Received: 23-06-2014
Accepted: 19-07-2014

ISSN: 2321-4902
Volume 2 Issue 2

Online Available at www.chemijournal.com

International Journal of Chemical Studies

Theoretical evaluation of optical refractive index in binary liquid mixtures of 1, 4-Dioxane with 1-Hexanol

Srinivasu Ch[1*], Anil Kumar K[2]

1. Department of Physics, Andhra Loyola College, Vijayawada-8, (A.P.), India.
2. Department of Physics, Sri Vani School of Engineering, Chevuturu, (A.P.), India.

Corresponding Author: Srinivasu Ch; Department of Physics, Andhra Loyola College, Vijayawada-8, (A.P.), India.

Refractive indices of the binary liquid mixture of 1, 4-dioxane with 1-hexanol have been evaluated at T=(298.15, 303.15,308.15,313.15 and 318.15) K over the entire composition range using Abbemat referometer. A comparative study on various mixing rules *viz.*, Arago-Biot (A-B), Gladstone-Dale (G-D), Newton's (Nn), Eyring and john (E-J), Lorentz-Lorentz (L-L), Heller (H), Eykman (Eyk), Oster (Os) and Weiner (W) relations to predicte the refractive index of the binary mixture at five studied temperatures calculated theoretically and the results discussed in terms of average percentage deviations. Further, the excess refractive indices have been computed and fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and standard errors.

Keyword: Refractive index, 1, 4-dioxane, 1-hexanol, Theoretical elevations, APD.

1. Introduction

The refractive indices measurements in binary and multi component liquid mixtures have been studied by several authors [1-4]. Physico-chemical calculations involving multiple phase systems require these predicted refractive index values of multi-component systems.

Refractive index measurements in combination with density and other analytical data are very useful in industry for common substances. Also, literature survey reveals that there is no such data on these mixtures.

In this paper, refractive indices of the binary liquid mixture of 1,4-dioxane with 1-hexanol have been evaluated at 298.15, 303.15, 308.15, 313.15 and 318.15 K of the liquid mixture reported here, with that various theoretical relations proposed by the Arago-Biot (A-B), Gladstone-Dale (G-D), Newton's (Nn), Eyring and john (E-J), Lorentz-Lorentz (L-L), Heller (H), Eykman (Eyk), Oster (Os) and Weiner (W) tested by many researchers [5-6], and then a comparative study have been made between the experimental data and the theoretically calculated values at five temperatures and the results discussed in terms of average percentage deviations (APD). From the experimental data one can calculate the excess refractive indices (n^E) and fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and there standard errors for the binary mixture studied.

2. Experimental Methods

1, 4-dioxane and 1-hexanol are purchased from Sigma Aldrich Company (U.S.A) used in the present work. Chemicals were further purified according to the methods described by Reddick et al [7]. The prepared binary samples were kept in airtight stopped glass bottles. Mole fractions of these samples were determined by measuring the mass of each component with a precision balance (Sartorius, model CP 225D, (0.01 mg). The uncertainty of the composition on a mole fraction basis was 0.0001. Refractive index is measured using Abbemat refractometer from Anton Paar are specifically developed for unique applications and can be used for calculating the refractive index in challenging environments. The instruments include a hermetically sealed stainless steel casing to endure harsh conditions. The refractive indices of the mixtures were me asured (0.00001) using an Abbemat. At the beginning, the standardization of the device at room temperature 298.15K was made with double distilled water and its refractive index is found to be 1.3328 it is in good agreement with the literature values [8]. The refractive indices of the pure liquids at the temperatures 298.15, 303.15 & 308.15 K are reported in table 1.

