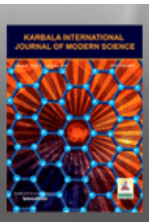

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Prediction of refractive indices and molecular radii of binary mixtures of Polyethylene glycol (PEG-200,400) and cyclic ethers: Insight into molecular interactions

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Keywords

Research Development, Industry, Sustainable Development, Binary Polymer Mixtures, Optical Parameters, Refractive Index, Mixing Rules, Molecular Radius.

RESEARCH PAPER

Prediction of Refractive Indices and Molecular Radii of Binary Mixtures of Polyethylene Glycol (PEG-200,400) and Cyclic Ethers: Insight into Molecular Interactions

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Abstract

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Keywords: Research development, Industry, Sustainable development, Binary polymer mixtures, Optical parameters, Refractive index, Mixing rules, Molecular radius

1. Introduction

Knowledge of the optical properties of the liquid mixtureis essential for theoretical and applied research. Laboratory research and industrial production require accurate and reliable values of thermo-dynamical properties of pure liquids and their mixtures [1]. The precise data on these properties help to reduce the overall cost of the production of ultrafine chemicals and pharmaceutical substances. Investigation of the behavior of multi-component mixtures of valuable industrial chemicals, therefore, has been preferred by several researchers [2−4]. The study of refractive index and density provides information about the fundamental behavior of liquid systems [5]. In fact, these intrinsic properties of liquid mixtures are of immense use in pharmaceutical research and opto-photon electronic applications [6]. Recently, many researchers have reported the refractive indices data for liquids and liquid mixtures based on a relatively simple measurement procedure [6]. To understand the correlation of refractive index and the compositions of multi-component systems, various mixing rules *viz.*, Lorentz-Lorenz [7], Gladstone-Dale [8], Wiener [9], Heller [10], Arago-Biot [11] and Eykman [12] have been employed by a number of workers. The average percentage deviation of these mixing rules, from their experimental values, provides

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information about the non-ideality of the system. Some available reports account for the drawbacks of mixing rules [13,14]. The most serious flaw, which is usually overlooked, is the inability to include the change in volume and refractivity during mixing. Aminabhavi et al. [14] provided a solution to such issues. Several researchers [15–17] have reported the performance of various mixing rules and concluded that the Lorentz–Lorenz, Gladstone–Dale, Wiener, Heller, and Arago -Biot relations performed noticeably well. In contrast, Eykman's and Oster's relations exhibit a higher percentage deviation than others, though the deviation is within experimental precision. Insight of reports [18–20] reveals that the refractive index can be theoretically determined for pure liquids, polymers, and their binary mixtures using various mixing rules. Some workers [17,18,21] successfully extended the theory of existing mixing rules of binary mixtures to ternary and quaternary mixtures.

Due to a wide range of applications in the pharmaceutical and cosmetic industry, polyethylene glycol was extensively studied by many researchers [22–27]. Recently, Ottani et al. [28] performed a refractometric and viscometrical study of PEG-200 and 400 with cyclic ethers (1,3-Dioxolane, Oxolane and Oxane) at 303.15 K. They also reported the deviations of these parameters from experimental values.

Keeping in mind the industrial importance of polyethylene glycol and the requirement for reliable and accurate refractive index data, five mixing rules of the refractive index such as Lorentz–Lorenz Relation (LLR), Gladstone–Dale Relation (GDR), Wiener Relation (WR), Heller Relation(HR) and Arago-Biot Relation (ABR) are employed to compute the refractive index values for the six binary polymer mixtures *viz.*, PEG-200 + 1,3-Dioxolane, PEG-200 + Oxolane, PEG-200 + Oxane, PEG-400 + 1,3-Dioxolane, PEG-400 + Oxolane, and PEG-400 + Oxane at 303.15 K, and atmospheric pressure. The relative merit of these mixing rules is also tested against the literature values.

The theoretical calculation of the molecular radius of pure liquids and their mixtures has attracted the attention of many workers [29–35] as this parameter reflects the structural features of liquids. The molecular radius is directly related to the molecular nature and the number of atoms present in the liquid. This parameter has been successfully used in well-established theories of the liquids, such as Scaled Particle Theory [29,30] and Collision Factor Theory (CFT) [31]. Pandey et al. [32] have computed the molecular radius for organic liquids and their mixtures using acoustical and thermodynamical methods. Ali et al. [33] have calculated the molecular radius for binary mixtures of benzenes and organic liquids using refractive index data. Shahla et al. [34] have computed the molecular radius of the organic liquid mixtures and utilized the results to explain the molecular structure of the systems. Recently, Sharma et al. [35] reported the molecular radius of pseudo-binary liquid mixtures using acoustical and refractive index methods. The present study employs the refractive index and ideal mixing methods to calculate the molecular radius of the binary polymer mixture under study. The computed values of r_m using the refractive index method are taken as a reference, following a well-established concept reported in the literature [32]. The values of the refractive index computed using the ideal mixing method are compared with standard values of the refractive index. The methodology used to predict the refractive indices and molecular radii of the chosen binary polymer mixtures in the present investigation has not yet been attempted.

