ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2010, *55*(8), 475-480

PROPERTY PREDICTION FOR BINARY AND TERNARY SYSTEMS WITH WATER, 1,4-DIOXANE AND ETHYLENE GLYCOL. II. REFRACTIVE INDEX

Olga IULIAN,[a] Amalia ŞTEFANIU,[b*] Oana CIOCÎRLAN[a] and Oana CROITORU[a]

[a] Dept. of Applied Physical Chemistry and Electrochemistry, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, 1 Polizu, 011061, Bucharest, Roumania
[b] Dept. of Pharmaceutical Biotechnologies, National Institute For Chemical - Pharmaceutical Research and Development – ICCF Bucharest, 112 Vitan Avenue, 031299, Bucharest, Roumania

Received February 12, 2010

Binary and ternary mixtures containing water, 1,4-dioxane and ethylene glycol were studied in order to experimentally determine and to calculate the refractive index properties at different temperatures (293.15 K, 303.15 K and 313.15 K) of the entire range of composition. Predictive equations such as Lorentz–Lorenz, Wiener, Heller, Gladstone–Dale, Arago–Biot and Edwards were used to calculate the refractive index properties and the accuracy of these methods was analyzed. The results can be used to obtain the property - composition curves for the studied mixtures with ethylene glycol. The Lorentz–Lorenz method with an advanced theoretical support can be used successfully for all systems.

INTRODUCTION

This work continue our research on thermodynamic properties of systems with glycols[1] and presents experimental data concerning refractive indices of the binary and ternary systems containing water, 1,4-dioxane and ethylene glycol between 293.15 and 313.15 K. The data for 298.15 K has been presented previously.[2]

The knowledge of refractive index property at different temperatures of liquid mixtures is an important step for their structure 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,[3] to estimate the boiling point with Meissner's[4] method or to estimate other properties such as viscosity[5] and other thermodynamic properties.

The studied systems have industrial utility; the water + organic type solvents are frequently used as chemical and biochemical reaction media. For managing the chemical process it is important to understand the influence on mixture behaviour of water and the compounds containing hydroxyl groups, the glycols having both hydrophilic and hydrophobic groups on property values.

In order to correlate the refractive index for liquid mixtures of a specified composition, the mixing rules of Lorentz-Lorenz, Wiener, Heller, Gladstone-Dale, Arago-Biot and Edwards are most frequently employed.[6] Lorentz-Lorenz equation can be applied to large areas of composition, the others are recommended to more diluted solutions. Wiener and Heller equations are valid only if the volumes are additive. Arago-Biot equations have the same advantages and disadvantages with the Gladstone-Dale equation: they gives the best results for systems with the behavior similar to the ideal comportment.

To our knowledge, a literature study shows that information regarding refractive indices is limited for binary mixtures with ethylene glycol[7,8] and

* Corresponding author: astefaniu@gmail.com

there are no literature data for ternary systems: water(1) + 1,4-dioxane(2) + ethylene glycol(3).

EXPERIMENTAL

Chemicals. The analytical-reagent-grade 1,4-dioxane from Merck was distilled at 374.15 K to collect the middle fractions; the water was distilled twice and the analytical-reagent-grade ethylene glycol (EG) from Merck p.a. was used without further purification.

The purity of the materials was checked by the means of gas chromatographic analysis. It was better than 99.5 mass%. The comparison between literature values and the pure component values of refractive index measured in this work is presented in Table 1.

Apparatus and procedure. The mixtures of the 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 indices of the mixtures at the sodium D-line were 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

Comparison of refractive indices of pure compounds with the literature data at 298.15 K

Refractive index, n_D	Pure compound		
	water	1,4-dioxane	ethylene glycol
Experimental	1.3324	1.4193	1.4300
Literature	1.3314 [9] 1.3325 [10] 1.3329 [11]	1.4200 [12] 1.4201 [13]	1.4306 [14] 1.4307 [13] 1.4310 [10]

RESULTS AND DISCUSSION

The obtained experimental refractive index data in this work for the binary systems: water (1) + ethylene glycol (2), 1,4-dioxane (1) + ethylene glycol (2), water (1)+1,4-dioxane (2) and for ternary system: water (1) +1,4-dioxane (2) +EG (3) are shown in Table 2.