3. Theory

The following mixing rules for refractive index of liquid mixtures are listed below:

Arago-Biot (A-B):

$$n = n_1\phi_1 + n_2\phi_2 \quad (1)$$

Gladstone-Dale (G-D):

$$n - 1 = (n_1 - 1)\phi_1 + (n_2 - 1)\phi_2 \quad (2)$$

Newton's (Nn) relation:

$$n^2 - 1 = (n_1^2 - 1)\phi_1 + (n_2^2 - 1)\phi_2 \quad (3)$$

Eyring and john (E-J):

$$n = n_1\phi_1^2 + 2(n_1 n_2)^{1/2}\phi_1\phi_2 + n_2\phi_2^2 \quad (4)$$

Lorentz-Lorentz (L-L):

$$\frac{n^2 - 1}{n^2 + 2} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right)\phi_2 \quad (5)$$

Heller (H):

$$\frac{n - n_1}{n_1} = \frac{3}{2}\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right]\phi_2 \quad (6)$$

Eykman (Eyk):

$$\frac{n^2 - 1}{n + 0.4} = \left(\frac{n_1^2 - 1}{n_1 + 0.4}\right)\phi_1 + \left(\frac{n_2^2 - 1}{n_2 + 0.4}\right)\phi_2 \quad (7)$$

Oster (Os):

$$\frac{(n^2 - 1)(2n^2 + 1)}{n^2} = \frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2}\phi_1 + \frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2}\phi_2 \quad (8)$$

Weiner (W):

$$\frac{n^2 - n_1^2}{n^2 + 2n_2^2} = \left(\frac{n^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2 \quad (9)$$

Where, n is the refractive index of the mixture. The variables n_1, n_2 are the refractive indices of the pure components, and ϕ_1, ϕ_2 are volume fractions of pure components respectively.

The volume fractions are obtained from, $\phi_1 = \frac{x_1 V_1}{\sum x_i V_i}$ and $\phi_2 = \frac{x_2 V_2}{\sum x_i V_i}$

(Where 'V_i' is the molar volume of the component)

From the measured refractive indices (n) of the binary mixture, the excess parameter (n^E) have been calculated using the equation

$$Y^E = Y_{mix} - (x_1 y_1 + x_2 y_2) \quad (10)$$

where x_1 and x_2 are mole fractions of 1,4-Dioxane and 1-hexanol respectively.

Further, the excess refractive index are fitted to Redlich – Kister polynomial equation of the form

$$Y^E = x_1(1 - x_1)\sum_{i=0}^{n} a_i (1 - 2x_1)^i \quad (11)$$

using least-squares regression method, the a_i coefficients are obtained by fitting above equation to the experimental values. The optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ)

$$\sigma = \left[\frac{\sum (Y_{\text{expt}} - Y_{calc})^2}{N - n} \right]^{1/2} \quad (12)$$

Where N is the number of measurements, n is the number of coefficients. The values of coefficients, a_i and the standard deviations, σ are presented in Table 4.

4. Results and Discussions

The experimental data with literature survey for refractive index has been given in table 1, and table 2 records the refractive index data of 1, 4-dioxnae with 1-butanol at the five temperatures (298.15, 303.15, 308.15, 313.15 and 318.15 K) studied. The experimental indices obtained for the binary mixture were compared with the predicted results for the mixing rules proposed by various theories. The average percentage deviations determined to assess their validity are shown in table 3. Further the excess refractive indices has been computed and fitted to the Redlich-Kister polynomial equation for finding their coefficients and standard errors are reported in table 4.