2. Theoretical formulation

Using experimental refractive index (n_{Lit}) and density (d) values for five pure liquids, e.g., PEG-200, PEG-400, 1,3-Dioxolane, Oxolane and Oxane, taken from the literature [28], following refractive index mixing rules are employed to estimate the values of the refractive index of six binary mixtures at different mole fractions (X_1) of PEG (200 and 400).

The Lorentz–Lorenz Relation (LLR) [7] is a widely accepted relation to predict the refractive index for multi-component liquid mixtures from the knowledge of refractive indices (n_1, n_2), and volume fractions (ϕ_1, ϕ_2) of pure components. Here suffixes 1 and 2 represent polymers (PEG-200 and PEG-400) and cyclic ethers (1,3-Dioxolane, Oxolane and Oxane), respectively. LLR has been extended to polymer mixtures as given below:

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

where $\phi_1 = X_1\overline{v}_1/(X_1\overline{v}_1 + X_2\overline{v}_2)$, and $\phi_2 = X_2\overline{v}_2/(X_1\overline{v}_1 + X_2\overline{v}_2)$

In the above equations, X_1 and X_2 are the mole fractions, $\overline{v}_1$ and $\overline{v}_2$ are the partial molar volumes; n_1 and n_2 are the refractive indices of polymers (PEG-200 and PEG-400) and cyclic ethers, respectively. In Eq. (1), the refractive index of polymer mixtures is denoted by n_{cal}. The same terminology is used in Eqs. (2)–(11).

The partial molar volumes $\overline{v}_1$ and $\overline{v}_2$ are calculated using the standard relations available in the literature [36].

$$\overline{v}_1 = V + (1 - X_1)\left(\frac{\partial V}{\partial X_1}\right)_{T,P,X_2} \tag{1a}$$

$$\overline{v}_2 = V + (1 - X_2)\left(\frac{\partial V}{\partial X_2}\right)_{T,P,X_2} \tag{1b}$$

In these equations, molar volume (V) is determined using the Response Surface Model (RSM) consisting of multi-linear interaction terms and given as;

$$V = \alpha_0 + \sum_{i=1}^{N-1} \alpha_i X_i + \sum_{i=1}^{N-1} \alpha_{ii} X_i^2 + \sum_{i \neq j}^{N-1} \alpha_{ij} X_i X_j + \sum_{i \neq j \neq k}^{N-1} \alpha_{ijk} X_i X_j X_k \tag{1c}$$

For binary system (N = 2), the above equation can be written as;

$$V = \alpha_0 + \alpha_1 X_1 + \alpha_{11} X_1^2 + \alpha_{12} X_1 X_2 \tag{1d}$$

In these equations, α_0, α_1, α_{11}, and α_{12} are the coefficients of the Response Surface Model. These are determined using an analytical tool Solver (MS–Excel). The calculated values of V (using Eq. (1d)) are plotted in Fig. 1, and the coefficients are reported in Table 1. The calculated values of $\overline{v}_1$, $\overline{v}_2$ and density for all the six binary polymer mixtures are presented in Table 2.

Gladstone–Dale Relation (GDR) is another refractive index mixing rule that is widely used in predicting the refractive index of dilute solutions having a slight difference in refractive indices of

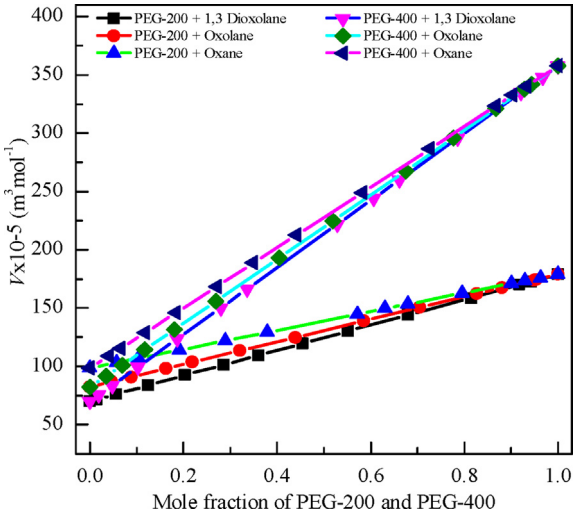

Fig. 1. Values of Molar volume (V) obtained using Eq. (1d).

Table 1. Coefficients of Eq. (1d) of molar volume (V) (in m^3mol^{-1}) at 303.15 K and 0.101 MPa.

System	$\alpha_0 \times 10^{-5}$	α_1	α_{11}	α_{12}
PEG −200 + 1,3-Dioxolane	7.02	0.08914	−0.08903	−0.08903
PEG 200 + Oxolane	8.22	0.08913	−0.08903	−0.08903
PEG 200 + Oxane	9.84	0.08912	−0.08904	−0.08904
PEG 400 + 1,3-Dioxolane	7.02	0.08926	−0.08897	−0.08897
PEG 400 + Oxolane	8.21	0.08925	−0.08897	−0.08897
PEG 400 + Oxane	9.83	0.08924	−0.08898	−0.08898

pure components of those binary solutions, i.e.$n_1 \approx n_2$. The relation is:

$$(n_{cal} - 1) = (n_1 - 1)\phi_1 + (n_2 - 1)\phi_2 \tag{2}$$

Wiener Relation (WR) is based upon volume additivity. It generally applies to bodies having spherically symmetrical shapes and is given by:

$$\frac{n_{cal}^2 - n_1^2}{n_{cal}^2 + 2n_2^2} = \left(\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right)\phi_2 \tag{3}$$

