are the adjustable parameters and calculated by fitting Δn data in eqn. e and are recorded in Table-3 along with respective standard deviations $\sigma(\Delta n)$. The experimental deviations in refractive index (Δn) data as well as values calculated by Redlich-Kister equation are shown in Figs. 1 and 2.

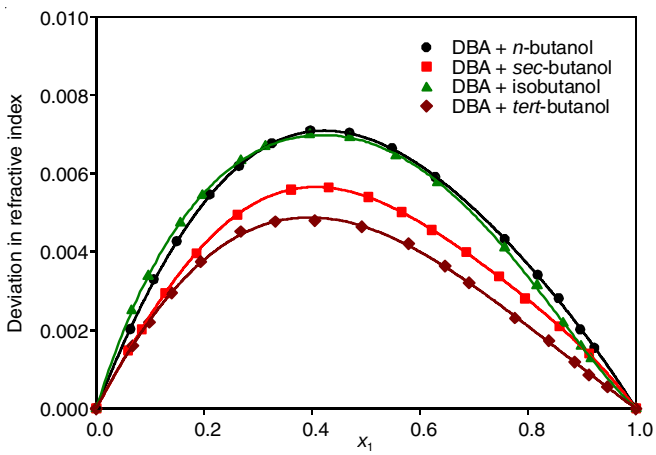

Fig. 1. Deviation in refractive index (Δn) with mole fraction of DBA (x_1) at 298.15 K. Experimental values (Symbols) and Redlich-Kister values (solid lines)

TABLE-3
REDLICH–KISTER EQUATION PARAMETERS ($A^{(j)}$) AND STANDARD DEVIATION (σ)

Temp. (K)	$A^{(1)}$	$A^{(2)}$	$A^{(3)}$	$A^{(4)}$	σ	$A^{(1)}$	$A^{(2)}$	$A^{(3)}$	$A^{(4)}$	σ
DBA (1) + *n*-butanol (2)						DBA (1) + *sec*-butanol (2)				
298.15	0.0276	-0.0092	0.0008	0.0026	2.49×10^{-5}	0.0217	-0.0096	0.0004	0.0062	1.56×10^{-5}
308.15	0.0271	-0.0084	0.0010	0.0021	3.12×10^{-5}	0.0208	-0.0105	-0.0012	0.0086	1.40×10^{-5}
318.15	0.0263	-0.0092	0.0014	0.005	4.99×10^{-5}	0.0198	-0.0109	-0.0031	0.0073	8.79×10^{-6}
DBA (1) + isobutanol (2)						DBA (1) + *tert*-butanol (2)				
298.15	0.0272	-0.0086	0.0014	-0.0072	2.77×10^{-5}	0.0185	-0.0092	-0.0002	0.001	4.27×10^{-5}
308.15	0.0265	-0.0082	0.0022	-0.0064	2.81×10^{-5}	0.0178	-0.0095	-0.0011	0.0033	5.32×10^{-5}
318.15	0.026	-0.0071	0.0023	-0.0076	2.39×10^{-5}	0.0171	-0.0093	-0.0025	0.0037	5.51×10^{-5}

