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REFRACTIVE INDEX IN BINARY AND TERNARY MIXTURES WITH DIETHYLENE GLYCOL, 1,4-DIOXANE AND WATER BETWEEN 293.15 - 313. 15K

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S-au determinat experimental şi s-au corelat indicii de refracţie pentru amestecurile binare şi ternare cu apă, 1,4-dioxan şi dietilenglicol la 293.15 K, 303.15 K şi 313.15 K pe întreaga gamă de compoziţii. Pentru a calcula indicii de refracţie s-au utilizat ecuaţiile predictive Lorentz–Lorenz, Wiener, Heller, Gladstone–Dale, Arago–Biot si Edwards; s-a analizat acurateţea de calcul a acestora. Valorile măsurate experimental pot fi utilizate pentru a obţine dependenţa proprietate - compoziţie pentru amestecurile cu glicoli studiate.Ecuaţia Lorentz-Lorentz, cu un suport teoretic avansat, poate fi utilizată cu succes pentru toate sistemele.

Refractive indices for binary and ternary mixtures containing water, 1,4-dioxane and diethylene glycol were experimentally measured and correlated at 293.15 K, 303.15 K and 313.15 K over the entire range of compositions. Lorentz–Lorenz, Wiener, Heller, Gladstone–Dale, Arago–Biot and Edwards predictive equations were used to calculate the refractive index; their accuracy was analyzed. The experimental values can be used to obtain the property - composition dependences for the studied mixtures with glycols. The Lorentz–Lorenz equation having an advanced theoretical support can be used successfully for all systems.

Keywords: refractive index, prediction, diethylene glycol

1. Introduction

The knowledge of refractive index of liquid mixtures at different temperatures is an important step for their structural characterization. Along with other thermodynamic data, refractive index values are also useful for practical purposes in engineering calculations. Refractive index is useful to assess purity of substances, to calculate the molecular electronic polarizability [1], to estimate the

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boiling point with Meissner's [2] method or to estimate properties such as viscosity [3] and other thermodynamic properties.

This work continue our research on thermodynamic properties of systems with glycols [4,5] and presents experimental data concerning refractive indices of the binary and ternary systems containing water, 1,4-dioxane and diethylene glycol between 293.15 and 313.15 K. The data for 298.15 K were presented previously [6].

The systems with water and compounds containing hydroxyl groups, like glycols having both hydrophilic and hydrophobic groups, are commonly used as chemical and biochemical reaction media.

The most frequently employed equations to correlate the refractive index for liquid mixtures with specified composition are those of Lorentz-Lorenz, Wiener, Heller, Gladstone-Dale, Arago-Biot and Edwards [7]. Lorentz-Lorenz equation can be applied for large composition domains, the others are recommended for more diluted solutions. Wiener and Heller equations are valid only if the volumes are additive. Arago-Biot equations have the same advantages and disadvantages as Gladstone-Dale equation: they give the best results for systems with near-ideal behavior.

By our knowledge, the binary mixtures with water and glycols [8,9] are scarcely studied and the binary and ternary systems with 1,4–dioxane and diethylene glycol have not been yet studied.

2. Experimental

Chemicals. The analytical-reagent-grade 1,4-dioxane from Merck was distilled at 374.15 K to collect the middle fraction; the water was twice distilled and the diethylene glycol (DEG) from Merck was distilled at 473.15 K in vacuum (around 3.87 kPa).

The purity of the materials was checked by gas chromatographic analysis (over 99.5 mass %). The comparison with literature of refractive index values for pure components is presented in Table 1.

Apparatus and procedure. The mixtures with desired composition were prepared volumetrically. The accuracy of the mole fraction was estimated at ±0.002. All mixtures were completely miscible over the whole composition range. Refractive index of the mixtures at the sodium D-line was measured with Abbe refractometer, thermostated with ± 0.05 K accuracy. The precision of the measurements was ±0.0001. An average of triplicate measurements was considered.

