

(An ISO 3297: 2007 Certified Organization) Vol. 4, Issue 12, December 2015

Refractive Properties for Binary Mixtures Containing DEC + o-xylene or m-xylene or pxylene

Srilakshmi Mandava^{1,*}, Narendra Kolla¹, Kavitha Chagarlamudi², Sarath Babu Anne³, Ratnakar Abbineni^{4,*}

Assistant Professor, Department of Chemistry, V. R. Siddhartha Engineering College, Vijayawada, India^{1,*} Assistant Professor, Department of Physics, V. R. Siddhartha Engineering College, Vijayawada, India¹ Assistant Professor, Department of Chemistry, V. R. Siddhartha Engineering College, Vijayawada, India² Associate Professor, Department of Chemical Engineering, NIT, Warangal, India³

Professor, Department of Chemistry, V. R. Siddhartha Engineering College, Vijayawada, India⁴

ABSTRACT: Refractive indices, n_D , and densities, ρ , of binary mixtures of diethyl carbonate (DEC) with o-xylene, mxylene, p-xylene have been measured by a Abbe refractometer and Anton Paar DSA 5000 density and sound analyser respectively at T = (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K. Some empirical and theoretical relations like Arago-Biot (A-B), Eykman (E), Eyring and John (E-J), Gladstone-Dale (G-D), Heller (H), Lorentz-Lorentz (L-L), Newton (N), Oster (Os) and Weiner (W) have been applied to study the dependence of the measured and derived quantities on temperature and on binary composition. Furthermore, refractive index deviations, Δn_D , molar refraction, R, and molar refraction deviation, ΔR have been examined, in order to identify the presence of solvent-cosolvent adducts in these binary solvent systems. The results obtained have been interpreted on the basis of specific intermolecular interactions between different species.

KEYWORDS: diethyl carbonate, refractive index, xylene, binary system, refractive index mixing rules.

I. INTRODUCTION

As a part of a study on thermodynamic and physico-chemical properties of binary liquid mixtures containing DEC as one of the components [1-3], we report here some investigations about refractive properties (and some related parameters) of binary liquid mixtures of DEC with o-xylene or m-xylene or p-xylene at different temperatures, T = (298.15 to 323.15) K.

Diethyl carbonate (DEC), the second member of dialkyl carbonates, provides an interesting case study for understanding conformational preferences in molecules containing the ethoxy groups, such as esters. The study of DEC is important because they are widely used [4-6] as ethylating and carbonylating reagents in organic synthesis. It is likewise utilized as solvents of nitro-cotton, cellulose ether, synthetic resin and natural resin in the textile printing and dyeing industry. It is utilized for preparing electrolyte in the capacitor and lithium battery. In the pharmaceutical industry, it is the basic ingredient of hard and is used to synthesize intermediate phenobarbital etc. It can also be used as fuel and lube additive, and finds application in the paint and plastic industry. Mixed xylenes are used as solvents and in the printing, rubber and leather industries. However, most mixed xylenes are separated and the individual isomers consumed in specific end-uses. P-xylene is used as a feedstock for terephthalic acid, a key component in polyethylene terephthalate (PET) resins. O-xylene is used in plasticisers, medicines, and dyes. Mixed xylenes are also a desirable gasoline, but are blended less often than toluene because there is a greater demand and higher value in their chemical applications.



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Refractive index deviations, molar refractions, molar refraction deviations were calculated from experimental data; the obtained results have been discussed in terms of the nature of the components of the mixture and the specific interactions between them. We have also applied several common mixing rules: Arago-Biot [7], Eykman [8], Eyring and John [9], Gladstone-Dale [10], Heller [11], Lorentz-Lorentz [12], Newton [13], Oster [14] and Weiner [15] to predict refractive indices of the mixtures from the experimental densities, and the refractive indices of the pure components. The relative applicability of these mixing rules has been tested by many researchers [16-20]. The major drawback of these mixing rules is their inability to account for change in volume and refractivity during mixing as they are based only on volume additivity [21].

II. MATERIALS AND METHODS

(a) Materials

DEC (Sigma Aldrich, Germany, mass fraction purity 0.98), xylenes (Sigma Aldrich, Germany, GC mass fraction purity 0.985), were used as such. Prior to experimental measurements, all the liquids were used after double-distillation, and partially degassed with a vacuum pump under nitrogen atmosphere. The purity of these solvents was ascertained by comparing the measured densities and refractive indices with the available literature [22-26] compiled in Table 1. The chemicals were stored in tightly sealed amber colored glass vials (8cm³) with screw caps having PFE septa, and securely sealed with parafilm to keep the atmospheric moisture absorption to minimum. Further, the chemicals were vacuum degassed, and the moisture content was reduced with the help of molecular vials, and was then stirred for more than 30 min to ensure total dissolution of the mixtures. The samples were taken from the vials with a syringe through the PFE septum.

