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Study Of Refractive Indices Of Binary Mixtures Composed Of Green Solvents Ethyl Lactate And Iso Propyl Alcohol

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Abstract: *Experimental liquids are chosen in green context. Refractive index is one of the fundamental properties used to characterize pure liquids and their mixtures. This paper presents the experimental data of refractive index of the binary liquid mixtures composed of green solvents ethyl lactate and iso propyl alcohol in the temperature range 303.15 to 318.15 K at an interval of 5 K and atmospheric pressure over the entire composition range. Deviation in refractive index as a function of volume fraction is computed and fitted to the Redlich–Kister type polynomial equation to obtain the binary coefficients and the standard deviations. Experimental data is used to test the applicability of different mixing rules for the system under investigation.*
Keywords*: binary liquid mixtures, green solvents, mixing rules,refractive index*

I. Introduction

Environment protection is one of the global challenges that needs to be constantly assessed. The manufacture, application and end usage of various consumer products used for the comfortable living can cause a potential toxic effect on human health and the environment.Chemical industries use many organic solvents at various stages like compound synthesis, separation, purification and transformation into end product. Solvents play key role in chemical analytical methods also. Most of the solvents used in industries are toxic and cause occupational health, safety and environmental problems. 'Green Chemistry', a new and safer approach for the synthesis and design of chemical processes and compounds is evolved to minimize or eliminate the risk of pollution on biosphere. It promotes the idea of green solvents (non toxic, benign to environment), replacement with safer solvent alternatives based on the 12 basic principles of green chemistry [1]. It is an essential driving force for the sustainable chemical processes [2].Development and the characterization of physico-chemical properties of green solvents is a continuous process in the field of science and technology. The knowledge of densities, refractive indices, viscosities, derived acoustic and thermodynamic parameters, solvent behaviour, molecular interactions and binding forces in pure and liquid mixtures is essential for any chemical industry in process design, transport equipment and engineering applications.

The present work is a continuation of our research on evaluation of thermo-physical properties (acoustic, volumetric, optical and spectral) of industrially significant green solvents and their binary liquid mixtures [3-5]. Solvent under investigation in this work are ethyl lactate (EL) and isopropyl alcohol (IPA). Both solvents are considered green [6]with wide spread applications. EL is 100% biodegradable with negligible eco-toxicity [7] and can be obtained from renewable feed stocks [8,9]. It is a promising bio-compatible media for organic synthesis [10] and a replacing solvent for NMP, toluene, xylene etc. [11]. On the other hand, IPA is used as a solvent for gums, shellac, essential oils, creosote and resins, for extraction of alkaloids etc. and also finds applications as de-icing agent for liquid fuels, dehydrating agent and synthetic flavouring adjuvant. Most of the commercial products have IPA as aco-solvent.

Owing to the industrial significance of the chosen solvents and unavailability of experimental data, the present work explores the study on refractive index measurement and its variation as a function of temperature and composition for the system (EL+IPA) under study.

II. Experimental

2.1. Chemicals

Ethyl lactate obtained from Fluka with 99.5 mole fraction purity is purified by distillation at 50 Torr [12]. Iso propyl alcohol from Sigma Aldrich with 99.5 mole fraction purity is dried first with calcium chloride followed by careful fractional distillation.

2.2. Apparatus and procedure

2.2.1. Sample preparation

Different compositions of binary liquid mixtures are freshly prepared gravimetrically on an electronic balance Citizon CX 285 N with an accuracy of 1×10^{-5} g, with readability 0.01/0.1 mg and repeatability (+/−) 0.03/0.1 mg and stored in air tight bottles to avoid mass loss on evaporation and absorption of atmospheric gases.

2.2.2. Measurement of Refractive Index

The refractive indices of pure liquids and their binary mixtures are measured at 589.3 nm using an automatic refractometer Abbemat HP (RXA170, Anton Paar, Austria) with a temperature controller that keeps the samples at working temperature. Calibration of the instrument before each series of measurement is carried out by measuring the refractive index of Millipore quality water and tetrachloroethylene according to operating manual instructions. The uncertainties in temperature and refractive index measurements are estimated to be within ±0.02 K and $\pm 4 \times 10^{-5}$ respectively.

For the system under study, data on density and ultrasonic velocity were reported elsewhere [3]. All experimental measurements are made at temperatures from 303.15 to 318.15 K with an interval of 5 K and at atmospheric pressure over the whole composition range. The experimental data on refractive index is given in Table 1.

