

Refractive Indices of Aqueous Solutions of Isomeric Butylamines at 303.15 K: Experimental and Correlative Approach

Muhammad A. R. Khan, Mohammed Sohel, Md. Ariful Islam, Faisal I. Chowdhury* and Shamim Akhtar
Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh

Abstract

Refractive indices (n_D) and densities (ρ) of water (W) + *n*-butylamine (NBA), + *sec*-butylamine (SBA) and + *tert*-butylamine (TBA) systems had been measured in the whole range of composition at 303.15 K, from which deviation in refractive index (Δn_D) molar refraction (R_m) and excess molar refraction (R_m^E) had been evaluated. All of the derived properties were fitted to appropriate polynomials. Δn_D were fitted to the Redlich-Kister polynomial equation. Values of Δn_D were all positive and R_m^E were all negative which were attributed to cross hydrogen bonding, specific interactions as well as interstitial accommodation effect. A comparative study of Lorentz-Lorenz (L-L), Weiner (W), Heller (H), Gladstone-Dale (G-D), Arago-Biot (A-B), Eykman (Ey), Newton (Nw), Eyring-John (E-J) and Oster (Os) relations for determining the refractive index of a liquid had been carried out to test their validity for the three binaries over the entire mole fraction range of butylamines at 303.15 K.

Keywords: Refractive indices, Excess molar refraction, Mixing relations, Isomeric butylamines.

1. Introduction

The extent of refraction can be reached through the refractive index (n_D), a characteristic optical property, which is a fundamental physical property of liquids and liquid mixtures. Also, n_D values are important for practical application in the calculation of electronic polarizability of molecule, boiling point estimation by Meissner's method or estimation of various thermodynamic properties. It measures the speed of light in material¹. In order to identify pure liquids and liquid mixtures accurately, this parameter has been used for many years. The values of n_D are essentially important for the development of alternatives in fuel substitutes, additives, and treatment of oils with chemicals². Comprehensive knowledge of fluids is required to clarify the nature of interactions between solute and solvent molecules as well as to design any technological processes. For many years, we have been working on various physico-chemical properties such as density, viscosity, refractive index, ultrasound velocity, etc., as well as their excess/deviation behavior to study molecular interaction in the liquid-liquid binary mixtures [3-11].

To characterize and understand the thermodynamic properties of fluids, n_D and ρ data have been used by many researchers [12-14]. The molecular interaction in a fluid mixture can also be assessed from the n_D and ρ of its pure components [15]. On the other hand, to determine the composition of an unknown mixture and the presence of molecular interactions in binary mixtures mixing rules have been

* Corresponding author. Tel.: +880-1836929291
E-mail address: faisal@cu.ac.bd

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used by Wankhede [16] and Sangita Sharma et al. [13]. The most common mixing rules are the Lorentz-Lorenz equation, Weiner relation, Heller's, Gladstone-Dale, Arago-Biot, Eykman, Newton, Eyring-John and Oster equations. In continuation of our earlier works [17-18], we reported the refractive indices of aqueous solutions with isomeric butylamines at 303.15 K and the results had been used to elucidate the nature and extent of interaction between the components and to verify commonly used mixing rules. Literature survey revealed that refractive indices of aqueous solutions with isomeric butylamines in any form, experimental or theoretical, was scanty, and this prompted us to conduct the present research.

2. Experimental Section

In order to prepare the required binary systems, liquids used were: *n*-butylamine (purity = 99.5%), *sec*-butylamine (purity = 99%), *tert*-butylamine (purity = 98%) and water. The chemicals were procured from Sigma-Aldrich Chemical Co. Ltd., and three times distilled water was used as a solvent for the preparation of aqueous solutions of butylamines. The liquids were used without further treatment. All the chemicals were kept under molecular sieves (4Å) for 2-3 weeks prior to use. The aqueous solutions at different compositions were made by volume using a pipette with an accuracy of $\pm 0.01 \text{ cm}^3$. Special caution was taken to prevent evaporation and also the introduction of moisture into the experimental samples.