(b) Apparatus and Procedure

All measurements on densities, ρ , were carried out on an Anton Paar DSA 5000 M densimeter. Calibration of the densimeter before carrying out experimental measurements was done with degassed water, which was triply distilled {CAS: 77-32-18-5; Anton Paar GmbH, liquid standard density, 0.9982 ± 0.00002 g*cm⁻³(293.15 K), literature density 0.9982 g*cm⁻³ (293.15 K, KNOVEL DIPPR); conductivity, $\kappa = 8\mu$ S}, and with dry air at atmospheric pressure in the experimental temperature range. The temperature inside the densimeter was controlled to ± 1·10⁻³ K by a built-in Peltier device. The reproducibility of the density measurements was ± 1·10⁻⁶ g·cm⁻³. The standard uncertainty of the density estimates was found to be within ± 5·10⁻⁵ g·cm⁻³. All of the solutions used in the measurements were made afresh on Sartorius CPA 225D balance having precision of ± 0.0001 g. Uncertainties in the solution concentration were estimated at ± 1·10⁻⁴ in calculations. All molar quantities expressed in this paper were based on the IUPAC relative atomic mass table [27]. A more detailed description and experimental procedure of these equipments can be found in literature reports [28, 29]. Refractive indices of the mixtures at the sodium D-line were determined with an Abbe refractometer equipped with a circulating water bath permitting to maintain the sample at constant temperature to within ±0.1K. The instrument is calibrates by measuring the refractive index of deionised water. The sample support was rinsed with acetone and dried with a paper towel.

III. THEORY

Looking at the literature, it is possible to extract many equations and empirical or theoretical models, due to various authors, accounting for the dependence of refractive properties on binary composition of liquid mixtures. With the aim of checking the effectiveness of these equations when applied to the systems here investigated, we have made a speculative test in order to compare their relative merits, basing the judgement on the average difference between experimental values and those calculated by the selected relationships. The 'mixing rules' tested here are the following:

Arago-Biot (A-B), assuming volume addivity, proposed the following relation for refractive index of binary mixtures: $n_m = \phi_1 n_1 + \phi_2 n_2$ (1)



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Eykman's (E) relation is represented as:

$$\left(\frac{n_m^2 - 1}{n_m + 0.4}\right) V_m = \left(\frac{n_1^2 - 1}{n_1 + 0.4}\right) \frac{M_1 x_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2 + 0.4}\right) \frac{M_2 x_2}{\rho_2}$$
(2)

where, symbols have their usual meaning.

Eyring and John (E-J) relation:

$$n = n_1 \phi_1^2 + 2(n_1 n_2)^{1/2} \phi_1 \phi_2 + n_2 \phi_2^2$$
(3)

Gladstone-dale (G-D) equation for predicting the refractive index of a binary mixture is as follows:

$$(n_m - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1)$$
 (4)

Heller's (H) relation is given by:

$$\left(\frac{n_m - n_1}{n_1}\right) = \frac{3}{2} \left(\frac{m^2 - 1}{m^2 + 2}\right) \phi_2 \tag{5}$$

Where m = $\frac{n_2}{n_1}$

The Lorentz-Lorentz (L-L) relation for refractive index is based on the change in the molecular polarizability with volume fraction:

$$\left(\frac{n_m^2 - 1}{n_m^2 + 2}\right) \frac{1}{\rho_m} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) \frac{w_1}{\rho_1} + \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) \frac{w_2}{\rho_2}$$
(6)

Newton (N) gave the following equation:

$$\left(n_{m}^{2}-1\right) = \phi_{1}\left(n_{1}^{2}-1\right) + \phi_{2}\left(n_{2}^{2}-1\right)$$
(7)

Oster (Os) relation:

$$\frac{\left(n^{2}-1\right)\left(2n^{2}+1\right)}{n^{2}} = \frac{\left(n_{1}^{2}-1\right)\left(2n_{1}^{2}+1\right)}{n_{1}^{2}}\phi_{1} + \frac{\left(n_{2}^{2}-1\right)\left(2n_{2}^{2}+1\right)}{n_{2}^{2}}\phi_{2}$$
(8)

Weiner's (W) relation is represented as:

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



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

In the above equations, n_m is the refractive index of the mixture; n_1 and n_2 are the refractive indices of the pure components 1 and 2 respectively. φ_i is volume fraction of component i. $\phi_i = x_i V_i / \sum x_i V_i$, V_i is the molar volume of component i and x_i is the mole fraction of component i.