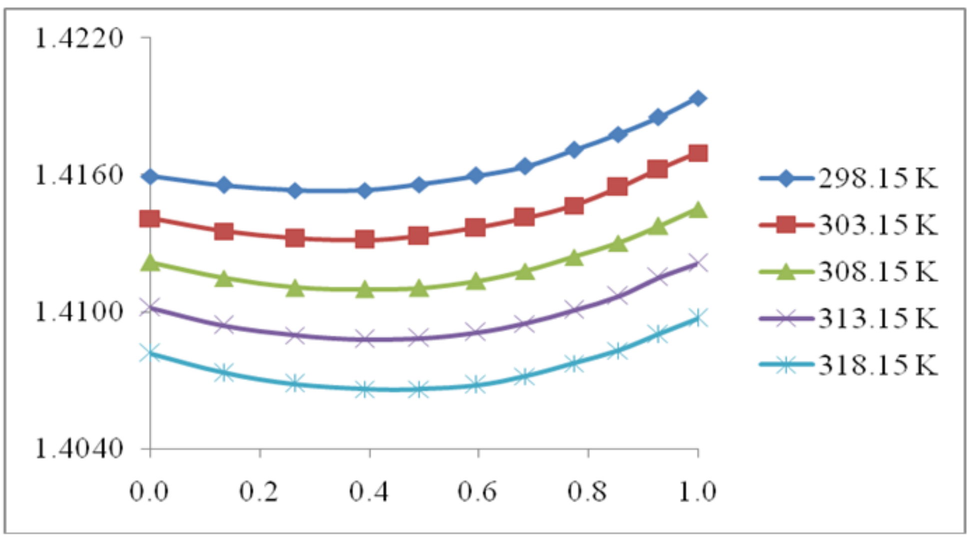

Fig 1: Variaton of Refractive index with mole fraction of 1, 4 dioxane.

A close glance of the table 2, fig 1 reveals that the refractive indices of the pure components and mixtures decrease with rise in temperature. The deviations of theoretical values from experimental one are temperature-independent for the system investigation. However, in case where the variation is significant with change in temperature, it can be used for interpreting the structure and interactions in the liquid by computing other dielectric, optical and acoustic properties using the experimental data. The H-bonds present in the hexanol play an vital role in reducing the experimental values of refractive index for the present system, which gives negative values of excess refractive indices (Fig 2) it indicates the presence of weak interactions are present in the system.

Table 1: Experimental and literature values of refractive indices for the binary mixture 1, 4-dioxane with 1-butanol

Compound	T (K)	Refractive Index(n)	
		Experimental	Literature
	298.15	1.4194	1.4199 [9,10]
1,4-dioxane	303.15	1.4170	1.4180 [11,12]
	308.15	1.4145	1.4167 [13]
	298.15	1.4159	1.4160 [14]
hexanol	303.15	1.4141	1.4141 [14]
	308.15	1.4122	-

Table 2(a): Refractive index, Excess Refractive indexes and different theories at 298.15 and 303.15K