Densities were measured by using the Anton Paar density meter (DSA 5000 M) with precision up to $\pm 10^{-6} \text{ g.cm}^{-3}$. The instrument was adjusted and calibrated with air and bi-distilled water at 303.15 K maintaining the temperature constant up to $\pm 0.01 \text{ K}$ (density of air = $0.001177 \text{ g.cm}^{-3}$ and density of water = $0.998205 \text{ g.cm}^{-3}$). n_D values were determined by using an Abbe Refractometer (60/ED, Bellingham+Stanley Ltd., Eng.) connected with a thermostatic water bath. Abbe Refractometer reading at a Na D-line was converted into the n_D value with the supplied Abbe utility software. The uncertainty in measured n_D was found to be ± 0.0002 .

From experimental refractive indices (n_D) deviation in refractive index (Δn_D), molar refraction (R_M) and excess molar refraction (R_M^E) were calculated. Deviation in refractive index (Δn_D) values were calculated by using the following equations.

$$\Delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \quad (1)$$

Observed molar refraction, R_M and its ideal value, $R_{M,id}$ could be calculated from equations (3) and (4) respectively:

$$R_M = \left(n_D^2 - 1 / n_D^2 + 2 \right) \left[\frac{x_1 M_1 + x_2 M_2}{\rho} \right] \quad (2)$$

$$R_M = \left(n_D^2 - 1 / n_D^2 + 2 \right) \left[\frac{(\varphi_1 M_1 + \varphi_2 M_2)}{\rho} \right] \quad (3)$$

Where, the volume fraction of *i*-th component, $\varphi_i = \frac{x_i V_i}{\sum x_i V_i}$

$$R_{M,id} = \varphi_1 R_{M1} + \varphi_2 R_{M2} \quad (4)$$

$$R_M^E = R_M - R_{M,id} \quad (5)$$

$$R_M^E = R_M - (\varphi_1 R_{M1} + \varphi_2 R_{M2}) \quad (6)$$

The following nine equations were used for the quantitative determination of refractive indexes of binary mixtures.

Arago-Biot (A-B):

$$n_D = n_{D1}\phi_1 + n_{D2}\phi_2 \quad (7)$$

Gladstone-Dale (G-D):

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

Lorentz-Lorentz (L-L):

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

Eykman (Eyk):

$$\frac{n_D^2 - 1}{n_D + 0.4} = \left(\frac{n_{D1}^2 - 1}{n_{D1} + 0.4}\right)\phi_1 + \left(\frac{n_{D2}^2 - 1}{n_{D2} + 0.4}\right)\phi_2 \quad (10)$$

Weiner (W):

$$\frac{n_D^2 - n_{D1}^2}{n_D^2 + 2n_{D2}^2} = \left[\frac{n_{D2}^2 - n_{D1}^2}{n_{D2}^2 + 2n_{D1}^2}\right]\phi_2 \quad (11)$$

Heller (H):

$$\frac{n_D - n_{D1}}{n_{D1}} = \frac{3}{2} \left[\frac{\left(\frac{n_{D2}}{n_{D1}}\right)^2 - 1}{\left(\frac{n_{D2}}{n_{D1}}\right)^2 + 2} \right] \phi_2 \quad (12)$$

Newton (N_w):

$$n_D^2 - 1 = (n_{D1}^2 - 1)\phi_1 + (n_{D2}^2 - 1)\phi_2 \quad (13)$$

Oster (O_s):

$$\frac{(n_D^2 - 1)(2n_D^2 + 1)}{n_D^2} = \frac{(n_{D1}^2 - 1)(2n_{D1}^2 + 1)}{n_{D1}^2}\phi_1 + \frac{(n_{D2}^2 - 1)(2n_{D2}^2 + 1)}{n_{D2}^2}\phi_2 \quad (14)$$

Eyring and John (E-J):

$$n_D = n_{D1}\phi_1^2 + 2(n_{D1}n_{D2})^{\frac{1}{2}}\phi_1\phi_2 + n_{D2}\phi_2^2 \quad (15)$$

In all these equations, n_D , n_{D1} and n_{D2} are the refractive index of the mixture, pure component-1 and pure component-2, respectively, and ϕ_i be Volume fraction of i -th component. Where, $\phi_i = \frac{x_i V_i}{\sum x_i V_i}$, x_i is the mole fraction and V_i is the molar volume of i -th component.