The n_m data of the mixtures have been used to calculate the excess refractive index using:

$$\mathbf{n}^{\rm E} = \mathbf{n}_{\rm m} - (\mathbf{x}_1 \mathbf{n}_1 + \mathbf{x}_2 \mathbf{n}_2) \tag{10}$$

With the aim of gathering further information about the specific intermolecular interactions in these binary systems, we have investigated the molar refraction, R, defined by the Lorentz-Lorentz equation:

$$\mathbf{R} = \left(\frac{n_m^2 - 1}{n_m^2 + 2}\right) V_m \tag{11}$$

where, $V_m = (x_1M_1 + x_2M_2)/\rho$ is the molar volume.

 Δn_D and ΔR were calculated using the following equations:

$$\Delta n_{\rm D} = n_{\rm D} - \phi_1 n_{\rm D1} - \phi_2 n_{\rm D2}$$
(12)
$$\Delta R = R - x_1 R_1 - x_2 R_2$$
(13)

where n_D is the refractive index of the mixture, ϕ_i is the volume fraction of component i. n_{Di} is the refractive index of component i, V_m is the molar volume of the mixture, x_i is the mole fraction, and R_i is the molar refraction of component i.

The deviations were further fitted to the Redlich-Kister polynomial equation [30]:

$$X^{E} = x_{1}(1-x_{1}) \sum_{i=1}^{5} A_{i}(1-2x_{1})^{i}$$
(14)

where X^E is the deviation in parameters and x_1 is the mole fraction of diethyl carbonate. The values of Redlich-Kister polynomial coefficients, A_i , were evaluated by the method of least squares and the standard deviation σ (X^E) was calculated as:

$$\sigma(X^{E}) = \left[\frac{\sum (X_{expt} - X_{cal})^{2}}{m - n}\right]^{1/2}$$
(15)

where m and n are the number of data points and parameters, respectively.

IV. RESULTS AND DISCUSSION

Experimental values of densities and refractive indices for the binary mixtures DEC + o-xylene, + m-xylene, + p-xylene have been reported in Table 2 at temperatures T = (298.15-323.15) K over the entire mole fraction range. Molar refraction, refractive index deviation, and molar refraction deviation calculated with equations. (11), (12), (13) have been shown in Figs. 1 (a to c) to 3 (a to c). The predicted refractive indices of the binary mixtures at each temperature



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

studied were compared with the experimentally measured values and the results are presented in terms of APD. The APD values for A-B, E, E-J, G-D, H, N, Os and W relations are presented in Table 4.

literature (298.15-	Liquids	T/K	Density, ρ/	′Kg·m ⁻³	Refractive i	values at T =	
			Experimental	Literature	Experimental	Literature	323.15) K.
		298.15	969.10	969 ²²	1.382458	1.38252 ²²	
		303.15	963.47	963 ²³	1.380170	1.3801^{23}	
	DEC	308.15	957.81	957.9^{22}	1.377869	1.37769^{22}	
	DEC	313.15	952.13	952^{23}	1.375586	1.3775^{23}	
		318.15	946.43	946.43 ²⁴	1.373301	-	
		323.15	940.69	940.77^{24}	1.370953	-	
		298.15	875.99	875.57^{25}	1.501212	1.5029^{25}	
		303.15	871.77	871.31 ²⁵	1.498275	1.5002^{25}	
	o-vylene	308.15	867.55	867.05 ²⁵	1.495559	1.4975^{25}	
	0-xylelle	313.15	863.31	862.79^{25}	1.492787	1.4948^{25}	
		318.15	859.05	858.53^{23}	1.490003	1.492125	
		323.15	854.77	855.5-0	1.48/226	-	
		298.15	859.86	860.02^{25}	1.494411	1.4948^{25}	
		303.15	855.55	855.74 ²⁵	1.491673	1.4922^{25}	
		308.15	851.23	851.45 ²⁵	1.488958	1.4896^{25}	
	m-xylene	313.15	846.90	846.9 ²⁶	1.486271	1.4870^{25}	
		318.15	842.56	842.4 ²⁶	1.483561	1.4844^{25}	
		323.15	838.19	838.3 ²⁶	1.480909	-	
		298.15	856.65	856.82 ²⁵	1.493042	1.4933^{25}	
		303.15	852.26	852.47 ²⁵	1.490210	1.4907^{25}	
	1	308.15	847.85	848.12 ²⁵	1.487460	1.4881^{25}	
	p-xylene	313.15	843.43	843.77 ²⁵	1.484715	1.4855^{25}	
		318.15	838.99	838.7 ²⁶	1.481953	1.4830^{25}	
		323.15	834.53	834.5 ²⁶	1.479233	-	