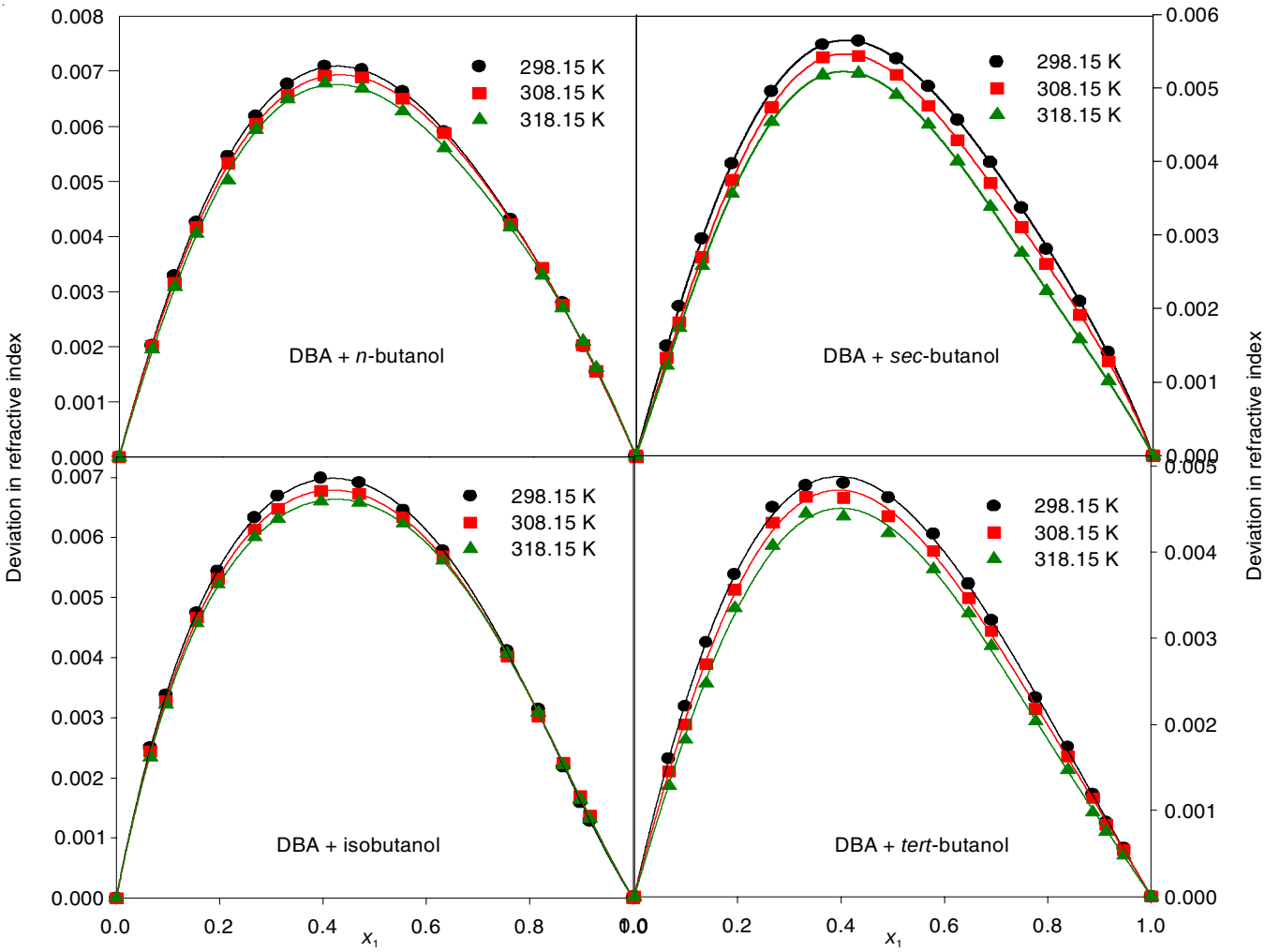

Fig. 2. Deviation in refractive index (Δn) with mole fraction of DBA (x_1). Experimental values (Symbols) and Redlich-Kister values (solid lines)

The refractive index (n_D) values were further predicted in terms of various correlations like Arago-Biot (A-B), Gladston-Dale (G-D), Lorentz (L-L), Heller (H), Weiner (W), Newton (Nw) and Erying-John (E-J) (eqns. 3-9). The details of these mixing rules was given in our earlier paper [45].

Arago-Biot (A-B):

$$n_D = n_{D1}\phi_1 + n_{D2}\phi_2 \tag{3}$$

Gladston-Dale (G-D):

$$n_D - 1 = (n_{D1} - 1)\phi_1 + (n_{D2} - 1)\phi_2 \tag{4}$$

Lorentz (L-L):

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \left(\frac{n_{D1}^2 - 1}{n_D^2 + 2}\right)\phi_1 + \left(\frac{n_{D2}^2 - 1}{n_D^2 + 2}\right)\phi_2 \tag{5}$$

Heller (H):

$$\frac{n_D - 1}{n_D} = \frac{3}{2}\left(\frac{\left(\frac{n_{D2}}{n_{D1}}\right) - 1}{\left(\frac{n_{D2}}{n_{D1}}\right) + 2}\right)\phi_2 \tag{6}$$

Weiner (W):

$$\frac{n_D^2 - n_{D1}^2}{n_D^2 + 2n_{D2}^2} = \left(\frac{n_{D2}^2 - n_{D1}^2}{n_{D2}^2 + 2n_{D2}^2}\right)\phi_2 \quad (7)$$

Newton (Nw):

$$n_D^2 - 1 = \left(n_{D1}^2 - 1\right)\phi_1 + \left(n_{D2}^2 - 1\right)\phi_2 \quad (8)$$

Erying-John (E-J):

$$n_D = n_{D1}\phi_1^2 + 2\left(n_{D1}n_{D2}\right)^{1/2}\phi_1\phi_2 + n_{D2}\phi_2^2 \quad (9)$$

In all the above mixing correlations n_{Di} (where i = 1 or 2) and n_D are the refractive index of pure components binary mixture. Here, ϕ_1 and ϕ_2 represent the volume fraction of pure components 1 and 2, respectively and can be given as:

$$\phi_1 = \frac{x_1 V_1}{\sum x_i V_i} \text{ and } \phi_2 = \frac{x_2 V_2}{\sum x_i V_i} \quad (10)$$

The details of these mixing rules was given elsewhere [45]. The results from various refractive index correlations were compared and found to agree well with the experimental data. The deviations in the experimental and theoretical results from various correlations are presented in the form of standard deviation (Table-4) and also in Fig. 3 (only at 298.15 K). A good agreement was observed for all the mixing relations.