Table 1:

Experimental and literature values of refractive index for pure compounds at 298.15 K

Refractive index, n_D	Pure compound		
	water	1,4-dioxane	diethylene glycol
Experimental	1.3324	1.4193	1.4424
Literature	1.3314 [10] 1.3325 [11] 1.3329 [12]	1.4200[13] 1.4201 [14]	1.4420 [15]

3. Results and discussions

The obtained experimental refractive index values for the binary systems: water + diethylene glycol, 1,4-dioxane + diethylene glycol and for ternary systems: water +1,4-dioxane +EG, water +1,4-dioxane + DEG at 293.15 K, 303.15 K and 313.15 are presented K in table 2. For 298.15 K, the variation of the refractive index with composition for water + 1,4-dioxane diethylene glycol ternary system is showed in Fig.1.

The obtained data were used to test the Lorentz-Lorenz, Wiener, Heller, Gladstone-Dale, Arago-Biot and Edwards mixing rules (Eqs. 1-6, respectively) in order to predict the refractive index of binary and ternary mixtures using refractive indices of pure components [16].

$$\frac{n^2-1}{n^2+2}=\varphi_1\frac{n_1^2-1}{n_1^2+2}+\varphi_2\frac{n_2^2-1}{n_2^2+2} \quad (1)$$

$$\frac{n^2-n_1^2}{n^2+2n_1^2}=\varphi_2\frac{n_2^2-n_1^2}{n_2^2+2n_1^2} \quad (2)$$

$$\frac{n-n_1}{n_1}=\frac{3}{2}\varphi_2\left(\frac{m^2-1}{m^2+2}\right) \quad m=n_2/n_1 \quad (3)$$

$$n-1=\varphi_1(n_1-1)+\varphi_2(n_2-1) \quad (4)$$

$$n=\varphi_1 n_1+\varphi_2 n_2 \quad (5)$$

$$\frac{n-1}{n}=\varphi_1\frac{n_1-1}{n_1}+\varphi_2\frac{n_2-1}{n_2} \quad (6)$$

In (1)-(6), n represents the refractive index of the mixture, n_1, n_2 are the refractive indices of pure components, φ_1, φ_2 are the volume fractions of components.

In order to evaluate the method accuracy, the standard deviation (σ) and the average percentage deviation (ε) were calculated as follows:

$$\sigma = \left[\frac{\sum_{i=1}^{n} (n_i^{exp} - n_i^{calc})^2}{n} \right]^{0.5} \tag{7}$$

$$\varepsilon = \frac{100}{n} \sum_{i=1}^{n} \frac{\left| n_i^{exp} - n_i^{calc} \right|}{n_i^{exp}} \tag{8}$$

where n_i^{exp}, n_i^{calc} are the experimental and calculated values and n are the number of experimental data.

The results of the predictive calculation for the refractive index, the standard deviation and average percentage deviation are presented in Table 3.

For the binary systems the method proposed by Lorentz-Lorenz, having an advanced theoretical support based on the additive property of the molar refractions of pure components, can be used with good results for all systems. Good results are obtained with Gladstone–Dale, Edwars, Heller and Wiener (very similar with Heller) models. Thus, the standard deviation range between 0.04 and 0.12, while the average percentage deviation, between 0.16 and 0.28, when using Lorentz-Lorenz equation.

For the ternary systems the best results are obtained, as in the case of binary systems, with Lorentz-Lorenz equation; appropriate results are given by Gladstone–Dale, Heller, Wiener and Edwards equations, cited in order of increasing error of calculation (0.3-0.7%).

Generally, the prediction for binary systems is better than for the ternary ones. From the Table 3 it can be seen that in all cases the Lorentz-Lorenz mixing rule gave the best results. In all cases the Arago-Biot equation gave poor prediction for both binary and ternary systems.