Table 1: Experimental values of density (ρ) and refractive index (n_D) of pure liquids along with the corresponding



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Table 2: Experimental values of density, ρ and refractive index, n_D for three binary mixtures at different temperatures.

x ₁	ρ (Ka m ⁻³)	n _D	ρ (Kam ⁻³)	n _D	ρ (Kam ⁻³)	n _D	
	$(\mathbf{Kg} \mathbf{m}^{*})$		$(\mathbf{Kg} \mathbf{m}^{*})$	20	$(\mathbf{Kg}\mathbf{m}^{*})$		
T = 298.15 K $T = 303.15 K$ $T = 308.15 K$							
0.0000	876.0	1.50121	871.8	1.49828	867.5	1.49556	
0.1007	885.3	1.49041	881.0	1.48779	876.6	1.48524	
0.1943	894.1	1.47918	889.6	1.47654	885.1	1.47400	
0.3017	904.2	1.46561	899.5	1.46298	894.9	1.46051	
0.4030	913.7	1.45331	908.9	1.45075	904.1	1.44829	
0.5047	923.2	1.44100	918.4	1.43852	913.4	1.43610	
0.6026	932.5	1.42921	927.4	1.42675	922.3	1.42435	
0.6977	941.4	1.41777	936.2	1.41538	930.9	1.41302	
0.8065	951.5	1.40496	946.1	1.40264	940.7	1.40033	
0.9000	960.0	1.39403	954.6	1.39175	949.0	1.38945	
1.0000	969.1	1.38246	963.5	1.38017	957.8	1.37787	
	T = 313.15 K		T = 31	8.15 K	T = 323.15 K		
0.0000	863.3	1.49279	859.0	1.49000	854.8	1.48723	
0.1007	872.2	1.48266	867.8	1.48022	863.4	1.47773	
0.1943	880.6	1.47150	876.0	1.46898	871.4	1.46651	
0.3017	890.2	1.45804	885.5	1.45563	880.7	1.45328	
0.4030	899.3	1.44578	894.4	1.44327	889.5	1.44087	
0.5047	908.4	1.43369	903.4	1.43125	898.4	1.42881	
0.6026	917.2	1.42196	912.1	1.41963	906.9	1.41727	
0.6977	925.7	1.41069	920.4	1.40834	915.1	1.40598	
0.8065	935.3	1.39794	929.9	1.39563	924.4	1.39333	
0.9000	943.5	1.38711	937.9	1.38483	932.4	1.38253	
1.0000	952.1	1.37559	946.4	1.37330	940.7	1.37095	
			DEC + m-xyle	ne			
	T = 298.15 K		T = 30	3.15 K	T = 308.15 K		
0.0000	859.9	1.49441	855.6	1.49167	851.2	1.48896	
0.1059	871.0	1.48235	866.6	1.47968	862.1	1.47703	
0.2070	881.8	1.47100	877.2	1.46836	872.6	1.46576	
0.3020	892.0	1.46040	887.3	1.45781	882.5	1.45526	
0.4098	903.9	1.44829	899.0	1.44574	894.1	1.44324	
0.5068	914.5	1.43735	909.5	1.43484	904.5	1.43239	
0.5982	924.9	1.42705	919.8	1.42456	914.7	1.42215	
0.6991	935.8	1.41573	930.6	1.41328	925.3	1.41091	
0.8038	947.2	1.40402	941.9	1.40161	936.5	1.39929	