In order to correlate measured and some derived properties, the following general polynomial equation was used:

$$Y = \sum_{i=0}^n a_i x_2^i \quad (16)$$

Here, Y represents refractive index, n_D , and molar refraction, R_M ; a_i is the fitting coefficient and

x_2 the mole fraction of isomeric butylamines.

And excess or deviation parameters had been correlated by Redlich-Kister polynomial equation of the form:

$$Z^E = x_2(1 - x_2) \sum_{i=0}^n A_i(1 - 2x_2)^i \quad (17)$$

with the standard deviation, σ , following

$$\sigma(Z^E) = \left[\sum \frac{(Z_{exp}^E - Z_{cal}^E)^2}{n-p} \right]^{1/2} \quad (18)$$

Here, Z^E represents Δn_D and R_m^E ; Z_{exp}^E and Z_{cal}^E are the experimental and calculated values of Z^E respectively and A_i is the i -th fitting coefficient, n the number of measurements, p the number of coefficients and the other terms have their usual significance.

3. Results and discussion

Refractive index (n_D) was measured for the binary solutions of W + NBA, W + SBA and W + TBA in the whole range of composition. Refractive Indices (n_D) of the above systems had been measured only at 303.15 K due to the boiling point of SBA (63 °C) and TBA (46 °C). These values along with deviation in refractive index (Δn_D), molar refraction (R_M) and excess molar refraction (R_M^E) are tabulated in Table 1, and comparative n_D values of W + NBA, + SBA and + TBA systems against mole fraction (x_2) for different molar ratios at 303.15 K are shown in Figure 1(a). In Figure 1(a), it is observed that initially n_D lines increase first up to $x_2 \approx 0.2$. After crossing this point, the n_D values rise very slowly with forking manner. In dilute region n_D lines run very closely, but in solute-rich region the order is as follows: W + NBA > W + SBA > W + TBA.

Comparative curve for Δn_D of W + NBA, W + SBA and W + TBA against mole fraction (x_2) and R_M and R_M^E against volume fraction (ϕ_2) for different molar ratios at 303.15 K is plotted in Figures 1(b-d), respectively. As can be seen in Figure 1(b), it is observed that Δn_D vs. x_2 curves are all positive, Δn_D of W + SBA is maximum and the broader maximum is found at $x_2 \approx 0.2$ to 0.3. Also, the broader maximum for the W + NBA system is observed to water-rich region whereas, that has appeared at $x_2 \approx 0.5$ for W + TBA system.

It is to be noted that, n_D is nothing but the ratio of the speed of light in a vacuum and that in the substance. Thus, it indicated the relative compactness of the medium. It depended on the density of solute and solvent molecules, polarizability, steric hindrance, as well as nature of intermolecular interaction of component molecules. One factor helped the light to pass through easier, another factor might create an obstacle to pass the light beam. As a result, deviation in n_D was found for the systems according to experimental observation.

In Figure 1(c), it is observed that molar refraction increased gradually for all the systems. Furthermore, the curves are almost identical and merge with each other. Molar Refraction depended on molar volume. Since the molar volume of isomeric butylamines was almost the same, so their molar refraction was almost identical. The excess molar refraction curve presented in Figure 1(d) reveals that the mixing of amines with water was accompanied by significant negative changes in molar refraction with minima at $\phi_2 \sim 0.5$. It is significant that the decreasing order of the values of R_M^E at $\phi_2 \sim 0.5$ follows W + TBA > W + SBA > W + NBA trend.

Moreover, for all the systems, observed excess molar refraction were negative as presented in Figure 1(d). In a previous study of Saleh et al. [17], values of V_m^E for these systems were negative and we obtained a highly resemble nature of variation of R_M^E in our present study. Generally, the magnitudes of R_M^E were different from V_m^E . The causes of negative excess molar volume were mainly hydrophobic

hydration, interstitial accommodation of molecules of one component into the structural network of molecules of the other component, favourable geometric fittings of molecules, size differences of molecules¹⁷. As for volume contraction, strong chemical interaction was responsible, similar reasons were also responsible for negative R_M^E . It is to be noted that, the order of hydrophobic capacity of hydrocarbon groups is $-CH_3 > -CH_2 > -CH$ [19]. Hence R_M^E of these systems should follow the order: $W + TBA > W + SBA > W + NBA$.