The obtained data were used to test the mixing rules of Lorentz-Lorenz, Wiener, Heller, Gladstone-Dale, Arago-Biot and Edwards (Eqs. 1-6, respectively) to predict the refractive index of binary and ternary mixtures using refractive indices of pure components.[15]

$$\frac{n^2-1}{n^2+2}=\sum_{i=1}^{r}\varphi_i\frac{n_i^{\,2}-1}{n_i^2+2}\;;\ \mathrm{i}=1,2,3;\ \mathrm{r}=2,3 \tag{1}$$

$$\frac{n^2-n_1^2}{n^2+2n_1^2}=\varphi_2\frac{n_2^2-n_1^2}{n_2^2+2n_1^2};\ \frac{n^2-n_1^2}{n^2+2n_1^2}=\varphi_2\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}+\varphi_3\frac{n_3^2-n_1^2}{n_3^2+2n_1^2} \tag{2}$$

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

$$\frac{n-n_1}{n_1}=\frac{3}{2}\varphi_2\left(\frac{m^2-1}{m^2+2}\right)+\frac{3}{2}\varphi_3\left(\frac{p^2-1}{p^2+2}\right);\ m=\frac{n_2}{n_1}\ \text{and}\ p=\frac{n_3}{n_1} \tag{3b}$$

$$(n-1)=\sum_{i=1}^{r}\varphi_i(n_i-1);\ \mathrm{i}=1,2,3;\ \mathrm{r}=2,3 \tag{4}$$

$$n=\sum_{i=1}^{r}\varphi_i n_i\;;\ \mathrm{i}=1,2,3;\ \mathrm{r}=2,3 \tag{5}$$

$$\frac{n-1}{n}=\sum_{i=1}^{r}\varphi_i\frac{n_i-1}{n_i};\ \mathrm{i}=1,2,3;\ \mathrm{r}=2,3 \tag{6}$$

n represents the refractive index of the mixture, n_i are refractive indices of pure components, φ_i are volume fractions of components.

In order to evaluate the accuracy of the methods, the standard deviation (σ) and the percent error (ε) was calculated:

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

$$\varepsilon = \frac{Y_i^{exp} - Y_i^{calc}}{Y_i^{exp}} 100 \quad (8)$$

Y_i^{exp}, Y_i^{calc} are the experimental and calculated values, n are the number of experimental data and m is the number of parameters.

The results of the predictive calculation for refractive index, the standard deviation and percent error defined by equations 7 and 8, are presented in Table 3.

Table 2

Refractive indices for binary and ternary mixtures at 293.15 K, 303,15 K and 313,15 K