X_1	n_{Exp}	n^E	n_{A-B}	n_{G-D}	n_{Nn}	n_{E-J}	n_{L-L}	n_H	n_{Eyk}	n_{Os}	n_W
298.15 K											
0.0000	1.4159	0.0000	1.4159	1.4159	1.4159	1.4159	1.4159	1.4159	1.4159	1.4159	1.4159
0.1327	1.4156	-0.0008	1.4164	1.4164	1.4164	1.4164	1.4164	1.4164	1.4164	1.4164	1.4164
0.2630	1.4153	-0.0015	1.4168	1.4168	1.4168	1.4168	1.4168	1.4168	1.4168	1.4168	1.4168
0.3906	1.4153	-0.0019	1.4172	1.4172	1.4172	1.4172	1.4172	1.4172	1.4172	1.4172	1.4172
0.4903	1.4156	-0.0021	1.4176	1.4176	1.4176	1.4176	1.4176	1.4176	1.4175	1.4175	1.4176
0.5947	1.4160	-0.0020	1.4179	1.4179	1.4179	1.4179	1.4179	1.4179	1.4179	1.4179	1.4179
0.6848	1.4164	-0.0019	1.4182	1.4182	1.4182	1.4182	1.4182	1.4182	1.4182	1.4182	1.4182
0.7732	1.4171	-0.0015	1.4185	1.4185	1.4185	1.4185	1.4185	1.4185	1.4185	1.4185	1.4185
0.8541	1.4178	-0.0011	1.4188	1.4188	1.4188	1.4188	1.4188	1.4188	1.4188	1.4188	1.4188
0.9273	1.4185	-0.0006	1.4191	1.4191	1.4191	1.4191	1.4191	1.4191	1.4191	1.4191	1.4191
1.0000	1.4194	0.0000	1.4194	1.4194	1.4194	1.4194	1.4194	1.4194	1.4194	1.4194	1.4194
303.15 K											
0.0000	1.4141	0.0000	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141
0.1327	1.4135	-0.0009	1.4144	1.4144	1.4144	1.4144	1.4144	1.4144	1.4144	1.4144	1.4144
0.2630	1.4132	-0.0016	1.4148	1.4148	1.4148	1.4148	1.4148	1.4148	1.4148	1.4148	1.4148
0.3906	1.4131	-0.0021	1.4152	1.4152	1.4152	1.4152	1.4152	1.4152	1.4152	1.4152	1.4152
0.4903	1.4133	-0.0022	1.4154	1.4154	1.4154	1.4154	1.4154	1.4154	1.4154	1.4154	1.4154
0.5947	1.4137	-0.0021	1.4157	1.4157	1.4157	1.4157	1.4157	1.4157	1.4157	1.4157	1.4157
0.6848	1.4141	-0.0019	1.4160	1.4160	1.4160	1.4160	1.4160	1.4160	1.4160	1.4160	1.4160
0.7732	1.4147	-0.0017	1.4163	1.4163	1.4163	1.4163	1.4163	1.4163	1.4163	1.4163	1.4163
0.8541	1.4154	-0.0011	1.4165	1.4165	1.4165	1.4165	1.4165	1.4165	1.4165	1.4165	1.4165
0.9273	1.4162	-0.0005	1.4167	1.4167	1.4167	1.4167	1.4167	1.4167	1.4167	1.4167	1.4167
1.0000	1.4170	0.0000	1.4170	1.4170	1.4170	1.4170	1.4170	1.4170	1.4170	1.4170	1.4170

Table 2(b): Refractive index, Excess Refractive indexes and different theories at 308.15 and 313.15 K

X_1	n_{Exp}	n^E	n_{A-B}	n_{G-D}	n_{Nn}	n_{E-J}	n_{L-L}	n_H	n_{Eyk}	n_{Os}	n_W
308.15 K											
0.0000	1.4122	0.0000	1.4122	1.4122	1.4122	1.4122	1.4122	1.4122	1.4122	1.4122	1.4122
0.1327	1.4115	-0.0010	1.4125	1.4125	1.4125	1.4125	1.4125	1.4125	1.4125	1.4125	1.4125
0.2630	1.4111	-0.0017	1.4127	1.4127	1.4127	1.4127	1.4127	1.4127	1.4127	1.4127	1.4127
0.3906	1.4110	-0.0021	1.4130	1.4130	1.4130	1.4130	1.4130	1.4130	1.4130	1.4130	1.4130
0.4903	1.4111	-0.0023	1.4133	1.4133	1.4133	1.4133	1.4133	1.4133	1.4133	1.4133	1.4133
0.5947	1.4114	-0.0022	1.4135	1.4135	1.4135	1.4135	1.4135	1.4135	1.4135	1.4135	1.4135
0.6848	1.4118	-0.0020	1.4137	1.4137	1.4137	1.4137	1.4137	1.4137	1.4137	1.4137	1.4137
0.7732	1.4124	-0.0016	1.4139	1.4139	1.4139	1.4139	1.4139	1.4139	1.4139	1.4139	1.4139
0.8541	1.4130	-0.0012	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141	1.4141
0.9273	1.4138	-0.0006	1.4143	1.4143	1.4143	1.4143	1.4143	1.4143	1.4143	1.4143	1.4143
1.0000	1.4145	0.0000	1.4145	1.4145	1.4145	1.4145	1.4145	1.4145	1.4145	1.4145	1.4145
313.15 K											
0.0000	1.4102	0.0000	1.4102	1.4102	1.4102	1.4102	1.4102	1.4102	1.4102	1.4102	1.4102
0.1327	1.4094	-0.0010	1.4104	1.4104	1.4104	1.4104	1.4104	1.4104	1.4104	1.4104	1.4104
0.2630	1.4090	-0.0017	1.4106	1.4106	1.4106	1.4106	1.4106	1.4106	1.4106	1.4106	1.4106
0.3906	1.4088	-0.0021	1.4109	1.4109	1.4109	1.4109	1.4109	1.4109	1.4109	1.4109	1.4109
0.4903	1.4089	-0.0023	1.4111	1.4111	1.4111	1.4111	1.4111	1.4111	1.4111	1.4111	1.4111
0.5947	1.4091	-0.0022	1.4113	1.4113	1.4113	1.4113	1.4113	1.4113	1.4113	1.4113	1.4113
0.6848	1.4095	-0.0020	1.4115	1.4115	1.4115	1.4115	1.4115	1.4115	1.4115	1.4115	1.4115
0.7732	1.4101	-0.0016	1.4117	1.4117	1.4117	1.4117	1.4117	1.4117	1.4117	1.4117	1.4117
0.8541	1.4107	-0.0012	1.4118	1.4118	1.4118	1.4118	1.4118	1.4118	1.4118	1.4118	1.4118
0.9273	1.4115	-0.0005	1.4120	1.4120	1.4120	1.4120	1.4120	1.4120	1.4120	1.4120	1.4120
1.0000	1.4121	0.0000	1.4121	1.4121	1.4121	1.4121	1.4121	1.4121	1.4121	1.4121	1.4121