Table 1. Refractive Index (n_D), deviation in refractive index, Δn_D , molar refraction, $R_M \cdot 10^6 / (m^3 \cdot mol^{-1})$ and excess molar refraction, $R_m^E \cdot 10^8 / (m^3 \cdot mol^{-1})$ of W + NBA, W + SBA and W + TBA systems for different molar ratios at 303.15 K.

x_2	ϕ_2	n_D	Δn_D	R_M	R_M^E
W + NBA					
1.0000	1.0000	1.3964	0.0000	24.185	0.00
0.8996	0.9803	1.3981	0.0030	23.475	-31.47
0.7991	0.9567	1.3982	0.0046	22.654	-66.08
0.6991	0.9281	1.3992	0.0074	21.824	-91.67
0.6014	0.8934	1.3973	0.0077	20.710	-133.35
0.4977	0.8463	1.3983	0.0117	19.562	-153.36
0.3970	0.7853	1.3962	0.0135	18.014	-185.73
0.2990	0.7033	1.3901	0.0127	16.003	-221.86
0.1992	0.5802	1.3806	0.0110	13.255	-249.35
0.0983	0.3772	1.3653	0.0086	9.442	-222.78
0.0000	0.0000	1.3326	0.0000	4.088	0.00
W + SBA					
1.0000	1.0000	1.38762	0.0000	24.185	0.00
0.8995	0.9807	1.39158	0.0097	23.486	-30.99
0.7993	0.9576	1.39273	0.0166	22.656	-67.55
0.6994	0.9295	1.39449	0.0241	21.819	-94.76
0.5976	0.8938	1.39539	0.0309	20.827	-122.11
0.4998	0.8499	1.39411	0.0352	19.567	-159.76
0.3984	0.7896	1.39305	0.0400	18.062	-188.91
0.2978	0.7062	1.38854	0.0412	15.901	-237.19
0.2003	0.5867	1.38143	0.0397	13.378	-249.07
0.0994	0.3848	1.36667	0.0308	9.535	-227.05
0.0000	0.0000	1.33021	0.0000	4.061	0.00
W + TBA					
1.0000	1.0000	1.3730	0.0000	24.451	0.00
0.8995	0.9815	1.3767	0.0037	23.803	-27.07
0.7999	0.9595	1.3812	0.0081	23.166	-45.90
0.6975	0.9319	1.3832	0.0101	22.251	-80.99
0.5995	0.8988	1.3847	0.0116	21.203	-118.37
0.4994	0.8554	1.3863	0.0133	19.969	-153.34
0.3984	0.7970	1.3857	0.0127	18.373	-193.98
0.2965	0.7142	1.3853	0.0123	16.384	-223.96
0.1985	0.5949	1.3778	0.0047	13.603	-258.87
0.0996	0.3961	1.3660	-0.0071	9.733	-240.49
0.0000	0.0000	1.3302	0.0000	4.061	0.00