Heller Relation (HR) is derived on the assumption of equivalence of light-scattering equations of Debye and Rayleigh and is given as:

$$\frac{n_{cal} - n_1}{n_1} = \frac{3}{2}\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right]\phi_2 \tag{4}$$

Arago-Biot Relation (ABR) provides the refractive index of a binary mixture based on the volume fraction average of the refractive indices of the pure components, as:

$$n_{cal} = n_1\phi_1 + n_2\phi_2 \tag{5}$$

The Eqs. (2)–(5) are taken from the literature [8–11]. These equations are re-written with minor changes in terminology and theoretical justifications for the present binary polymer mixtures.

Besides, predicting refractive indices of six binary systems at 303.15 K, for various compositions, some other parameters such as deviation in refractive index (Δn_{Lit}), reduced free volume ($\Delta(V/R_m)$) and molecular radius (r_m) [32] are also determined. The following relations have been used for their computations:

$$\Delta n_{Lit} = n_{Lit} - \sum_{i=1}^{2} \phi_i n_i \tag{6}$$

$$\Delta(V/R_m) = \left(\frac{{n_{Lit}}^2 + 2}{{n_{Lit}}^2 - 1}\right) - \frac{\sum_{i=1}^{2} X_i \overline{v}_i}{\sum_{i=1}^{2} X_i R_{mi}} \tag{7}$$

where R_{mi} is the molar refraction of the ith components, given by

Table 2. Density (d), partial molar volume ($\bar{v}_1$) of PEG-(200 and 400) (1) and partial molar volume ($\bar{v}_2$) of cyclic ethers(2) at 303.15 K and 0.101 MPa.

PEG-200(1) + 1,3 Dioxolane(2)				PEG-200(1) + Oxolane (2)				PEG-200 (1) + Oxane(2)			
X_1	d[a](kgm^{-3})	$\bar{v}_1$(cm^3mol^{-1})	$\bar{v}_2$(cm^3mol^{-1})	X_1	d*(kgm^{-3})	$\bar{v}_1$(cm^3mol^{-1})	$\bar{v}_2$(cm^3mol^{-1})	X_1	d* (kgm^{-3})	$\bar{v}_1$(cm^3mol^{-1})	$\bar{v}_2$(cm^3mol^{-1})
0	1052.68	179.04	70.37	0	876.36	179.04	82.28	0	874.31	178.98	98.51
0.0141	1055.02	179.03	70.37	0.0471	899.73	179.04	82.28	0.0568	897.67	179.06	98.58
0.0565	1061.48	179.02	70.35	0.0884	918.36	179.03	82.28	0.1041	915.62	179.11	98.64
0.124	1070.32	178.99	70.33	0.1622	947.88	179.02	82.27	0.1912	945.76	179.18	98.70
0.2029	1078.82	178.97	70.30	0.2191	967.88	179.01	82.25	0.289	975.66	179.22	98.75
0.2859	1086.2	178.94	70.28	0.3201	998.55	178.99	82.24	0.379	1000.14	179.24	98.77
0.3599	1091.65	178.93	70.27	0.4394	1028.57	178.98	82.23	0.572	1044.73	179.23	98.76
0.4548	1097.53	178.92	70.26	0.5854	1058.37	178.98	82.23	0.6305	1056.53	179.21	98.74
0.5515	1102.49	178.92	70.25	0.7046	1078.52	178.99	82.24	0.679	1065.74	179.20	98.72
0.6794	1107.79	178.94	70.27	0.8261	1096.04	179.01	82.26	0.7954	1086.2	179.14	98.67
0.8142	1112.23	178.97	70.31	0.8799	1103	179.02	82.26	0.9006	1102.75	179.10	98.63
0.9175	1115.06	179.01	70.35	0.95	1111.45	179.03	82.28	0.9292	1106.97	179.09	98.61
0.9424	1115.67	179.02	70.36	0.953	1111.8	179.03	82.28	0.9631	1111.84	179.07	98.60
1	1117.01	179.05	70.38	1	1117.01	179.05	82.30	1	1117.01	179.05	98.58
PEG-400(1) + 1,3 Dioxolane(2)				**PEG-400(1) + Oxolane(2)**				**PEG-400(1) + Oxane(2)**			
0	1052.68	357.79	70.37	0	876.36	357.88	82.28	0	874.31	357.81	98.51
0.0187	1059.32	357.72	70.31	0.0343	910.4	357.71	82.11	0.0405	907.72	357.69	98.39
0.0474	1067.67	357.64	70.23	0.0688	937.92	357.57	81.97	0.0655	925.17	357.63	98.33
0.1026	1079.46	357.53	70.12	0.1171	968.43	357.43	81.84	0.1183	956.05	357.55	98.25
0.1865	1090.9	357.44	70.02	0.1806	998.83	357.31	81.71	0.1836	986.11	357.47	98.17
0.2794	1098.82	357.40	69.99	0.2695	1029.4	357.22	81.62	0.2716	1016.87	357.41	98.11
0.3361	1102.28	357.40	69.98	0.4046	1060.41	357.20	81.60	0.3489	1037.55	357.39	98.09
0.5284	1109.97	357.44	70.03	0.5197	1078.4	357.25	81.66	0.4415	1057.07	357.39	98.09
0.6065	1112.06	357.46	70.05	0.6744	1095.71	357.36	81.76	0.5822	1079.33	357.44	98.14
0.6612	1113.29	357.49	70.07	0.7762	1104.33	357.44	81.84	0.726	1096.12	357.51	98.22
0.786	1115.54	357.55	70.14	0.8676	1110.74	357.53	81.93	0.8677	1108.83	357.60	98.30
0.9215	1117.4	357.64	70.23	0.9283	1114.44	357.59	81.99	0.9037	1111.6	357.62	98.32
0.9672	1117.94	357.67	70.25	0.9433	1115.3	357.60	82.01	0.9336	1113.81	357.63	98.34
1	1118.31	357.68	70.27	1	1118.31	357.68	82.08	1	1118.31	357.68	98.39