Table 2(c): Refractive index, Excess Refractive indexes and different theories at 318.15 K

X_1	n_{Exp}	n^E	n_{A-B}	n_{G-D}	n_{Nn}	n_{E-J}	n_{L-L}	n_H	n_{Eyk}	n_{Os}	n_W
318.15 K											
0.0000	1.4082	0.0000	1.4082	1.4082	1.4082	1.4082	1.4082	1.4082	1.4082	1.4082	1.4082
0.1327	1.4073	-0.0011	1.4084	1.4084	1.4084	1.4084	1.4084	1.4084	1.4084	1.4084	1.4084
0.2630	1.4068	-0.0017	1.4086	1.4086	1.4086	1.4086	1.4086	1.4086	1.4086	1.4086	1.4086
0.3906	1.4066	-0.0022	1.4087	1.4087	1.4087	1.4087	1.4087	1.4087	1.4087	1.4087	1.4087
0.4903	1.4066	-0.0023	1.4089	1.4089	1.4089	1.4089	1.4089	1.4089	1.4089	1.4089	1.4089
0.5947	1.4068	-0.0023	1.4091	1.4091	1.4091	1.4091	1.4091	1.4091	1.4091	1.4091	1.4091
0.6848	1.4072	-0.0021	1.4092	1.4092	1.4092	1.4092	1.4092	1.4092	1.4092	1.4092	1.4092
0.7732	1.4077	-0.0016	1.4093	1.4093	1.4093	1.4093	1.4093	1.4093	1.4093	1.4093	1.4093
0.8541	1.4083	-0.0012	1.4095	1.4095	1.4095	1.4095	1.4095	1.4095	1.4095	1.4095	1.4095
0.9273	1.4090	-0.0006	1.4096	1.4096	1.4096	1.4096	1.4096	1.4096	1.4096	1.4096	1.4096
1.0000	1.4097	0.0000	1.4097	1.4097	1.4097	1.4097	1.4097	1.4097	1.4097	1.4097	1.4097

Table 3: APD for the binary mixture at different temperatures using different mixing rules