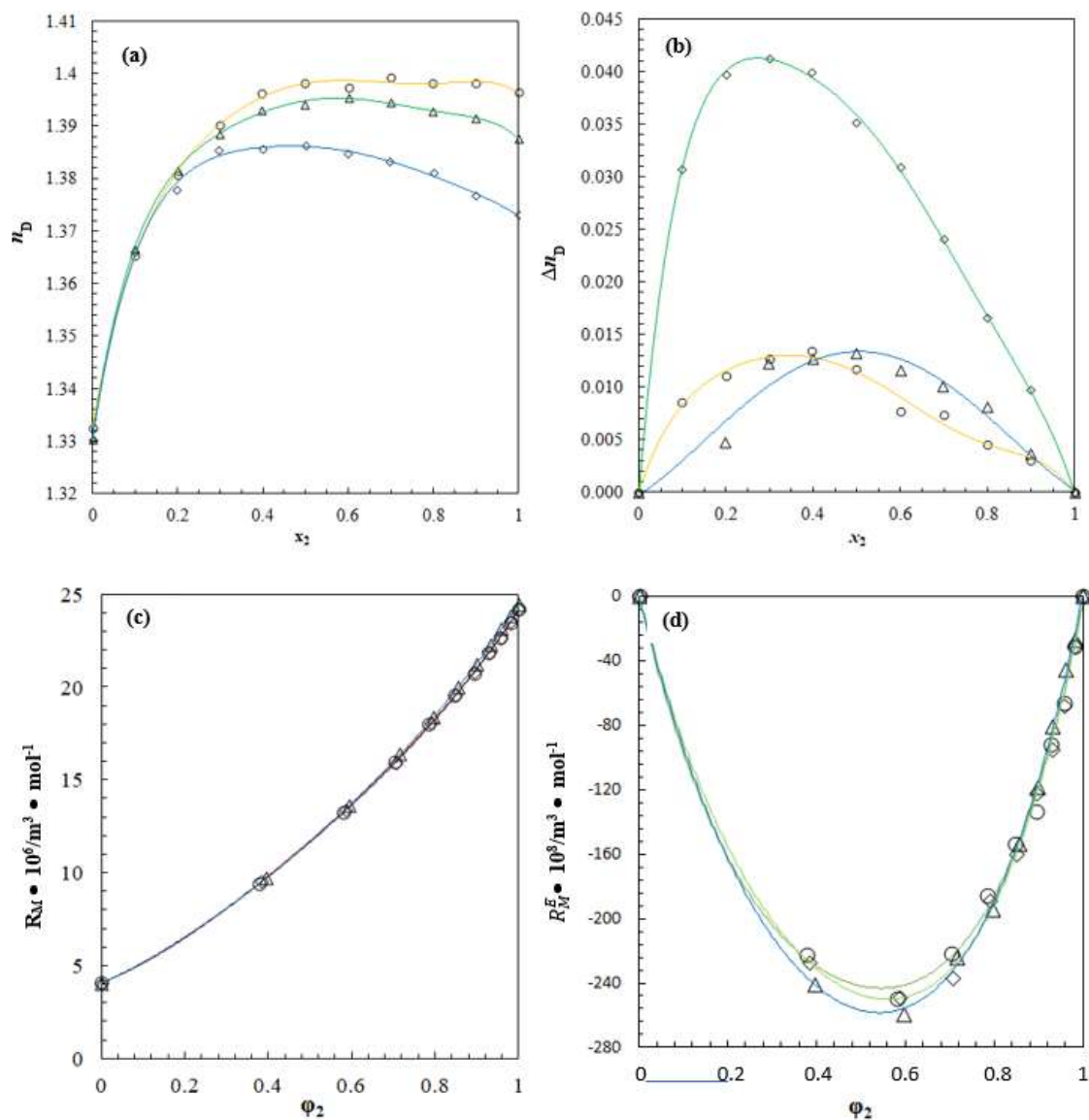


Figure 1: Comparative diagrams of refractive indices (n_D), deviations in refractive index (Δn_D), molar refractions (R_M) and excess molar refractions (R_M^E) for W + NBA, W + SBA, and W + TBA systems against compositions of butylamines at 303.15 K: (a) n_D vs. x_2 ; (b) Δn_D vs. x_2 ; (c) R_M vs. ϕ_2 and (d) R_M^E vs. ϕ_2 . Solid lines represent polynomial fittings. Data points for W + NBA, W + SBA, and W + TBA are represented by O, ◇, and Δ, respectively.

The coefficients for n_D and R_M (Equation 16) along with R^2 and those for Δn_D and R_M^E (Equation 17) and their standard deviation (Equation 18) for W + NBA, + SBA and + TBA systems at 303.15 K are presented in Tables 2 and 3, respectively. In order to correlate the experimental n_D value, different mixing relations are known as Arago-Biot (A-B), Gladstone-Dale (G-D), Lorentz-Lorentz (L-L), Eykman (Eyk), Weiner (W), Heller (H), Newton (N), Oster (Os) and Eyring-John (E-J) were used. The correlating ability of each of Equations 7-15 was tested by calculating average deviations between the experimental and calculated refractive indices. The average deviations were calculated for the binary

systems of W + NBA, + SBA and + TBA. Experimental refractive index and calculated refractive index for different mixing relations of W + NBA, + SBA and + TBA systems for different molar ratios at 303.15K are listed in Table 4 and graphically represented in Figures 2(a-c), respectively. Their comparative curve is shown in Figure 2(d) and average deviations are tabulated in Table 5.