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

-	0.9023	958.0	1.39305	952.5	1.39068	946.9	1.38841	
	1.0000	969.1	1.38246	.38246 963.5		957.8	8 1.37787	
		T = 313.15 K		T = 318	3.15 K	T = 323.15 K		
	0.0000	846.9	1.48627	842.6	1.48356	838.2	1.48091	
	0.1059	857.6	1.47441	853.1	1.47176	848.6	1.46917	
	0.2070	868.0	1.46318	863.3	1.46058	858.7	1.45801	
	0.3020	877.8	1.45272	873.0	1.45016	868.2	1.44761	
	0.4098	889.2	1.44073	884.3	1.43823	879.4	1.43572	
	0.5068	899.5	1.42993	894.4	1.42747	889.3	1.42499	
	0.5982	909.5	1.41972	904.3	1.41728	899.1	1.41483	
	0.6991	920.0	1.40852	914.7	1.40612	909.4	1.40370	
	0.8038	931.0	1.39694	925.6	1.39458	920.1	1.39219	
	0.9023	941.4	1.38612	935.8	1.38383	930.2	1.38147	
	1.0000	952.1	1.37559	946.4	1.37330	940.7	1.37095	
				DEC + p-xylen	e			
		T = 298.15 K		T = 302	3.15 K	T = 30)8.15 K	
	0.0000	856.6	1.49304	852.3	1.49021	847.9	1.48746	
	0.0995	867.7	1.48120	863.3	1.47845	858.8	1.47583	
	0.2104	880.1	1.46970	875.5	1.46707	870.8	1.46444	
	0.3088	891.2	1.45860	886.4	1.45591	881.6	1.45328	
	0.4002	901.2	1.44857	896.3	1.44596	891.4	1.44340	
	0.5154	914.4	1.43586	909.4	1.43330	904.3	1.43085	
	0.6003	923.9	1.42640	918.8	1.42385	913.6	1.42138	
	0.7120	936.4	1.41417	931.2	1.41172	925.9	1.40929	
	0.7988	946.3	1.40451	941.0	1.40212	935.6	1.39972	
	0.8992	957.7	1.39352	952.2	1.39115	946.6	1.38881	
	1.0000	969.1	1.38246	963.5	1.38017	957.8	1.37787	
		T = 313.15 K		T = 318.15 K		T = 323.15 K		
	0.0000	843.5	1.48472	839.1	1.48195	834.7	1.47923	
	0.0995	854.2	1.47314	849.7	1.47054	845.2	1.46794	
	0.2104	866.2	1.46187	861.5	1.45926	856.8	1.45672	
	0.3088	876.8	1.45071	872.0	1.44817	867.2	1.44567	
	0.4002	886.5	1.44093	881.5	1.43845	876.6	1.43608	
	0.5154	899.2	1.42835	894.1	1.42601	889.0	1.42356	
	0.6003	908.5	1.41891	903.3	1.41651	898.0	1.41443	
	0.7120	920.6	1.40688	915.2	1.40447	909.8	1.40210	
	0.7988	930.1	1.39733	924.7	1.39496	919.2	1.39264	
	0.8992	941.1	1.38648	935.5	1.38415	929.9	1.38183	
_	1.0000	952.1	1.37559	946.4	1.37330	940.7	1.37095	
-								



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

Table 3: Adjustable parameters A_i with the standard deviations σ for deviation in refractive index (Δn_D) and deviation in molar refraction (ΔR) for binary mixtures at temperatures T = (298.15 - 323.15) K

T (K)	A ₁	A_2	A ₃	A ₄ A ₅		σ		
		DEC + o-xylene						
			Δ	n _D				
298.15	-1.19E-03	-3.72E-03	2.97E-03	-1.07E-02	1.04E-02	6.05E-05		
303.15	-6.78E-04	-3.67E-03	2.35E-03	-1.25E-02	1.43E-02	5.20E-05		
308.15	-3.96E-04	-3.93E-03	3.65E-03	-1.29E-02	1.37E-02	4.74E-05		
313.15	-1.80E-05	-3.99E-03	4.50E-03	-1.41E-02	1.35E-02	3.31E-05		
318.15	5.67E-04	-4.10E-03	4.55E-03	-1.61E-02	1.63E-02	1.92E-05		
323.15	1.02E-03	-4.50E-03	5.82E-03	-1.72E-02	1.72E-02	3.72E-05		
			4	۱R				
298.15	2.60E-02	-3.01E-02	1.77E-02	-6.34E-02	6.09E-02	3.81E-04		
303.15	3.01E-02	-3.00E-02	1.40E-02	-7.51E-02	8.51E-02	3.35E-04		
308.15	3.33E-02	-3.17E-02	1.95E-02	-7.98E-02	8.67E-02	3.00E-04		
313.15	3.66E-02	-3.25E-02	2.77E-02	-8.74E-02	8.28E-02	2.24E-04		
318.15	4.19E-02	-3.32E-02	2.66E-02	-1.02E-01	1.02E-01	1.21E-04		
323.15	4.60E-02	-3.64E-02	3.50E-02	-1.08E-01	1.10E-01	2.05E-04		
			DEC +	m-xylene				
			Δ	n _D				
298.15	4.90E-03	3.39E-03	-4.41E-03	-4.57E-03	-2.33E-03	1.32E-05		
303.15	5.01E-03	3.43E-03	-4.77E-03	-4.87E-03	-1.49E-03	1.53E-05		
308.15	5.10E-03	3.33E-03	-4.88E-03	-4.73E-03	-1.04E-03	1.53E-05		
313.15	5.21E-03	3.32E-03	-5.29E-03	-4.78E-03	-9.01E-05	2.29E-05		
318.15	5.35E-03	3.42E-03	-5.92E-03	-4.98E-03	1.47E-03	2.23E-05		
323.15	5.47E-03	3.57E-03	-6.07E-03	-5.36E-03	2.07E-03	2.43E-05		
			Z	۱R				
298.15	7.73E-02	1.94E-02	-2.63E-02	-2.66E-02	-1.17E-02	7.56E-05		
303.15	7.91E-02	1.96E-02	-2.92E-02	-2.81E-02	-6.30E-03	8.48E-05		
308.15	8.09E-02	1.93E-02	-3.10E-02	-2.78E-02	-2.26E-03	1.12E-04		
313.15	8.29E-02	1.95E-02	-3.41E-02	-2.88E-02	5.29E-03	1.48E-04		
318.15	8.51E-02	2.01E-02	-3.78E-02	-3.00E-02	1.40E-02	1.43E-04		
323.15	8.72E-02	2.09E-02	-3.90E-02	-3.19E-02	1.75E-02	1.64E-04		
			DEC +	p-xylene				
			Δ	n _D				
298.15	-1.10E-03	8.70E-04	6.65E-04	9.31E-05	-2.58E-04	3.13E-05		
303.15	-9.02E-04	9.99E-04	4.90E-04	-1.86E-04	1.44E-04	2.92E-05		
308.15	-8.04E-04	9.95E-04	8.22E-04	-1.79E-04	-8.09E-05	2.76E-05		
313.15	-6.95E-04	1.10E-03	1.01E-03	-3.08E-04	1.41E-04	2.78E-05		
318.15	-5.40E-04	1.14E-03	1.23E-03	-2.54E-04	-1.41E-04	2.96E-05		
323.15	-4.15E-04	1.15E-03	1.23E-03	-3.94E-04	2.09E-04	2.87E-05		
			L	١R				
298.15	5.13E-03	9.44E-03	7.52E-03	-1.43E-03	-3.72E-03	1.84E-04		