water (1) + EG (2)		1,4-dioxane (1) + EG (2)		water (1) + 1,4-dioxane (2)		water (1)+1,4-dioxane (2)+EG (3)					
X_1	n	X_1	n	X_1	n	X_1	X_2	n	X_1	X_2	n
T = 293.15 K											
0.0000	1.4318	0.0000	1.4318	0.0000	1.4222	0.1465	0.4273	1.4234	0.8500	0.1048	1.3762
0.0941	1.4285	0.0998	1.4304	0.1007	1.4201	0.3031	0.3482	1.4190	0.1474	0.2559	1.4252
0.2006	1.4250	0.1987	1.4292	0.1995	1.4185	0.4976	0.2507	1.4111	0.2984	0.2104	1.4202
0.2452	1.4230	0.2991	1.4281	0.3422	1.4152	0.6987	0.1507	1.3962	0.5000	0.1501	1.4112
0.3963	1.4167	0.3977	1.4271	0.4256	1.4138	0.8492	0.0754	1.3752	0.6999	0.0900	1.3953
0.5010	1.4102	0.4977	1.4261	0.5379	1.4093	0.1504	0.7191	1.4205	0.8498	0.0451	1.3738
0.5984	1.4030	0.6012	1.4252	0.6640	1.4026	0.2963	0.5923	1.4174	0.1497	0.1303	1.4261
0.7039	1.3925	0.7017	1.4244	0.7530	1.3956	0.4988	0.4214	1.4104	0.3006	0.1047	1.4211
0.8072	1.3780	0.8006	1.4236	0.8197	1.3858	0.7005	0.2494	1.3978	0.4995	0.0752	1.4110
0.8992	1.3602	0.9003	1.4229	0.8710	1.3772	0.8504	0.1250	1.3779	0.6990	0.0453	1.3944
1.0000	1.3330	1.0000	1.4222	0.9130	1.3667	0.1502	0.5949	1.4219	0.8493	0.0199	1.3721
				0.9470	1.3555	0.3007	0.4901	1.4172	0.0534	0.8976	1.4215
				0.9760	1.3441	0.5021	0.3491	1.4105	0.0551	0.0491	1.4299
				1.0000	1.3330	0.7012	0.2096	1.3971	0.9496	0.0252	1.3511
T = 303.15 K											
0.0000	1.4287	0.0000	1.4287	0.0000	1.4170	0.1465	0.4273	1.4199	0.8500	0.1048	1.3747
0.0941	1.4265	0.0998	1.4273	0.1007	1.4155	0.3031	0.3482	1.4152	0.1474	0.2559	1.4218
0.2006	1.4229	0.1987	1.4259	0.1995	1.4138	0.4976	0.2507	1.4078	0.2984	0.2104	1.4171
0.2452	1.4212	0.2991	1.4246	0.3422	1.4109	0.6987	0.1507	1.3933	0.5000	0.1501	1.4079
0.3963	1.4145	0.3977	1.4234	0.4256	1.4085	0.8492	0.0754	1.3731	0.6999	0.0900	1.3920
0.5010	1.4085	0.4977	1.4223	0.5379	1.4049	0.1504	0.7191	1.4168	0.8498	0.0451	1.3720
0.5984	1.4012	0.6012	1.4212	0.6640	1.3990	0.2963	0.5923	1.4136	0.1497	0.1303	1.4230
0.7039	1.3904	0.7017	1.4201	0.7530	1.3909	0.4988	0.4214	1.4068	0.3006	0.1047	1.4179
0.8072	1.3768	0.8006	1.4191	0.8197	1.3827	0.7005	0.2494	1.3945	0.4995	0.0752	1.4081
0.8992	1.3591	0.9003	1.4181	0.8710	1.3742	0.8504	0.1250	1.3752	0.6990	0.0453	1.3921

1.0000	1.3320	1.0000	1.4170	0.9130	1.3637	0.1502	0.5949	1.4179	0.8493	0.0199	1.3703
				0.9470	1.3534	0.3007	0.4901	1.4141	0.0534	0.8976	1.4165
				0.9760	1.3428	0.5021	0.3491	1.4071	0.0551	0.0491	1.4269
				1.0000	1.3320	0.7012	0.2096	1.3939	0.9496	0.0252	1.3493
T = 313.15 K											
0.0000	1.4260	0.0000	1.4260	0.0000	1.4131	0.1465	0.4273	1.4166	0.8500	0.1048	1.3718
0.0941	1.4235	0.0998	1.4245	0.1007	1.4110	0.3031	0.3482	1.4122	0.1474	0.2559	1.4189
0.2006	1.4202	0.1987	1.4231	0.1995	1.4100	0.4976	0.2507	1.4049	0.2984	0.2104	1.4144
0.2452	1.4188	0.2991	1.4217	0.3422	1.4075	0.6987	0.1507	1.3911	0.5000	0.1501	1.4063
0.3963	1.4120	0.3977	1.4204	0.4256	1.4053	0.8492	0.0754	1.3709	0.6999	0.0900	1.3899
0.5010	1.4060	0.4977	1.4192	0.5379	1.4012	0.1504	0.7191	1.4123	0.8498	0.0451	1.3695
0.5984	1.3985	0.6012	1.4179	0.6640	1.3951	0.2963	0.5923	1.4092	0.1497	0.1303	1.4204
0.7039	1.3882	0.7017	1.4167	0.7530	1.3880	0.4988	0.4214	1.4032	0.3006	0.1047	1.4158
0.8072	1.3745	0.8006	1.4155	0.8197	1.3798	0.7005	0.2494	1.3909	0.4995	0.0752	1.4058
0.8992	1.3575	0.9003	1.4143	0.8710	1.3703	0.8504	0.1250	1.3722	0.6990	0.0453	1.3897
1.0000	1.3300	1.0000	1.4131	0.9130	1.3617	0.1502	0.5949	1.4139	0.8493	0.0199	1.3682
				0.9470	1.3516	0.3007	0.4901	1.4108	0.0534	0.8976	1.4128
				0.9760	1.3409	0.5021	0.3491	1.4038	0.0551	0.0491	1.4241
				1.0000	1.3300	0.7012	0.2096	1.3909	0.9496	0.0252	1.3480