Table 2. Coefficients, a_i , of equation 16, expressing refractive index, n_D , molar refraction, $R_M \cdot 10^6 / (m^3 \cdot mol^{-1})$, excess molar refraction $R_m^E \cdot 10^8 / (m^3 \cdot mol^{-1})$ and R^2 value of W + NBA, W + SBA and W + TBA systems for different molar ratios at 303.15 K.

Property	a_0	a_1	a_2	a_3	a_4	a_5	R^2
W + NBA							
n_D	1.3329	0.4040	-1.0500	1.4290	-0.9945	0.2752	1.0000
R_M	4	8	20	-20	10		0.9999
R_M^E	0.1	-1000	2000	-2000	1000		0.9961
W + SBA							
n_D	1.3305	0.4859	-1.5900	2.6871	-2.2464	0.7209	0.9986
R_M	4	10	20	-20	10		0.9999
R_M^E	0.04	-1000	2000	-2000	1000		0.9974
W + TBA							
n_D	1.3305	0.4837	-1.6710	2.8510	-2.3899	0.7688	0.9977
R_M	4	9	20	-10	8		1.0000
R_M^E	0.02	-1000	2000	-1000	800		0.999

Table 3: Coefficients, A_i , of equation (17), expressing deviation in refractive index (Δn_D) and standard deviation, σ , according to equation 18 of W + NBA, + SBA and + TBA systems for different molar ratios at 303.15 K.

Property	A_0	A_1	A_2	A_3	A_4	A_5	σ
W + NBA							
Δn_D	0.0457	-0.0542	-0.007	0.1244	0.055	-0.1612	0.00083
W + SBA							
Δn_D	0.1434	-0.0913	0.0544	-0.0692	0.1118	-0.0282	0.00054
W + TBA							
Δn_D	0.0501	-0.0183	0.0673	0.0223	-0.2706	0.193	0.00071

In Figure 2(a), it is observed that the average deviation in refractive indices of the W + NBA system was found to be about 6% according to Weiner relation (w). In Figure 2(b), the average deviation in refractive indices of the W + SBA system was found to be about 1% according to Arago-Biot (A-B) and Gladstone-Dale (G-D) relations. And for W + TBA system [Figure 2(c)], the Average Deviations in refractive index were 2% estimated from Gladstone-Dale (G-D) and Lorentz-Lorentz (L-L) relations. The lowest values were observed for W + NBA system estimated by Weiner Relation, for W + SBA system by Arago-Biot and Gladstone-Dale relation and for W + TBA system by Gladstone-Dale and Lorentz-Lorentz relations which were fitted best.

Table 4. Experimental refractive index, n_D and calculated refractive index, n_D from different mixing relations of W + NBA, W + SBA and W + TBA systems for different molar ratios at 303.15 K.