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

303.15	7.31E-03	9.77E-03	7.81E-03	-2.34E-03	-3.37E-03	2.05E-04
308.15	9.12E-03	1.01E-02	9.14E-03	-3.86E-03	-3.83E-03	1.83E-04
313.15	1.10E-02	1.03E-02	1.03E-02	-4.05E-03	-2.65E-03	1.79E-04
318.15	1.30E-02	1.04E-02	1.11E-02	-3.87E-03	-2.14E-03	1.82E-04
323.15	1.50E-02	1.03E-02	1.22E-02	-4.40E-03	-2.25E-03	2.02E-04

Table 4: Values of average percentage deviations (APD) in experimentally and theoretically calculated refractive indices using various mixing rules at different temperatures.

T/K	A-B	Е	E-J	G-D	Н	L-L	Ν	Os	W
DEC(1) + o-xylene(2)									
298.15	0.0083	0.1277	0.0337	0.0083	0.0608	0.0609	-0.0425	0.1604	0.0290
303.15	0.0166	0.1350	0.0418	0.0166	0.0687	0.0687	-0.0337	0.1676	0.0372
308.15	0.0230	0.1409	0.0481	0.0230	0.0749	0.0747	-0.0272	0.1735	0.0435
313.15	0.0298	0.1469	0.0547	0.0298	0.0813	0.0810	-0.0202	0.1794	0.0501
318.15	0.0395	0.1560	0.0644	0.0395	0.0908	0.0903	-0.0102	0.1884	0.0598
323.15	0.0488	0.1647	0.0736	0.0488	0.0999	0.0993	-0.0007	0.1971	0.0690
DEC (1) -	+ m-xylene	(2)							
298.15	0.0249	0.1317	0.0477	0.0249	0.0708	0.0719	-0.0206	0.1611	0.0433
303.15	0.0282	0.1346	0.0509	0.0282	0.0739	0.0748	-0.0171	0.1640	0.0465
308.15	0.0303	0.1360	0.0528	0.0303	0.0756	0.0765	-0.0148	0.1653	0.0484
313.15	0.0325	0.1377	0.0549	0.0325	0.0776	0.0783	-0.0125	0.1670	0.0506
318.15	0.0350	0.1397	0.0574	0.0350	0.0800	0.0805	-0.0097	0.1690	0.0530
323.15	0.0375	0.1418	0.0598	0.0375	0.0823	0.0827	-0.0072	0.1711	0.0554
DEC (1) -	+ p-xylene	(2)							
298.15	0.0174	0.1207	0.0394	0.0174	0.0622	0.0628	-0.0266	0.1492	0.0351
303.15	0.0194	0.1219	0.0413	0.0194	0.0639	0.0643	-0.0243	0.1503	0.0370
308.15	0.0209	0.1229	0.0426	0.0209	0.0654	0.0654	-0.0227	0.1512	0.0384
313.15	0.0225	0.1239	0.0441	0.0225	0.0666	0.0667	-0.0208	0.1522	0.0399
318.15	0.0242	0.1249	0.0457	0.0242	0.0680	0.0680	-0.0189	0.1532	0.0415
323.15	0.0256	0.1260	0.0471	0.0256	0.0693	0.0691	-0.0173	0.1542	0.0429

The basis of these mixing rules of refractive index is Electromagnetic theory of light, which treats the molecules as dipoles or assemblies of dipoles by an external field. Refractive index dependent on the nature of liquid, pressure and temperature and is directly related to a number of physical parameters of the liquid such as dielectric constant, density, molar refractivity etc. Here an attempt has been made to study the validity of nine mixing rules for predicting the refractivity of binary liquid system, over the entire mole fraction range.