Table 2

Refractive index for binary and ternary mixtures at different temperatures

water (1)+ DEG (2)		1,4-dioxane (1) + DEG (2)		water(1)+1,4-dioxane(2)+DEG(3)					
X_1	n	X_1	n	X_1	X_2	n	X_1	X_2	n
T = 293.15 K									
0.0000	1.4427	0.0000	1.4427	0.1574	0.4213	1.4335	0.6993	0.2100	1.4059
0.0762	1.4411	0.1106	1.4406	0.3031	0.3521	1.4299	0.8498	0.1044	1.3898
0.1833	1.4386	0.2175	1.4385	0.4879	0.2576	1.4238	0.1446	0.2557	1.4390
0.2744	1.4362	0.3223	1.4364	0.6981	0.1511	1.4109	0.2960	0.2106	1.4358
0.3829	1.4330	0.4254	1.4343	0.8495	0.0751	1.3887	0.5008	0.1496	1.4277
0.4722	1.4300	0.5269	1.4322	0.1525	0.7157	1.4251	0.7006	0.0895	1.4134
0.5828	1.4239	0.6252	1.4301	0.3009	0.5891	1.4222	0.8501	0.0450	1.3908
0.7040	1.4132	0.7211	1.4281	0.5004	0.4178	1.4131	0.1465	0.1315	1.4418
0.8084	1.3986	0.8167	1.4261	0.7000	0.2503	1.4028	0.2993	0.1048	1.4381
0.8448	1.3912	0.9109	1.4241	0.8499	0.1249	1.3874	0.5010	0.0744	1.4308
0.8900	1.3802	1.0000	1.4222	0.1546	0.5914	1.4296	0.6015	0.2454	1.4159
0.9315	1.3662			0.2987	0.4889	1.4258	0.8492	0.0206	1.3928
0.9551	1.3559			0.5008	0.3484	1.4186			
0.9795	1.3428								
1.0000	1.3330								
T = 303.15 K									
0.0000	1.4421	0.0000	1.4421	0.1574	0.4213	1.4308	0.6993	0.2100	1.4026
0.0762	1.4401	0.1106	1.4395	0.3031	0.3521	1.4254	0.8498	0.1044	1.3777
0.1833	1.4378	0.2175	1.4370	0.4879	0.2576	1.4201	0.1446	0.2557	1.4353
0.2744	1.4356	0.3223	1.4345	0.6981	0.1511	1.4060	0.2960	0.2106	1.4321
0.3829	1.4328	0.4254	1.4320	0.8495	0.0751	1.3834	0.5008	0.1496	1.4108
0.4722	1.4296	0.5269	1.4295	0.1525	0.7157	1.4206	0.7006	0.0895	1.4108
0.5828	1.4229	0.6252	1.4270	0.3009	0.5891	1.4177	0.8501	0.0450	1.3878
0.7040	1.4129	0.7211	1.4245	0.5004	0.4178	1.4108	0.1465	0.1315	1.4391
0.8084	1.3983	0.8167	1.4220	0.7000	0.2503	1.3991	0.2993	0.1048	1.4359
0.8448	1.3907	0.9109	1.4194	0.8499	0.1249	1.3761	0.5010	0.0744	1.4278
0.8900	1.3794	1.0000	1.4170	0.1546	0.5914	1.4246	0.6015	0.2454	1.4114