[a] Ref. [28]

$$R_{mi} = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) v_i \quad (8)$$

Here, v_i is the molar volume of the ith component. The suffix $i = 1, 2$ is used for the values of pure components *viz.*, polymer and cyclic ethers, respectively.

Refractive indices (n_{Lit}) of the binary polymer mixtures in conjunction with molar volume (V) can be utilized to compute the molecular radius (r_{m}) using the following relations [32]:

$$r_m = \left[\left\{\left(\frac{3}{4\pi N}\right) r_f\right\} V\right]^{1/3} \quad (9)$$

where r_{f} is the space-filling factor and given as

Table 3. Refractive index values viz.*, from literature* (n_{Lit}) *and computed* (n_{cal}) *for PEG-200(1) + 1,3 Dioxolane(2), PEG-200(1) + Oxolane(2) and PEG-200(1) + Oxane(2) at 303.15 K.*

X_1	n_{Lit}[a]	n_{cal}				
		LLR (Equation (1))	GDR (Equation (2))	WR (Equation (3))	HR (Equation (4))	ABR (Equation (5))
PEG 200 (1) + 1,3-Dioxolane (2)						
0	1.3962	1.3962	1.3962	1.3962	1.3958	1.3962
0.0141	1.3985	1.3983	1.3983	1.3983	1.3979	1.3984
0.0565	1.4041	1.4041	1.4042	1.4042	1.4039	1.4046
0.124	1.4124	1.4120	1.4123	1.4122	1.4120	1.4131
0.2029	1.4203	1.4198	1.4201	1.4200	1.4198	1.4212
0.2859	1.4272	1.4265	1.4269	1.4268	1.4267	1.4283
0.3599	1.4325	1.4316	1.4320	1.4319	1.4318	1.4334
0.4548	1.4381	1.4372	1.4375	1.4374	1.4374	1.4390
0.5515	1.4428	1.4420	1.4423	1.4422	1.4422	1.4437
0.6794	1.4481	1.4473	1.4475	1.4474	1.4474	1.4486
0.8142	1.4524	1.4519	1.4520	1.4520	1.4520	1.4527
0.9175	1.4552	1.4549	1.4549	1.4549	1.4549	1.4552
0.9424	1.4558	1.4555	1.4556	1.4556	1.4556	1.4558
1	1.4570	1.4570	1.4570	1.4570	1.4570	1.4570
PEG 200 (1) + Oxolane (2)						
0	1.4025	1.4025	1.4025	1.4025	1.4022	1.4025
0.0471	1.4236	1.4077	1.4078	1.4078	1.4075	1.4078
0.0884	1.4268	1.4118	1.4120	1.4119	1.4117	1.4121
0.1622	1.4331	1.4184	1.4186	1.4186	1.4184	1.4189
0.2191	1.4391	1.4229	1.4231	1.4231	1.4229	1.4236
0.3201	1.4451	1.4298	1.4301	1.4300	1.4299	1.4307
0.4394	1.4491	1.4366	1.4368	1.4368	1.4367	1.4376
0.5854	1.4528	1.4434	1.4436	1.4436	1.4435	1.4442
0.7046	1.4570	1.4480	1.4482	1.4481	1.4481	1.4487
0.8261	1.4600	1.4521	1.4522	1.4522	1.4522	1.4525
0.8799	1.4623	1.4537	1.4538	1.4538	1.4538	1.4540
0.9500	1.4628	1.4557	1.4557	1.4557	1.4557	1.4559
0.9530	1.4631	1.4558	1.4558	1.4558	1.4558	1.4560
1	1.4570	1.4570	1.4570	1.4570	1.4570	1.4570
PEG 200 (1) + Oxane (2)						
0	1.4165	1.4165	1.4165	1.4165	1.4163	1.4165
0.0568	1.4206	1.4205	1.4205	1.4205	1.4204	1.4196
0.1041	1.4237	1.4235	1.4236	1.4236	1.4234	1.4220
0.1912	1.4289	1.4286	1.4287	1.4287	1.4286	1.4264
0.2890	1.4342	1.4336	1.4337	1.4337	1.4336	1.4311
0.3790	1.4383	1.4377	1.4378	1.4378	1.4377	1.4352
0.5720	1.4457	1.4451	1.4451	1.4452	1.4452	1.4431
0.6305	1.4476	1.4470	1.4471	1.4471	1.4471	1.4453
0.6790	1.4492	1.4486	1.4486	1.4486	1.4486	1.4470
0.7954	1.4525	1.4519	1.4520	1.4520	1.4520	1.4510
0.9006	1.4547	1.4547	1.4547	1.4547	1.4547	1.4542
0.9292	1.4555	1.4553	1.4554	1.4554	1.4554	1.4550
0.9631	1.4563	1.4562	1.4562	1.4562	1.4562	1.4560
1	1.457	1.4570	1.4570	1.4570	1.4570	1.4570