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015



Fig. 1(a) : Plots of molar refraction, R against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + oxylene.



Fig. 1(b) : Plots of molar refraction, R against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + m-xylene.

From Figure 1 (a-c) it can be observed that the molar refraction values are almost equal for all the mixtures at all the temperatures studied. And it can also be observed that the values of molar refraction increase with increase in temperature but the increase is small.



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015



Fig. 1(c) : Plots of molar refraction, R against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + p-xylene.

In Figure 2 (a) for DEC+ o-xylene, Δn_D shows positive and negative values, with the maximum value at $x_1 = 0.1007$ and minimum value at $x_1 = 0.6977$. The same trends have been observed at all temperatures studied.



Fig. 2(a) : Plots of deviation in refractive index, Δn_D against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + o-xylene.

From Figure 2(b) it can be observed that the Δn_D shows positive values over the entire composition range, with the maximum value at $x_1 = 0.6143$ for all temperatures for DEC + m-xylene. Whereas from Figure 2(c) for DEC + p-xylene, it can be observed that the Δn_D shows negative and positive values. More negative is observed at $x_1 = 0.3080$ and more positive is observed at $x_1 = 0.7997$.



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015



Fig. 2(b) : Plots of deviation in refractive index, Δn_D against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + m-xylene.

From Figure 2 (a-c) more negative value (-0.0005) of Δn_D can be observed for DEC + o-xylene when compared to other two mixtures. The larger negative deviations of DEC with o-xylene clearly suggest that the –CH₃ group at oposition makes o-xylene molecules to pack themselves more favorably in the structure of DEC molecules in the solution than in the pure state.



Fig. 2(c) : Plots of deviation in refractive index, Δn_D against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + p-xylene.

Thus, we conclude that for xylenes the experimental results show that the position of $-CH_3$ groups, rather than their number, is significant in deciding the extent of negative deviations in Δn_D . The lowest deviations for the calculated refractive indices have been obtained by using Newton equation, whereas the Eykman equation gives the highest deviations at all temperatures for all the mixtures studied.



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015



Fig. 3(a) : Plots of deviation in molar refraction, $\Delta \mathbf{R}$ against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + o-xylene.

The deviations in molar refraction, ΔR [Figure 3(a-c)], from the linear dependence on mole fraction reveals that it is positive for all the three binary mixtures investigated. More positive deviation is observed at x₁=0.1943 in figure 3(a), at x₁=0.6143 in figure 3(b) and at x₁=0.79 in figure 3(c).



Fig. 3(b) : Plots of deviation in molar refraction, $\Delta \mathbf{R}$ against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + m-xylene.

It also supports the behavior that is observed in figure 2(a-c). The increases in values of ΔR with increase in temperature have been observed from figure 3(a-c).



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015



Fig. 3(c) : Plots of deviation in molar refraction, $\Delta \mathbf{R}$ against mole fraction, x_1 of DEC at T = (298.15-323.15) K for DEC + p-xylene.

The deviations of theoretical values from experimental ones are temperature-independent. This may be attributed to the fact that variation in refractive index with temperature is compensated by the change in density of the liquid mixture. However, in cases 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 acoustical properties using experimental data. If the concept of excess volume (which is an indirect measure of interaction) is taken into consideration in various mixing rules, the deviation between the observed and theoretical values of refractive index may be reduced [31].

V. CONCLUSION

Density and refractive index values are measured experimentally and various mixing rules of refractive index were used to test their validity for binary mixtures. 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. Negative and positive deviations are observed between experimental and theoretical values calculated by using various theories/models. The lowest deviations for the calculated refractive indices have been obtained by using Newton equation, whereas the Oster relation gives the highest deviations at all temperatures for all the mixtures studied