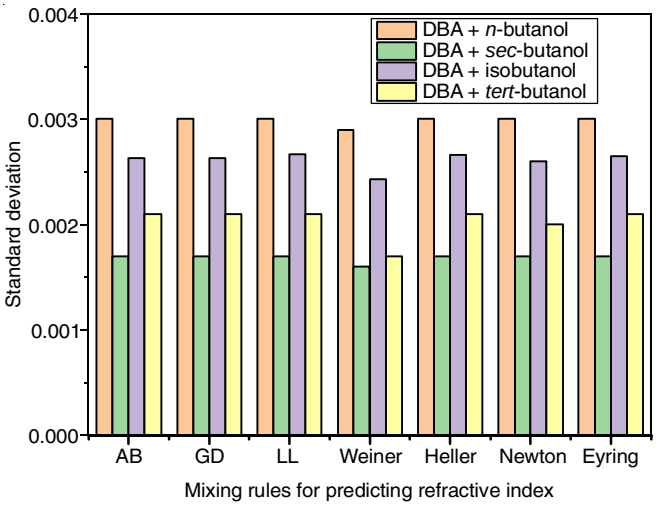

Fig. 3. Standard deviation in n_D calculated by various correlations (eqns. 3-9) for binary DBA (1) + butanol (2) at 298.15 K

Deviations in refractive index (Δn) for DBA (1) + *n*-butanol (2) or + *sec*-butanol (2) or + isobutanol (2) or + *tert*-butanol (2) are positive (Fig. 1). The positive value of Δn denotes the interactive interactions between DBA and isomeric butanol molecules. In the present binary mixtures, the presence of polar function group (-NH and -OH) also addressed the presence of stronger H-bonding between unlike molecules which lead to positive deviation in Δn. Further, negative V_m^E values for all the binary mixture also support the strong H-bonding between unlike molecules (Fig. 4). The Δn values for equimolar mixtures of DBA (1) + isomeric butanol (2) follow the sequence: *n*-butanol > isobutanol > *sec*-butanol > *tert*-butanol. The branching at the carbon atom attached to the hydroxyl group obstruct the approach/interaction of hydroxyl hydrogen (OH^-) of butanol and -NH group of amines [43]. Thus Δn value decreases for with increase in branching of butyl group and found to be maximum for *n*-butanol and minimum for *tert*-butanol.

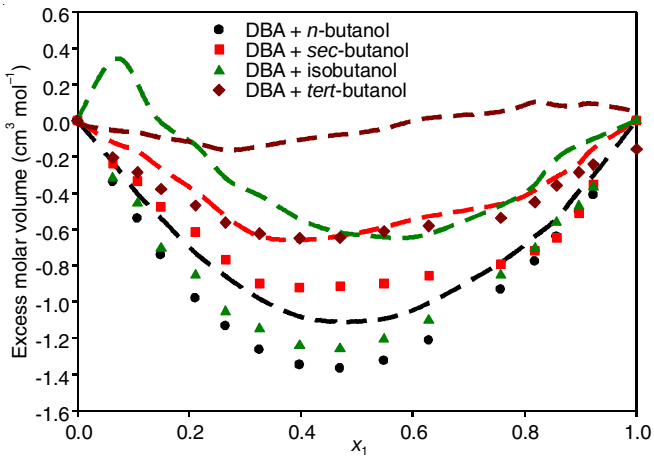

Fig. 4. Excess molar volume (V_m^E) *versus* mole fraction of DBA (x_1) at 298.15 K. Experimental values (Symbols) and Nakata & Sakurai model [25] (dashed lines)

Excess volume from refractive index [25]

For the prediction of V_m^E values from n_D data, the Nakata and Sakurai model (Model I) is used. According to this model

$$V_m^E = \sum_{i=1}^{2}\left[\left(f(n_{Di}) - f(n_D)\right)\left(\frac{x_i V_i}{f(n_D)}\right)\right] \quad (11)$$