[a] Ref. [28]

$$r_f = \frac{(n_{Lit}^2 - 1)}{(n_{Lit}^2 + 2)} \tag{10}$$

The Eq. (9) is a non-acoustic method to estimate the molecular radius (r_m) of liquid mixtures.

The molecular radius (r_m) can also be computed using the ideal mixing relation [20]. The standard form of r_m as extended to binary mixtures, is

$$r_m = X_1 r_1 + X_2 r_2 \tag{11}$$

$$r_1 = \left[\left\{\left(\frac{3}{4\pi N}\right)\frac{(n_1^2 - 1)}{(n_1^2 + 2)}\right\} v_1\right]^{1/3} \tag{11a}$$

$$r_2 = \left[\left\{\left(\frac{3}{4\pi N}\right)\frac{(n_2^2 - 1)}{(n_2^2 + 2)}\right\} v_2\right]^{1/3} \tag{11b}$$

Table 4. Refractive index values viz. *literature* (n_{Lit}) *and computed* (n_{cal}), *for PEG-400(1) + 1,3 Dioxolane(2), PEG-400(1) + Oxolane(2) and PEG-400(1) + Oxan (2) at 303.15 K.*

X_1	n_{Lit}[a]	n_{cal}				
		LLR (Equation (1))	GDR (Equation (2))	WR (Equation (3))	HR (Equation (4))	ABR (Equation (5))
PEG 400 (1) + 1,3-Dioxolane (2)						
0	1.3962	1.3962	1.3962	1.3962	1.3957	1.3962
0.0187	1.4029	1.4020	1.4021	1.4021	1.4017	1.4033
0.0474	1.4129	1.4095	1.4098	1.4097	1.4094	1.4121
0.1026	1.4226	1.4206	1.4211	1.4208	1.4206	1.4246
0.1865	1.4274	1.4321	1.4328	1.4324	1.4323	1.4364
0.2794	1.4428	1.4406	1.4413	1.4409	1.4408	1.4445
0.3361	1.4463	1.4445	1.4451	1.4447	1.4447	1.4480
0.5284	1.4547	1.4535	1.4539	1.4536	1.4536	1.4556
0.6065	1.4570	1.4560	1.4563	1.4561	1.4561	1.4577
0.6612	1.4567	1.4575	1.4577	1.4576	1.4576	1.4589
0.7860	1.4609	1.4603	1.4604	1.4603	1.4603	1.4611
0.9215	1.4629	1.4627	1.4627	1.4627	1.4627	1.4629
0.9672	1.4635	1.4633	1.4634	1.4633	1.4633	1.4634
1	1.4638	1.4638	1.4638	1.4638	1.4638	1.4638
PEG 400 (1) + Oxolane (2)						
0	1.4025	1.4025	1.4025	1.4025	1.4021	1.4025
0.0343	1.4117	1.4104	1.4107	1.4106	1.4103	1.4133
0.0688	1.4191	1.4170	1.4174	1.4172	1.4170	1.4216
0.1171	1.4273	1.4245	1.4250	1.4247	1.4245	1.4302
0.1806	1.4354	1.4320	1.4327	1.4323	1.4322	1.4384
0.2695	1.4426	1.4398	1.4405	1.4401	1.4400	1.4459
0.4046	1.4503	1.4480	1.4486	1.4482	1.4481	1.4528
0.5197	1.4544	1.4528	1.4533	1.4530	1.4530	1.4564
0.6744	1.4586	1.4575	1.4578	1.4576	1.4576	1.4598
0.7762	1.4607	1.4599	1.4601	1.4600	1.4600	1.4614
0.8676	1.4620	1.4617	1.4618	1.4617	1.4617	1.4626
0.9283	1.4629	1.4627	1.4627	1.4627	1.4627	1.4632
0.9433	1.4632	1.4629	1.4630	1.4630	1.4630	1.4633
1	1.4638	1.4638	1.4638	1.4638	1.4638	1.4638
PEG 400 (1) + Oxane (2)						
0	1.4165	1.4165	1.4165	1.4165	1.4163	1.4165
0.0405	1.4236	1.4227	1.4228	1.4227	1.4225	1.4243
0.0655	1.4268	1.4259	1.4261	1.4260	1.4258	1.4282
0.1183	1.4331	1.4318	1.4320	1.4319	1.4318	1.4347
0.1836	1.4391	1.4375	1.4378	1.4376	1.4376	1.4409
0.2716	1.4451	1.4435	1.4438	1.4436	1.4436	1.4469
0.3489	1.4491	1.4475	1.4479	1.4477	1.4476	1.4506
0.4415	1.4528	1.4514	1.4517	1.4515	1.4515	1.4541
0.5822	1.4570	1.4559	1.4561	1.4560	1.4559	1.4577
0.7260	1.4600	1.4593	1.4594	1.4593	1.4593	1.4604
0.8677	1.4623	1.4619	1.4619	1.4619	1.4619	1.4624
0.9037	1.4628	1.4624	1.4625	1.4624	1.4624	1.4628
0.9336	1.4631	1.4629	1.4629	1.4629	1.4629	1.4631
1	1.4638	1.4638	1.4638	1.4638	1.4638	1.4638