REFERENCES

- [1] M. Srilakshmi, T. Srinivasa Krishna, K. Narendra, Ranjan Dey and A. Ratnakar. "J. Mol. Liq.", Vol. 211, pp. 854-867, 2015.
- K. Narendra, B. Sudhamsa, M. Sarath Babu and T.S. Krishna. "J. App. Sol. Chem. Modeling", Vol. 4(2), pp. 119-127, 2015. [2]
- [3] B. Sudhamsa, M. Sarath Babu, K. Narendra. "International Letters of Chemistry Physics and Astronomy", Vol. 19(1), pp. 1-7, 2014.
- [4] Zhiyuan Zeng, Wen-I Liang, Ying-Hao Chu, Haimei Zheng. "Faraday Discussions", Vol. 176, pp. 95-107, 2015.
- W. Martindale, The Extra Pharmacopoeia, Pharmaceutical Press, London, 1989 [5]
- M. C.Annesini, R. De Sanctis, I. Kikic, R. Marrelli. "J. Chem. Eng. Data", Vol. 29, pp. 39-41, 1984. [6]
- D.F.J. Arago and J.B. Biot, "Mem. Acad. Fr.", 7, 1806. [7]

- [8] J.F. Eykman, "Rec. Trav. Chim.", Vol. 14, pp. 185, 1895.
 [9] H. Eyring and M.S. John, *Significant liquid structures*, John Wiley, New York, 1969.
- F. Gladstone and D. Dale, "Philos. Trans. R. Soc. ", Vol. 148, pp. 887, 1858. W. Heller, "Phys. Rev. ", Vol. 68, pp.5, 1945. [10]
- [11]
- H.A. Lorentz, "Weid. Ann. ", Vol. 9, pp. 641, 1880. [12]
- S.S. Kurtz and A.L. Ward, "J Franklin Inst.", Vol. 222, pp. 563, 1936. [13]
- G. Oster, "Chem. Rev." Vol. 43, pp. 319, 1948. [14]



(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

- O. Weiner, "Leipz. Ber." Vol. 62, pp. 256, 1910. [15]
- [16]
- S. Parveen, S. Singh, D. Shukla, M. Yasmin, M. Gupta, J.P. Shukla, "J. Solution Chem.", Vol. 41, pp. 156-172, 2012. K. Narendra, P. Narayana Murthy, Ch. Srinivasu, "Asian Journal of Applied Sciences", Vol. 4(5), pp. 535-541, 2011. [17]
- B. Sudhamsa, M. Sarath Babu and K. Narendra. "Journal of applicable Chemistry", Vol. 3(3), pp. 1272-1276, 2014. [18]
- [19]
- M.C. Saxena, "Indian J Chem.", Vol. 10, pp. 636, 1998. T. Srinivasa Krishna, B. Munibhadrayya, S. Govardhana Rao, Sk. Fakruddin, K. Narendra. "Golden Research Thoughts", Vol. 3(10), pp. 1-[20] 4, 2014.
- T. M. Aminabhavi, "J. Chem. Eng. Data", Vol. 29, pp. 54, 1984. [21]
- L. Mosterio, E. Mascato, B.E. de Cominges, T.P. Iglesias, J.L. Legido. "J. Chem. Thermodyn." Vol. 33, pp. 787-801, 2001. M.V. Ratnam, Sudhir Mohite, M. Nandini. "J. Mol. Liq.", Vol. 17, pp. 229-236, 2013. E.R. Lopez, L.Lugo, M.J.P. Comunas, J. Garcia, J. Fernandez. "J. Chem. Thermodyn.", Vol. 32, pp. 743-754, 2000. Anil K. Nain, Prakash Chandra, Jata D. Pandey, and Swarita Gopal. "J. Chem. Eng. Data", Vol. 53, pp. 2654–2665, 2008. [22]
- [23]
- [24]
- [25]
- [26] Cheng-Ying Song, Hong-Zhi Shen, Jian-Hong Zhao, Liu-Cheng Wang, and Fu-An Wang. "J. Chem. Eng. Data", Vol. 53, pp. 1110–1115, 2008.
- International Union of Pure and Applied Chemistry. Inorganic Chemistry Division, Commission on Atomic Weights and Isotopic [27] Abundances. "Pure Appl. Chem.", Vol. 58, pp. 1677–1692, 1986.
- T. Srinivasa Krishna, M. Gowrisankar, K. Thomas S S Raju, S GovardhanRao, B. Munibhadrayya, "J. Mol. Liq.", Vol. 206, pp. 350-358, [28] 2015.
- S. Govardhana Rao, T. Madhu Mohan, T. Vijaya Krishna, K. Narendra, B. Subba Rao, "J. Mol. Liq.", Vol. 211, pp. 1009–1017, 2015. O. Redlich, T.A. Kister, "Ind. Eng. Chem.", Vol. 40, pp. 345-348, 1984. [29]
- [30]
- T.M. Aminabhavi and P. Munk, "Macromolecules", Vol. 12, pp. 1186, 1979. [31]