An example for the variation of the refractive index with composition is illustrated in Fig. 1 which present the calculated refractive indices with Gladstone-Dale equation for ternary systems: water (1)+1,4-dioxane (2)+ethylene glycol (3) at 298.15 K.

For 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, standard deviations and the percent error using Lorentz-Lorenz equation range from 0.05 at 0.12, respectively 0.16 at 0.28. Poor results are obtained with the Biot-Arago model, especially in the case of 1.4-dioxane with ethylene glycol or water. Generally, the results for binary systems are better than for ternary mixtures.

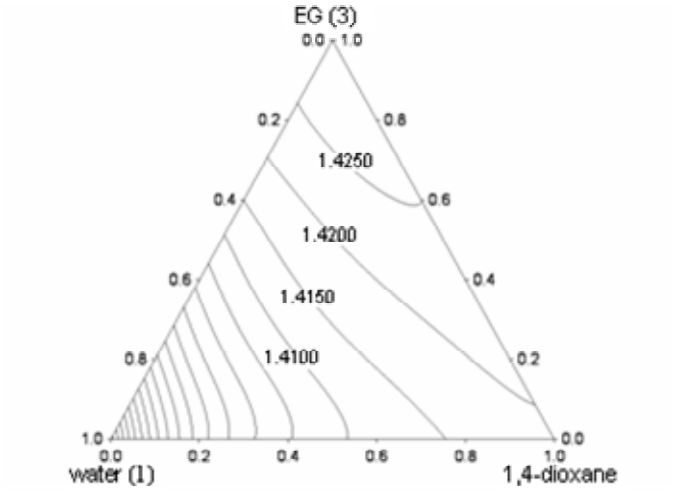

Fig. 1 – Refractive index versus composition for the ternary system water (1)+1,4-dioxane(2)+EG(3) at 298.15K, (—) prediction with Gladstone–Dale model.

Table 3

Results of prediction standard deviations (σ) and percent error (ε) with different models at 293.15 K, 303,15 K and 313,15 K

System	T, K	Model											
		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+ EG	293.15	0.108	0.26	0.189	0.32	0.238	0.39	0.118	0.27	0.925	0.75	0.134	0.29
	303.15	0.073	0.21	0.231	0.37	0.286	0.43	0.082	0.21	0.947	0.75	0.104	0.25
	313.15	0.102	0.25	0.233	0.37	0.286	0.43	0.106	0.25	1.065	0.80	0.144	0.30
1,4-dioxane+ EG	293.15	0.126	0.28	0.007	0.06	0.007	0.06	0.110	0.26	0.384	0.49	0.159	0.31
	303.15	0.107	0.26	0.046	0.17	0.047	0.17	0.088	0.23	0.411	0.50	0.144	0.30
	313.15	0.116	0.27	0.068	0.20	0.068	0.20	0.094	0.24	0.483	0.55	0.161	0.32
water+ 1,4-dioxane	293.15	0.090	0.23	0.432	0.49	0.462	0.53	0.073	0.21	1.413	0.93	0.167	0.33
	303.15	0.068	0.20	0.404	0.48	0.434	0.51	0.052	0.17	1.300	0.89	0.142	0.30
	313.15	0.048	0.16	0.398	0.48	0.427	0.51	0.040	0.15	1.173	0.84	0.104	0.25
water+ 1,4-dioxane+ EG	293.15	0.190	0.35	0.285	0.42	0.337	0.48	0.174	0.34	1.472	0.97	0.271	0.42
	303.15	0.242	0.40	0.297	0.44	0.349	0.49	0.214	0.38	1.682	1.05	0.344	0.48
	313.15	0.335	0.48	0.299	0.44	0.348	0.48	0.293	0.44	1.984	1.16	0.461	0.56