[a] Ref. [28]

where r_1 and r_2 are the radii of the pure component 1 (PEG-200 and PEG-400) and component 2 (1,3-Dioxolane, Oxolane and Oxane), respectively. These radii are, in actual fact, the radii of sphere-equivalent polarizability volumes of corresponding molecules.

3. Results and discussion

In the present study, the refractive indices of six binary mixtures at 303.15 K and atmospheric pressure, have been computed using five refractive index mixing rules *viz.*, Lorentz–Lorentz, Gladstone

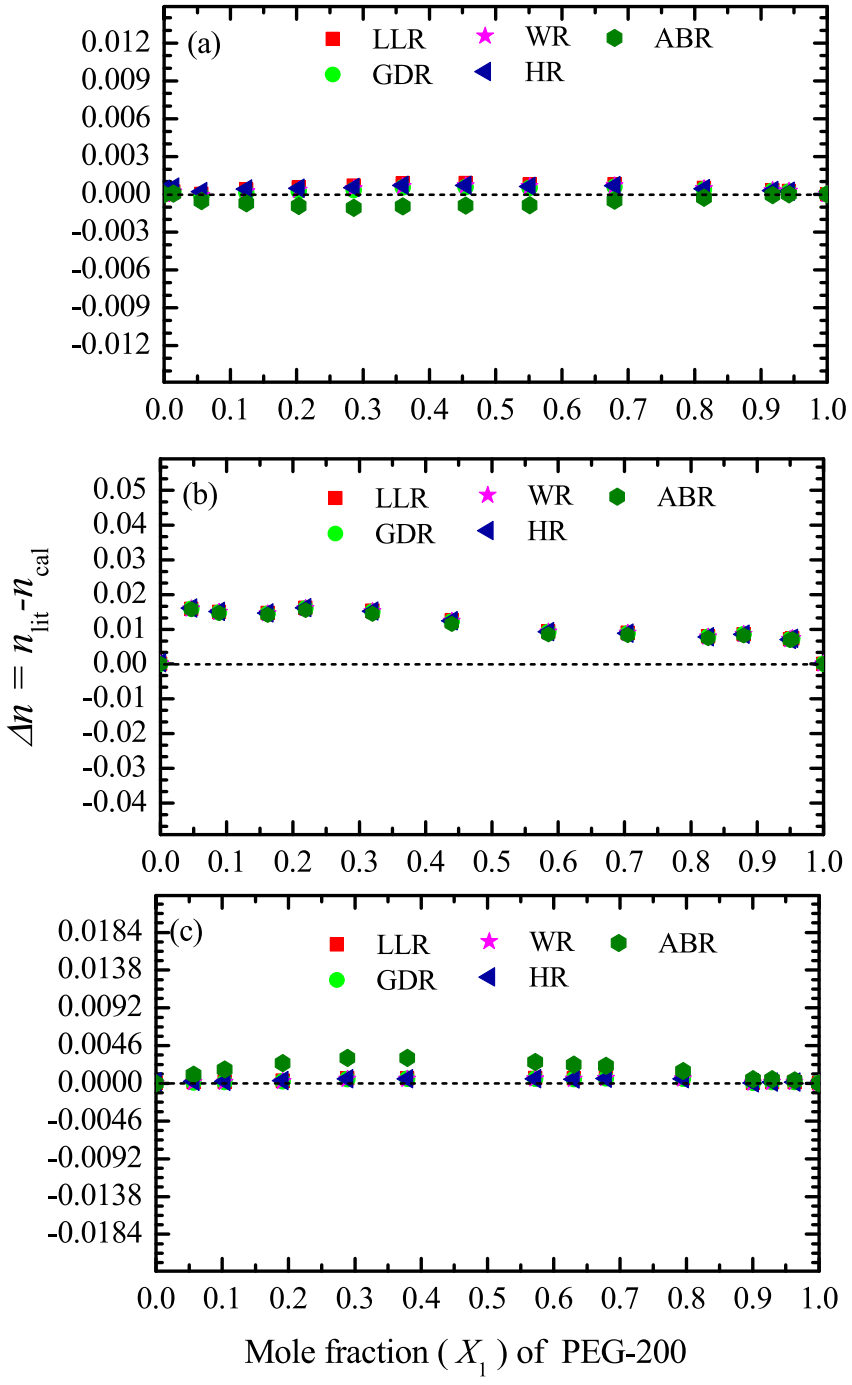

Fig. 2. Deviation (Δn) of (a) PEG-200 + 1,3 Dioxolane (b) PEG-200 + Oxolane (c) PEG-200 + Oxane at various mole fractions (X_1) of PEG-200.