X_2	n_D	A - B	G - D	L - L	Eyk	W	H	NW	E - J	Os
W + NBA system										
1.0000	1.3963	1.3963	1.3963	1.3964	1.3964	1.4004	1.3958	1.3964	1.3964	1.3964
0.8996	1.3981	1.3951	1.3951	1.3951	1.3951	1.3991	1.3946	1.3951	1.3951	1.3951
0.7991	1.3982	1.3936	1.3936	1.3935	1.3936	1.3975	1.3931	1.3937	1.3936	1.3936
0.6991	1.3992	1.3918	1.3918	1.3917	1.3918	1.3955	1.3913	1.3919	1.3917	1.3918
0.6014	1.3973	1.3896	1.3896	1.3894	1.3895	1.3932	1.3891	1.3897	1.3895	1.3896
0.4977	1.3983	1.3866	1.3866	1.3864	1.3865	1.3899	1.3861	1.3868	1.3865	1.3867
0.3970	1.3962	1.3827	1.3827	1.3824	1.3826	1.3858	1.3823	1.3829	1.3826	1.3828
0.2990	1.3901	1.3774	1.3774	1.3772	1.3773	1.3802	1.3771	1.3778	1.3773	1.3776
0.1992	1.3806	1.3696	1.3696	1.3693	1.3695	1.3718	1.3693	1.3700	1.3694	1.3698
0.0983	1.3653	1.3566	1.3566	1.3563	1.3565	1.3581	1.3564	1.3570	1.3565	1.3568
0.0000	1.3326	1.3326	1.3326	1.3326	1.3326	1.3326	1.3326	1.3326	1.3326	1.3326
W + NBA										
1.0000	1.3876	1.3964	1.3964	1.3964	1.3796	1.3897	1.3861	1.3811	1.3340	1.3804
0.8995	1.3916	1.3951	1.3951	1.3951	1.3770	1.3883	1.3848	1.3787	1.3227	1.3779
0.7993	1.3927	1.3936	1.3936	1.3935	1.3736	1.3866	1.3831	1.3757	1.3078	1.3747
0.6994	1.3945	1.3918	1.3918	1.3917	1.3688	1.3844	1.3811	1.3715	1.2857	1.3702
0.5976	1.3954	1.3896	1.3896	1.3894	1.3634	1.3817	1.3786	1.3667	1.2618	1.3651
0.4998	1.3941	1.3866	1.3866	1.3864	1.3542	1.3780	1.3751	1.3586	1.2162	1.3564
0.3984	1.3931	1.3827	1.3827	1.3824	1.3413	1.3729	1.3703	1.3472	1.1536	1.3442
0.2975	1.3885	1.3774	1.3774	1.3772	1.3219	1.3656	1.3635	1.3299	1.0600	1.3258
0.2003	1.3814	1.3696	1.3696	1.3693	1.2822	1.3534	1.3520	1.2938	0.8649	1.2876
0.0994	1.3667	1.3566	1.3566	1.3563	1.3521	1.3534	1.3520	1.3525	1.3520	1.3523
0.0000	1.3302	1.3326	1.3326	1.3326	1.3302	1.3302	1.3302	1.3302	1.3302	1.3302
W+ TBA										
1.0000	1.3730	1.3477	1.3964	1.3964	1.3658	1.3741	1.3720	1.3671	1.3228	1.3664
0.8995	1.3767	1.3421	1.3951	1.3951	1.3636	1.3731	1.3711	1.3652	1.3126	1.3644
0.7999	1.3812	1.3334	1.3936	1.3935	1.3604	1.3718	1.3699	1.3624	1.2965	1.3614
0.6975	1.3832	1.3247	1.3918	1.3917	1.3571	1.3703	1.3685	1.3594	1.2809	1.3583
0.5995	1.3847	1.3092	1.3896	1.3894	1.3517	1.3684	1.3667	1.3547	1.2525	1.3532
0.4994	1.3863	1.2868	1.3866	1.3864	1.3439	1.3658	1.3642	1.3479	1.2117	1.3459
0.3984	1.3857	1.2507	1.3827	1.3824	1.3319	1.3621	1.3606	1.3373	1.1472	1.3346
0.2965	1.3853	1.1970	1.3774	1.3772	1.3142	1.3567	1.3556	1.3216	1.0542	1.3177
0.1985	1.3778	1.0827	1.3696	1.3693	1.2784	1.3479	1.3471	1.2893	0.8674	1.2834
0.0996	1.3660	1.3472	1.3566	1.3563	1.3471	1.3479	1.3471	1.3473	1.3471	1.3473
0.0000	1.3302	1.3302	1.3326	1.3326	1.3302	1.3302	1.3302	1.3302	1.3302	1.3302