From the Table 3, it can be seen that in all cases the Lorentz-Lorenz mixing rule give the best results.

For the ternary system 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 – 0.5%).

The Arago-Biot equation gives in all cases poor prediction for the refractive indices of both binary and ternary systems.

The influence of the temperature is not conclusive.

CONCLUSIONS

The refractive indices for three binary and one ternary systems were measured at various temperatures (293.15 K, 303.15 K and 313.15 K).

The experimental data were utilized to test the capability prediction of Lorentz-Lorenz, Wiener, Heller, Gladstone-Dale, Arago-Biot and Edwards models.

Generally, the prediction methods represent well the experimental data. The calculated values with Lorentz-Lorenz equation agree very well with the experimental data. As could be expected, calculated refractive indices with Arago-Biot equation are unsatisfactory.

The obtained data on refractive index *versus* molar fraction are practically useful in determining the composition of binary and ternary mixtures with glycols.

REFERENCES

1. O. Iulian, I. Niță, O. Ciocîrlan, M. Catrinciuc and A. Fedeleș, *Rev. Chim. (Bucureşti*), **2009**, *60*, 972-975.
2. O. Iulian, A. Ştefaniu and O. Ciocîrlan, *RICCCE XVI*, 9-12 sept. **2009**, Sinaia, Roumania, P-38, p. S III. 139-147, ISBN: 978-606-521-349-4RICCCE.
3. L.B. Kier and L.H. Hall, "Molecular Connectivity in Chemistry and Drug Research", San Diego**,** Academic Press, 1976.
4. C.E. Rechsteiner, "Boiling point", in "Handbook of Chemical Property Estimation", W.J. Lyman, W.F. Reehl and D. H.Rosenblatt (Eds.), American Chemical Society, Washington, 1990.
5. R.T. Lagemann*, J. Am. Chem. Soc*., **1945,** *67*, 498-499.
6. M. Catrinciuc, O. Iulian, I. Niță and M. Iosif*, Analele Universității "Ovidius" Constanța*, *seria Chimie*, **2005**, *2,* 336–340.

7. J. Allan and A.S. Teja, *Can. J. Chem. Eng.,* **1991**, *69*, 986–991.
8. A.M. Awwad, A.H. Al-Dujaili and H.E. Salman, *J. Chem. Eng. Data*, **2002**, *47,* 421–424.
9. T.M. Aminabhavi and B. Gopalakrishna, *J. Chem. Eng. Data*, **1995**, *40,* 856–861.
10. N.G. Tsierkezos and I.E. Molinou*, J. Chem. Eng. Data*, **1998**, *43*, 989–993.
11. B.S. Hawrylak Andrecyk, C.-E. Gabriel, K. Garcie and R. Palepu, *J. Solution Chem*., **1998**, *27*, 827–841.
12. A. Penas, E. Calvo, M. Pintos, A. Amigo and R. Bravo, *J. Chem. Eng. Data*, **2005**, *45*, 682–685.
13. J.N. Nayak, M.I. Aralaguppi and T.M. Aminabhavi, *J. Chem. Eng. Data*, **2003**, *48*, 1152–1156.
14. J.A. Riddick, W.B. Bunger and T.K. Sakano, "Techniques of Organic Chemistry", vol. II., John Wiley and Sons, New York, 1985.
15. A.Z. Tasic, B.D. Djordjevic and D.K. Grozdanic, *J. Chem. Eng. Data*, **1992**, *37*, 310-313.