TABLE-4
STANDARD DEVIATIONS ($\sigma(n_D)$) IN n_D FROM VARIOUS MIXINIG RULES

Binary system	Temp. (K)	$\sigma(n_D)$						
		A-B	G-D	L-L	Weiner	Heller	Newton	Eyring
DBA (1) + *n*-butanol (2)	298.15	0.0030	0.0030	0.0030	0.0029	0.0030	0.0030	0.0030
	308.15	0.0030	0.0030	0.0030	0.0029	0.0030	0.0030	0.0030
	318.15	0.0030	0.0030	0.0030	0.0029	0.0030	0.0030	0.0030
DBA (1) + *sec*-butanol (2)	298.15	0.0017	0.0017	0.0017	0.0016	0.0017	0.0017	0.0017
	308.15	0.0017	0.0017	0.0017	0.0016	0.0017	0.0017	0.0017
	318.15	0.0018	0.0018	0.0018	0.0017	0.0018	0.0017	0.0018
DBA (1) + isobutanol (2)	298.15	0.0026	0.0026	0.0027	0.0024	0.0027	0.0026	0.0027
	308.15	0.0026	0.0026	0.0026	0.0024	0.0026	0.0026	0.0026
	318.15	0.0026	0.0026	0.0026	0.0024	0.0026	0.0026	0.0026
DBA (1) + *tert*-butanol (2)	298.15	0.0021	0.0021	0.0021	0.0017	0.0021	0.0020	0.0021
	308.15	0.0021	0.0021	0.0022	0.0017	0.0021	0.0020	0.0021
	318.15	0.0022	0.0022	0.0023	0.0018	0.0022	0.0021	0.0022

In the above equation, the specific refraction is presented as:

$$\frac{f(n_D)}{\rho} = \sum_{i=1}^{2} w_i \frac{f(n_{Di})}{\rho_i} \quad (12)$$

In eqns. 11 and 12, subscript '*i*' represent the pure component DBA (1) or butanol (2) and absence of subscript represent property of binary mixtures and w = mass fraction; ρ = density; n_D = refractive index; x = mole fraction; V = molar volume; $f(n_D)$ = function of refractive index.

Excess molar volume (V_m^E) were predicted from the at the temperature 298.15 K for the DBA (1) + butanol isomers with the incorporation of L-L mixing rules and results are compared with experimental excess molar volume data in Fig. 4. This theory predicts the sign and shape of V_m^E *versus* x_1 curves but the quantitative comparison is not very impressive.

The Δ*n* values for DBA (1) + isomeric butanols (2) at equimolar mixtures follow the sequence: *n*-butanol > isobutanol > *sec*-butanol > *tert*-butanol. The refractive index is an index of speed of light, varied with density of the medium. With increase in density of the medium n_D also increases. As in the binary mixtures of DBA + *n*-butanol, *n*-butanol is highly approachable due to straight chain molecule and form strong H-bonding with DBA, causes maximum increase in density and hence the refractive index. Consequently, Δ*n* is highly positive and maximum in this case. As *tert*-butanol has maximum branching at the carbon atom attached to hydroxyl group among all the isomers of butanol, therefore, offer maximum steric hindrance to hydroxyl hydrogen to interact with -NH group. This weakens the H-bonding between both the components to the minimum. Consequently density as well as Δ*n* should be minimum for *tert*-butanol mixture [46,47]. This is what we have observed (Fig. 1). The least interaction of DBA and *tert*-butanol may also attribute to the higher exposed hydrophobic part due to its geometry, which makes it less approachable towards DBA causes less specific interactions.

Temperature also affects values. As temperature increases from 298.15 K to 308.15 K, the Δ*n* values decreases which is due to decrease in density of the medium owing to weakening of intermolecular H-bonding. The effect of temperature on Δ*n* values for DBA+ *tert*-butanol is higher in comparison to DBA+ *n*-butanol or *sec*-butanol or isobutanol. It is because of the lesser interactions of DBA + *tert*-butanol molecule which are further more effected by the increase in temperature.

Conclusion

The refractive index for the binary mixtures of dibutylamine (DBA) + isomeric butanol were measured and Δ*n* values were determined in the temperature range 298.15 K to 308.15 K. The Δ*n* values for all the binary mixtures are found positive and magnitude of Δ*n* for DBA (1) + isomeric butanol (2) at equimolar mixtures follow the sequence: *n*-butanol > isobutanol > *sec*-butanol > *tert*-butanol. This trend is observed as a result of cumulative effect of molecular interactions between unlike molecules and packing of the molecules in binary mixtures. The negative values of Δ*n* represent the specific molecular interactions. Moreover, highest value of in DBA + *n*-butanol shows higher magnitude of specific interactions which is least in case of DBA + *tert*-butanol. The results were well explained on the basis of size, shape and geometry of the molecules. The refractive index data were also analyzed in terms of various mixing correlations and found to be in good agreement with experimental results. Nakata & Sakurai model [25] was applied to predict the V_m^E values from refractive index data of pure as well as their binary mixtures and it predict the sign and shape of excess molar volume (V_m^E) *versus* mole fraction (x_i) curves for the present binary systems.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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