Dale, Wiener, Heller and Arago -Biot. The required experimental values of refractive index (n_{Lit}) and density (d) have been taken from the literature [28]. The refractive indices of the binary polymer systems, under study are computed using Eqs. (1)–(5) and reported in Tables 3 and 4. The deviations; $\Delta n = n_{Lit}$-n_{cal} of the computed refractive indices (n_{cal}) from their corresponding literature data (n_{Lit}) have also been determined for all the binary mixtures. These deviations are plotted against the mole fraction (X_1) of PEG-200 and PEG-400 in Figs. 2 and 3, respectively. The average percentage deviations of refractive indices for each mixing rule are reported in Table 5.

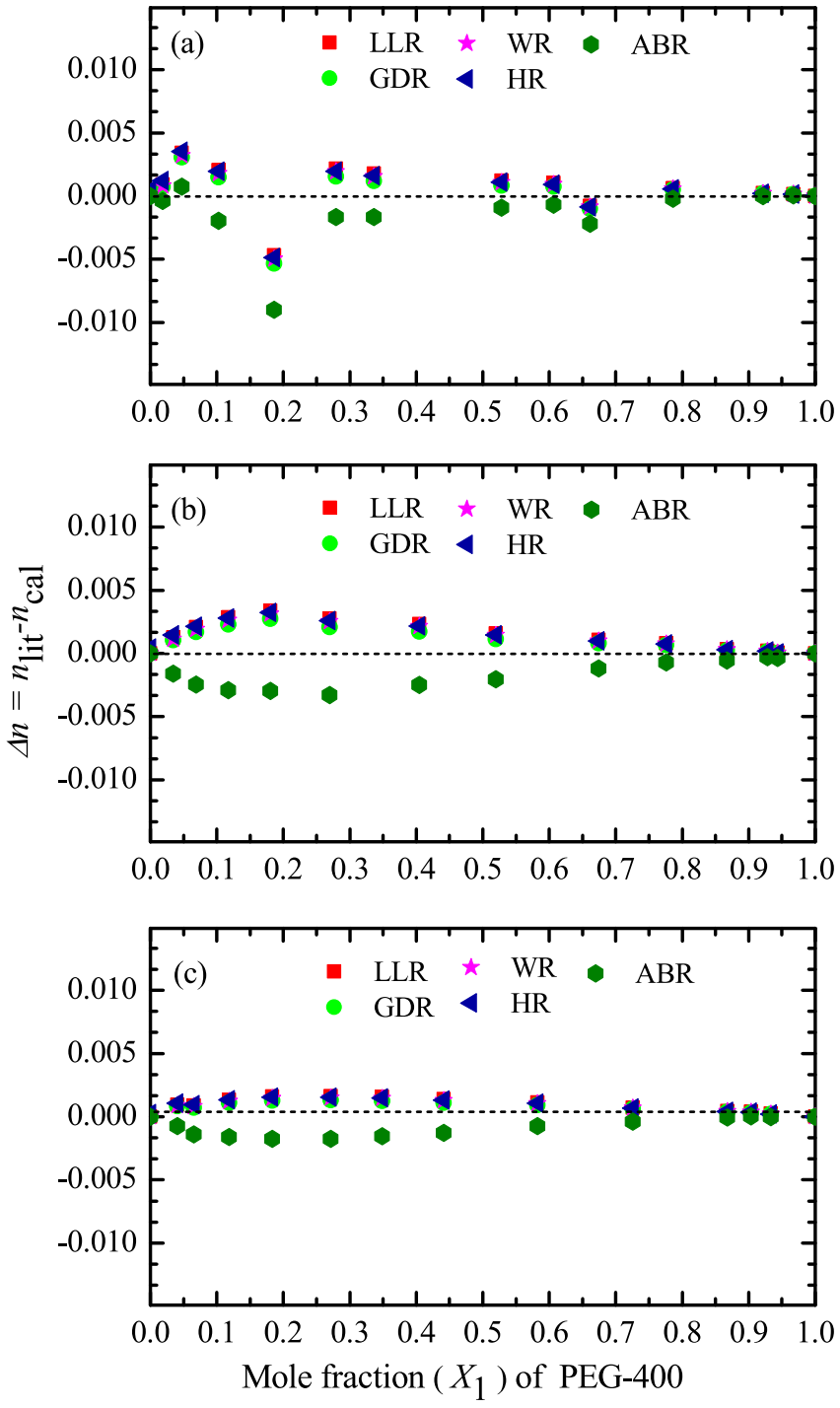

Fig. 3. Deviation (Δn) of (a) PEG-400 + 1,3 Dioxolane (b) PEG-400 + Oxolane (c) PEG-400 + Oxane at various mole fraction (X_1) of PEG-400.

Table 5. Average percentage deviation of refractive indices for the binary mixtures of PEG-200 and PEG-400 with 1,3-Dioxolane, Oxolane and Oxane at 303.15 K.