Rules	298.15K	303.15k	308.15K	313.15k	318.15k
n_{A-B}	-0.08361	-0.08842	-0.09188	-0.09280	-0.09560
n_{G-D}	-0.08361	-0.08842	-0.09188	-0.09280	-0.09560
n_{Nn}	-0.08365	-0.08845	-0.09190	-0.09281	-0.09561
n_{E-J}	-0.08359	-0.08841	-0.09187	-0.09279	-0.09559
n_{L-L}	-0.08357	-0.08839	-0.09186	-0.09278	-0.09559
n_{H}	-0.08357	-0.08839	-0.09186	-0.09278	-0.09559
n_{Eyk}	-0.08351	-0.08835	-0.09183	-0.09277	-0.09558
n_{Os}	-0.08348	-0.08833	-0.09182	-0.09276	-0.09557
n_{W}	-0.08360	-0.08841	-0.09187	-0.09279	-0.09559

Table 4: Coefficients (a_i) and standard deviation (σ) for 1,4 Dioxane + hexanol system at different temperatures

Property	T (K)	a_0	a_1	a_2	a_3	a_4	σ (10^2)
	298.15	-0.0083	0.0009	0.0004	0.0006	0.0006	0.0031
	303.15	-0.0087	0.0006	-0.0020	0.0004	0.0055	0.0060
n^E	308.15	-0.0091	0.0007	0.0006	-0.0005	-0.0007	0.0029
	313.15	-0.0090	0.0008	-0.0006	-0.0012	0.0020	0.0049
	318.15	-0.0094	0.0012	0.0015	-0.0026	-0.0027	0.0041

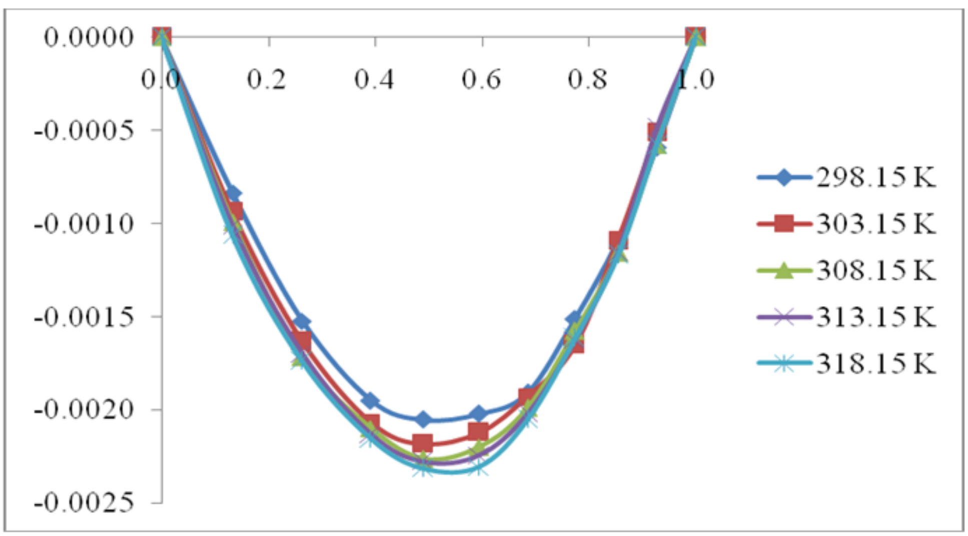

Fig 2: Variation of Excess refractive index with mole fraction of 1, 4 dioxane

The refractive index values were predicted from nine theoretical relations shows excellent agreement with the experimental values. The average percentage deviations for the system under investigation are exhibited negative values. It may applicable to isotropic bodies of spherically symmetrical shape and it proposes volume additivity which is the reason for the deviations obtained in the present study. Also, the negative deviations decrease with rise in temperature and increase in chain length of alcohols and alkanols [15-16].

5. Conclusion

From the above investigations it may be concluded that all the mixing rules discussed are interrelated in a simple quantitative manner and perform well within the limits of experimental error are observed between experimental and theoretical values calculated from various theories/models.