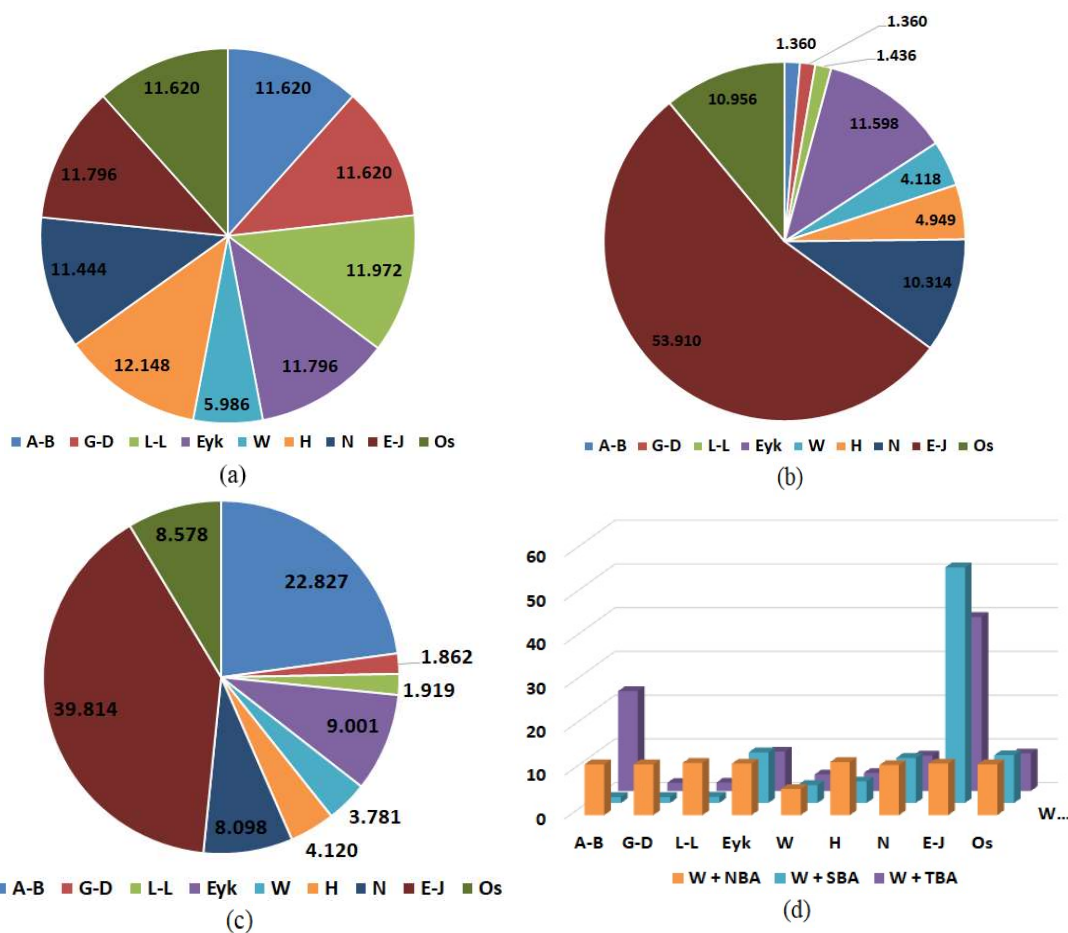


Figure 2. Comparison of predicted n_D values for the systems: (a) W+NBA, (b) W+SBA, (c) W+TBA, and (d) their average deviations at 303.15 K.

Table 5. Average deviations* in the refractive index from different mixing relations of W + NBA, W + SBA and W + TBA systems for different molar ratios at 303.15 K

System	A – B	G – D	L - L	Eyk	W	H	N	E – J	nOs
W + NBA	0.00066	0.00066	0.00068	0.00067	0.00034	0.00069	0.00065	0.00067	0.00066
W + SBA	0.00036	0.00036	0.00038	0.00307	0.00109	0.00131	0.00273	0.01427	0.00290
W + TBA	0.00809	0.00066	0.00068	0.00319	0.00134	0.00146	0.00287	0.01411	0.00304

* $[(n_{obsd} - n_{calcd}) / n]$, n_{obsd} = Observed, n_{calcd} = Calculated, n = Number of Data Sets

3. Conclusion

A systematic study of aqueous solutions of isomeric butylamines was performed at different concentrations and 303.15 K through a refractometric method by using density data. The refractive indices values and other related parameters provided valuable information to understand the solute-solvent interactions in the aqueous solutions. Excess molar refraction (R_M^E) played an important role in

these systems which indicated significant contraction between solute and solvent molecules due to which structural rearrangements took place. The decreasing order of R_M^E was as $W + TBA > W + SBA > W + NBA$. Moreover, nine mixing rules as Arago-Biot (A-B), Gladstone-Dale (G-D), Lorentz-Lorentz (L-L), Eykman (Eyk), Weiner (W), Heller (H), Newton (N), Oster (Os) and Eyring-John (E-J) had been tested to verify them computing the average deviations in refractive indices. For $W + NBA$ system, Weiner relation, for $W + SBA$ system, Arago-Biot and Gladstone-Dale relation and $W + TBA$ system, Gladstone-Dale and Lorentz-Lorentz relations were fitted best. These findings will be useful for future studies of liquid-liquid mixtures and chemical engineering applications.

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