0.9315	1.3654			0.2987	0.4889	1.4221	0.8492	0.0206	1.3894
0.9551	1.3552			0.5008	0.3484	1.4159			
0.9795	1.3425								
1.0000	1.3320								
				T = 313.15 K					
0.0000	1.4415	0.0000	1.4415	0.1574	0.4213	1.4289	0.6993	0.2100	1.4002
0.0762	1.4396	0.1106	1.4386	0.3031	0.3521	1.4220	0.8498	0.1044	1.3692
0.1833	1.4374	0.2175	1.4358	0.4879	0.2576	1.4175	0.1446	0.2557	1.4327
0.2744	1.4349	0.3223	1.4330	0.6981	0.1511	1.4024	0.2960	0.2106	1.4295
0.3829	1.4323	0.4254	1.4302	0.8495	0.0751	1.3796	0.5008	0.1496	1.4090
0.4722	1.4289	0.5269	1.4274	0.1525	0.7157	1.4174	0.7006	0.0895	1.4090
0.5828	1.4223	0.6252	1.4246	0.3009	0.5891	1.4146	0.8501	0.0450	1.3857
0.7040	1.4125	0.7211	1.4218	0.5004	0.4178	1.4093	0.1465	0.1315	1.4372
0.8084	1.3977	0.8167	1.4189	0.7000	0.2503	1.3965	0.2993	0.1048	1.4342
0.8448	1.3897	0.9109	1.4160	0.8499	0.1249	1.3680	0.5010	0.0744	1.4257
0.8900	1.3787	1.0000	1.4131	0.1546	0.5914	1.4212	0.6015	0.2454	1.4083
0.9315	1.3645			0.2987	0.4889	1.4195	0.8492	0.0206	1.3869
0.9551	1.3542			0.5008	0.3484	1.4140			
0.9795	1.3422								
1.0000	1.3300								

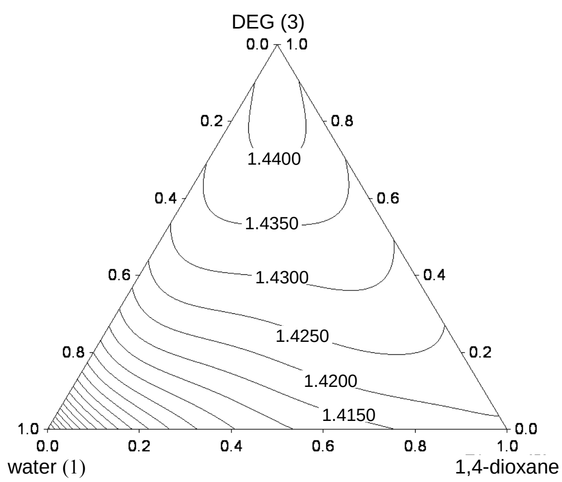

Fig. 1. Refractive index prediction versus composition for the ternary system water(1)+1,4-dioxane(2)+DEG(3) at 298.15K using Gladstone–Dale model

Table 3

Standard deviations (σ) and average percentage deviation (ε) as results of predictive models at different temperatures

System	T, K	Lorentz–Lorenz		Wiener		Heller		Gladstone–Dale		Arago –Biot		Edwards	
		$\sigma \cdot 10^2$	ε (%)	$\sigma \cdot 10^2$	ε (%)	$\sigma \cdot 10^2$	ε (%)	$\sigma \cdot 10^2$	ε (%)	$\sigma \cdot 10^2$	ε (%)	$\sigma \cdot 10^2$	ε (%)
water+ DEG	293.15	0.122	0.28	0.245	0.37	0.306	0.44	0.136	0.29	1.126	0.82	0.154	0.31
	303.15	0.103	0.26	0.255	0.37	0.313	0.44	0.114	0.27	1.079	0.81	0.136	0.29
	313.15	0.062	0.18	0.291	0.40	0.350	0.47	0.069	0.20	1.005	0.78	0.090	0.22
1,4-dioxane+ DEG	293.15	0.056	0.18	0.019	0.10	0.018	0.10	0.053	0.17	0.137	0.28	0.064	0.19
	303.15	0.044	0.16	0.005	0.05	0.003	0.04	0.042	0.16	0.132	0.28	0.051	0.17
	313.15	0.040	0.16	0.012	0.08	0.014	0.09	0.038	0.15	0.149	0.30	0.048	0.17
water+ 1,4-dioxane+ DEG	293.15	0.204	0.35	0.661	0.66	0.736	0.71	0.216	0.36	1.349	0.91	0.172	0.31
	303.15	0.380	0.41	0.461	0.55	0.526	0.60	0.361	0.38	1.928	1.12	0.468	0.49
	313.15	0.674	0.61	0.405	0.50	0.452	0.55	0.633	0.58	2.522	1.30	0.808	0.69