Table 1: Experimental refractive indices (n) for the binary mixtures of EL with IPA at T = (303.15, 308.15, 313.15 and 318.15) K.

x1	Refractive index (n)			
	303.15K	308.15K	313.15K	318.15K
0.0000	1.3735	1.3714	1.3676	1.3651
0.0758	1.3795	1.3779	1.3746	1.3735
0.1517	1.3846	1.3832	1.3804	1.3790
0.2265	1.3890	1.3876	1.3850	1.3834
0.3105	1.3931	1.3917	1.3892	1.3876
0.4027	1.3970	1.3956	1.3932	1.3916
0.4960	1.4000	1.3986	1.3963	1.3947
0.6121	1.4029	1.4015	1.3993	1.3977
0.7327	1.4054	1.4036	1.4014	1.3997
0.8610	1.4072	1.4051	1.4030	1.4005
1.0000	1.4084	1.4061	1.4038	1.4014

III. Theory

Refractive index deviation is calculated on volume fraction basis as below.

$$\Delta_{\phi} n = n - n^{id} \qquad (1)$$

Where n^{id} is the refractive index for ideal mixture and is given by the relation:

$$n^{id} = \phi_1 n_1 + \phi_2 n_2 \qquad (2)$$

Where n_1, n_2 are the refractive indices of pure components 1 (EL) and 2 (IPA) respectively.

3.1 Refractive Index mixing rules

A number of mixing rules of refractive index have been proposed for liquid mixtures in terms of the refractive indices of the pure components. The accuracy of different mixing rules in the prediction of the refractive index of binary mixtures of (EL+IPA) is evaluated using the following equations.

Arago-Biot [13] proposed the simplest equation for predicting refractive index of the mixture by considering the direct volume fraction average of the refractive index of each component n_i, and is expressed as below.

$$n = \sum_{i=1}^{2} n_i \phi_i \qquad (3)$$

The Gladstone-Daleequation [14, 15]accounts for the effect of volume changeupon mixing and is given below.

$$n - 1 = \sum_{i=1}^{2} (n_i - 1)\phi_i \qquad (4)$$

Considering volume additivity, Newton equation[16] takes the following form.

$$n^2 - 1 = \sum_{i=1}^{2} (n_i^2 - 1)\phi_i \qquad (5)$$

Eyring and John [17] relation is given by

$$n = n_1 \phi_1^2 + 2(n_1 n_2)^{1/2} \phi_1 \phi_2 + n_2 \phi_2^2 \qquad (6)$$

The most systematic mixing rule is the Lorentz-Lorenz equation [18], based on an argument that led to the Clausius-Mossotti equation for the dielectric constant of polarizable molecules which assumes ideal mixing of thepolarizability.

$$\frac{n^2-1}{n^2+2}=\sum_{i=1}^{2}\left(\frac{n_i^2-1}{n_i^2+2}\right)\phi_i \quad (7)$$

Based on the measurement of light scattering, Heller [19]proposed a new mixing rule as below.

$$\frac{n-n_1}{n_1}=\frac{3}{2}\left(\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right)\phi_2 \quad (8)$$

Another mixing rule proposed by Eykman [20] is given as below.

$$\frac{n^2-1}{n^2+0.4}=\sum_{i=1}^{2}\left(\frac{n_i^2-1}{n_i^2+0.4}\right)\phi_i \quad (9)$$

Oster [21] relation is given by

$$\frac{\left(n^2-1\right)\left(2n^2+1\right)}{n^2}=\sum_{i=1}^{2}\left(\frac{\left(n_i^2-1\right)\left(2n_i^2+1\right)}{n_i^2}\right)\phi_i \quad (10)$$

Wiener equation [22] takes the following form

$$\frac{n^2-n_1^2}{n^2+2n_1^2}=\left(\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right)\phi_2 \quad (11)$$

The Average Absolute Deviation (APD, %) of experimental refractive index is calculated by the relation

$$AAD=\frac{100}{n}\sum_{i=1}^{n}\left(\left|\frac{n_{cal}}{n_{\exp}}-1\right|\right) \quad (12)$$

where $n_{\exp}$ is experimental refractive index and n_{cal} is the value calculated from various mixing rules and 'n' is the number of data points.

The Maximal deviation (*M Dev*) is given by

$$MDev=100*\max\left|\frac{n_{cal}}{n_{\exp}}-1\right| \quad (13)$$

IV. Results And Discussion

It is evidentfrom Table 1 that refractive index decreases with increase in temperature and increases with the increased mole fraction of ethyl lactate.Refractive index deviation ($\Delta_{\phi}n$) function is calculated on a volume fraction basis as suggested byBrocos et.al, [23] and its variation with volume fraction and temperature is represented in Fig. 1. Refractive index deviation is observed positive (Fig. 1) over the entire composition and at the experimental temperatures.