6. References

1. Amalendu P, Kumar A. Excess Molar Volumes, Viscosities, Refractive. Indices of Diethylene Glycol Dimethyl Ether with Dimethyl Carbonate, Diethyl Carbonate, and Propylene Carbonate at (298.15, 308.15, and 318.15) K. J chem eng data 1998; 43:143-147.
2. Pandey JD, Vyas V. Speed of sound, viscosity and refractive index of multicomponent systems: theoretical predictions from the properties of pure components. J mol liq 1999; 81:123-133.
3. Al-Dujaili AH, Yassen AA *et al.* Refractive Indices, Densities, and Excess Properties of 4-(2-Hydroxyethyl) morpholine + Water at (298.15, 308.15, and 318.15) K. J chem eng Data 2000; 45:647-649.
4. Tejraj M, Aminabhavi, Mrityunjaya I. Aralaguppi *et al.* Densities, viscosities, refractive indices, and speeds of sound for methyl acetoacetate + aliphatic alcohols (C1-C8). J chem eng data 1993; 38:31-39.
5. Narendra K, Narayana MP, Srinivasu C. Refractive Indices of Binary Liquid Mixture at Different Temperatures. Asian J Appl Sciences 2011; 4(5):535-541.
6. Mehra R. Application of refractive index mixing rules in binary systems of hexadecane and heptadecane with n-alkanols at different temperatures, Proc Indian Acad Sci (Chem Sci). 2003; 115(2):147–154.
7. Reddick JA, Bunger WB, sukano TK Physical properties and Methods of Purification 2, Fourth Edition, McGraw-Hill, New York, 1986.
8. Martinez-Reina M. Refractive indices. Densities and Excess properties of binary mixtures of ethanol with hexane, heptane, octane and water at (293.15, 298.15, 303.15, and 308.15)K, Revista Bistua, Facultad de Ciencias Basicas 2010; 8(2):1.
9. Giner B, Lafuente C *et al.* Volumetric and refractive properties of binary mixtures containing 1, 4-dioxane and Chloroalkanes. J Chem Thermodyn 2007; 39:148–157.
10. Anil K, Chandra NP *et al.* Densities, Refractive Indices, and Excess Properties of Binary Mixtures of 1,4-Dioxane with Benzene, Toluene, o-Xylene, m-Xylene, p-Xylene, and Mesitylene at Temperatures from (288.15 to 318.15) K, Journal of Chemical & Engineering Data 2008; 53(11):2654–2665.
11. Aminabhavi TM, Patil VB. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Ethylbenzene With N,N-Dimethylacetamide, Tetrahydrofuran, N,N-Dimethylformamide, 1,4-Dioxane, Dimethyl Sulfoxide, Bromoform and 1-Chloronaphthalene in theTemperature Interval (298.15-308.15) K. J Chem Eng Data 1998; 43:497-503.
12. Jyoti N, Nayak MI, Aralaguppi *et al*, Thermodynamic Properties of Water + Tetrahydrofuran and Water + 1,4-Dioxane Mixtures at (303.15, 313.15, and 323.15) K. J Chem Eng Data 2004; 49:468-474.
13. Shipra B, Nirmal P *et al*, Thermodynamic and acoustical studies of binary mixtures of diethyl malonate at 308.15K. Physics and Chemistry of Liquids 2005; 43(3):309–316.
14. Angel P, Pilar B *et al*, Refractive Indexes of Binary Mixtures of Tetrahydrofuran with 1-Alkanols at 25 °C and Temperature Dependence of n and ρ for the Pure Liquids. Journal of Solution Chemistry 2002; 31(5).
15. Tejraj M, Aminabhavi HTS *et al.* Densities, refractive indices, speeds of sound, and shear viscosities of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, and diethyl succinate in the temperature range from 298.15 to 318.15 K. J Chem Eng Data 1994; 39:251-260.
16. Roque R, Mariana HU *et al*, Densities and refractive indexes of binary mixtures in the system methyl isobutyl ketone-2-butanol Mathematical relations obtained. J Chem Eng Data 1980; 25:318-320.