4. Conclusions

Two binary and one ternary systems containing diethylene glycol were studied in order to obtain the refractive index data at different temperatures (293.15 K, 303.15K and 313.15K). The experimental data were used to test the capability prediction of Lorentz-Lorenz, Wiener, Heller, Gladstone-Dale, Arago-Biot and Edwards models.

All prediction methods represent generally well the experimental data. The best results were obtained with Lorentz-Lorenz equation. As expected, the calculated refractive index with Arago-Biot equation is unsatisfactory.

The obtained data on refractive index are useful in determining the composition of binary and ternary mixtures with diethylene glycol.

R E F E R E N C E S

[1] *L.B. Kier, L.H. Hall*, "Molecular Conectivity in Chemistry and Drug Research", San Diego**,** Academic Press, 1976

[2] *C.E. Rechsteiner*, "Boiling Point, in Handbook of Chemical Property Estimation", W.J. Lyman, W.F. Reehl and D. H. Rosenblatt, Editors, Washington, American Chemical Society, 1990

[3] *R.T. Lagemann,* J. Am. Chem. Soc., **vol. 67**, 1945, pp. 498-499

[4] *O. Iulian, I. Nita, O. Ciocirlan, M. Catrinciuc, A. Fedeles*, Rev. Chimie, Bucuresti, **vol. 60**, no.9 , 2009, pp. 972-975

[5] *A. Fedeles, O. Ciocirlan, O. Iulian,*, UPB Sci. Bull., series B, **vol.71**, no.4, 2009, pp. 100-106

[6] *O. Iulian, A. Stefaniu, O. Ciocarlan*, 16th Romanian International Conference on Chemistry and Chemical Engineering, Sinaia, 9-12 sept. 2009, Romania, S-3 P-38, pp. S III. 139-147, ISBN: 978-606-521-349-4RICCCE

[7] *M. Catrinciuc, O. Iulian, I. Nita, M. Iosif,* Analele Universității „Ovidius" Constanța, Seria: Chimie, **vol. 2** (XVI), 2005, pp. 336–340

[8] *J. Allan, A.S. Teja*, Can. J. Chem. Eng., **vol. 69**, 1991, pp. 986–991

[9] *R.R. Dreisbach*, *A.K. Doolittle*, AIChE J., **vol. 6,** 1960, pp. 150, 153, 157

[10] *T.M. Aminabhavi, B. Gopalakrishna*, J. Chem. Eng. Data, **vol. 40**, 1995, pp. 856–861

[11] *N.G. Tsierkezos, I.E. Molinou*, J. Chem. Eng. Data, **vol**. **43**, 1998, pp. 989–993

[12] *B.S. Hawrylak Andrecyk, C.-E. Gabriel, K. Garcie, R. Palepu,* J. Solution Chem., **vol. 27**, 1998, pp. 827–841

[13] A. *Penas, E. Calvo, M. Pintos, A. Amigo, R. Bravo*, J. Chem. Eng. Data, **vol. 45***,* 2005, pp. 682–685

[14] *J.N. Nayak, M.I. Aralaguppi, T.M. Aminabhavi*, J. Chem. Eng. Data, **vol.48,** 2003, pp.1152–1156

[15] *R. M. Tombaugh, H.S. Choguill,* Water Trans. Kansas Acad. Sci.*,* **vol. 54**, 1951, pp. 411-419

[16] *A.Z. Tasic, B.D. Djordjevic, D.K. Grozdanic*, J. Chem. Eng. Data, **vol. 37,** 1992, pp. 310-313.