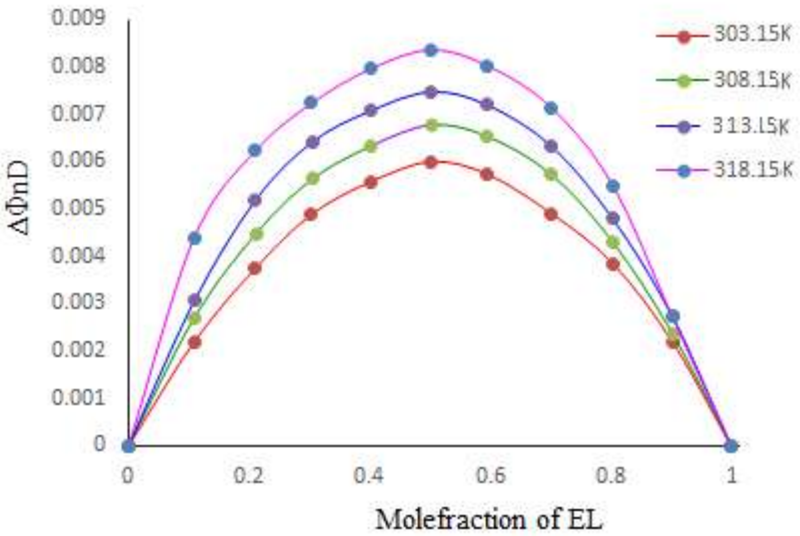

Fig.1.Variationof refractive index deviation ($\Delta_{\phi} n$) function withmolefractionof EL(x_1)

The behaviour of $\Delta_{\phi} n$ as a function of mole fraction is similar to that of V_m^E [3] which suggested the operation of disruptive forces upon mixing. The refractive index deviation has also been fitted with the Redlich-Kister polynomial smoothing equation and fitting parameters are given in Table 2.

Table 2: Coefficients of the Redlich–Kister equation, together with the standard deviations of $\Delta_{\phi} n$ for the binary mixtures of EL with IPA at T= (303.15, 308.15, 313.15 and 318.15) K.

Property	T /K	A0	A1	A2	A3	A4	□
n	303.15	0.023988	-0.00011	-0.00606	-0.00199	0.008994	7.86E-05
	308.15	0.027084	-0.00153	-0.00118	0.003368	0.002792	4.87E-05
	313.15	0.029886	-6.3E-06	0.002443	0.000582	-0.00045	6.53E-05
	318.15	0.033424	-0.00295	0.003796	0.019576	0.006724	0.000125

The accuracy of different mixing rules in the prediction of the refractive index of binary mixtures of (EL+IPA) is tested by the equations proposed by Arago–Biot (A-B), Gladstone – Dale (G-D), Newton (Nw), Eyring-John (E-J), Lorentz– Lorenz (L-L), Heller, Eykman (Eyk), Oster and Wiener. Average absolute deviations (AAD ,%) and maximal deviation ($MDev$) quantities have been analyzedto estimate the predicting abilitiesof different mixing rules, and are given in Table 3.

Table 3: Average absolute deviation (AAD,%) for the predictive estimation of refractive index of (EL+IPA) mixtures using different equations

T/K	Deviations	A-B	G-D	Nw	E-J	L-L	Heller	Eykman	Oster	Wiener
303.15	AAD	0.25460	0.25460	0.24986	0.25697	0.25919	0.59045	0.26558	0.26883	0.25608
	Mdev	0.42928	0.42928	0.42144	0.43320	0.43685	0.82144	0.44742	0.45279	0.43172
308.15	AAD	0.29234	0.29234	0.28764	0.29469	0.29687	0.62468	0.30321	0.30644	0.29380
	Mdev	0.48527	0.48527	0.47750	0.48916	0.49276	0.87014	0.50324	0.50858	0.48769
313.15	AAD	0.32820	0.32820	0.32308	0.33076	0.33311	0.67530	0.34003	0.34356	0.32979
	Mdev	0.53629	0.53629	0.52783	0.54052	0.54440	0.94777	0.55584	0.56167	0.53891
318.15	AAD	0.37663	0.37663	0.37147	0.37921	0.38156	0.72369	0.38854	0.39211	0.37823
	Mdev	0.60058	0.60058	0.59205	0.60484	0.60873	1.00789	0.62027	0.62618	0.60322

From the table it is evident that the best prediction ability (lower AAD) corresponds to Newton equation at all experimental temperatures. MDev values alsosupport the same. Except Heller, all other mixing rules have very close predicting abilities suggesting that the proposed equations satisfactorily correlates the refractive index with experimental temperatures and whole composition range.

V. Conclusions

Refractive indices of the binary mixtures of ethyl lactate with isopropyl alcohol are determined experimentally at temperatures from 303.15 to 318.15 K over the entire composition range. Deviation in refractive index is computed and analyzed interms of operating forces prevailing in the mixtures. Deviation parameter is fitted to Redlich–Kister type polynomial equation. Predicting abilities of different mixing rules are evaluated by computing AAD, MDev parameters. Except Heller, all other mixing rules have very close predicting abilities of refractive index and the one suggested by Newton is the best.

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