System	LLR	GDR	WR	HR	ABR
PEG 200 (1) + 1,3-Dioxolane (2)	0.0311	0.0202	0.0238	0.0316	0.0340
PEG 200 (1) + Oxolane (2)	0.6865	0.6778	0.6803	0.6867	0.6570
PEG 200 (1) + Oxane (2)	0.0228	0.0200	0.0193	0.0227	0.1052
PEG 400 (1) + 1,3-Dioxolane (2)	0.0949	0.0838	0.0899	0.0971	0.0971
PEG 400 (1) + Oxolane (2)	0.0924	0.0723	0.0849	0.0917	0.1037
PEG 400 (1) + Oxane (2)	0.0606	0.0496	0.0558	0.0602	0.0561

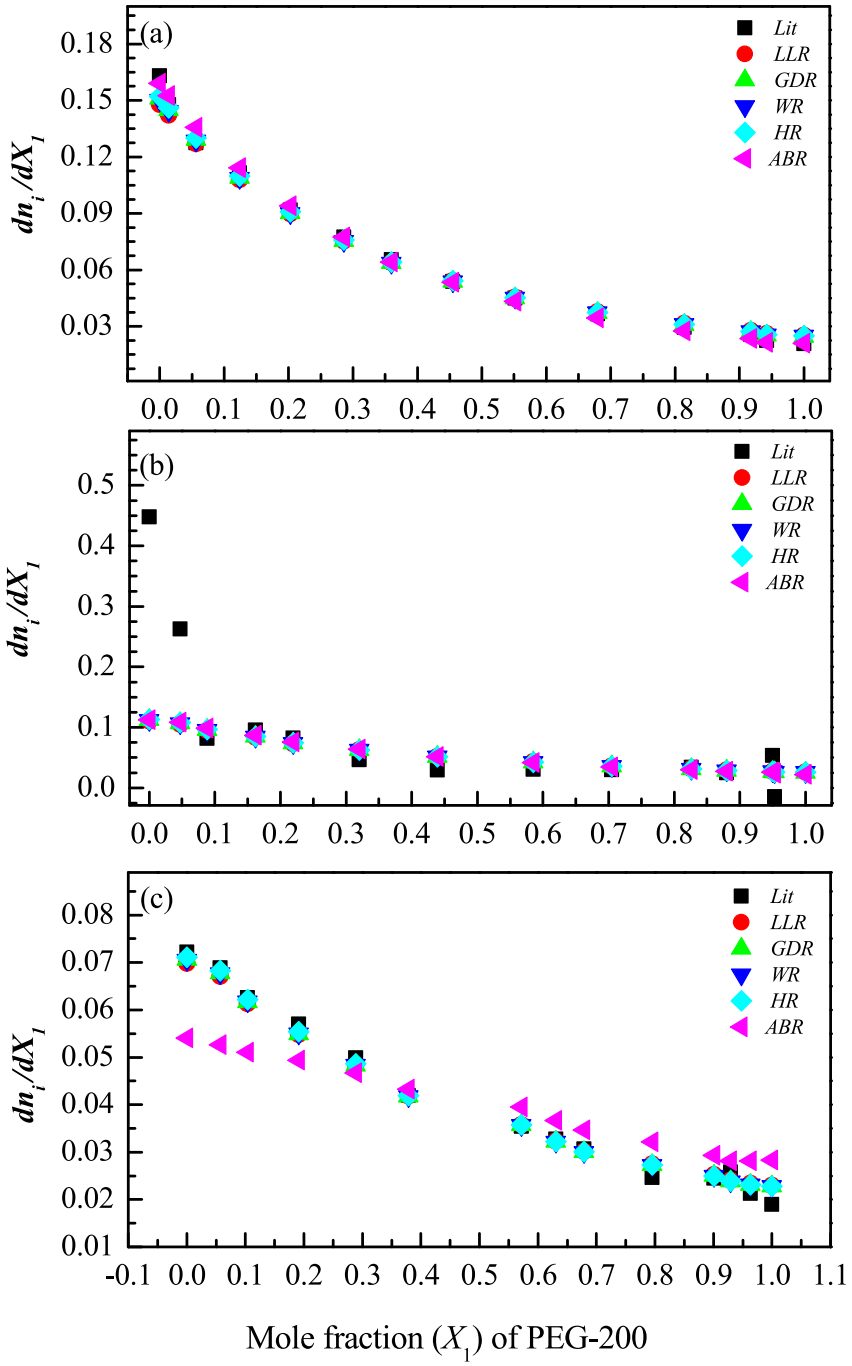

Fig. 4. Comparison of dn_i/dX_1 (i = Lit, LLR, GDR, WR, HR, and ABR) *values for (a) PEG-200 + 1,3 Dioxolane (b) PEG-200 + Oxolane (c) PEG-200 + Oxane at various mole fractions*(X_1) *of PEG-200 in polymer mixture.*

A perusal of Tables 3 and 4 indicates that the refractive indices computed using five mixing rules are in good agreement with their corresponding literature values for all the binary mixtures studied here. This conclusion is in conformity with the results reported in Figs. 2 and 3. The validity of the Lorentz–Lorenz relation and Arago -Biot relation can be inferred based on the minimum change in volume on mixing the constituents of these binary mixtures [15,17]. The nearly equal values of refractive indices ($n_1 \approx n_2$) of the pure components allow for the good performance of GDR relation [21] for these binary mixtures. Figure 2 reveals that the deviation (Δn) is less than 0.02, which is well within the

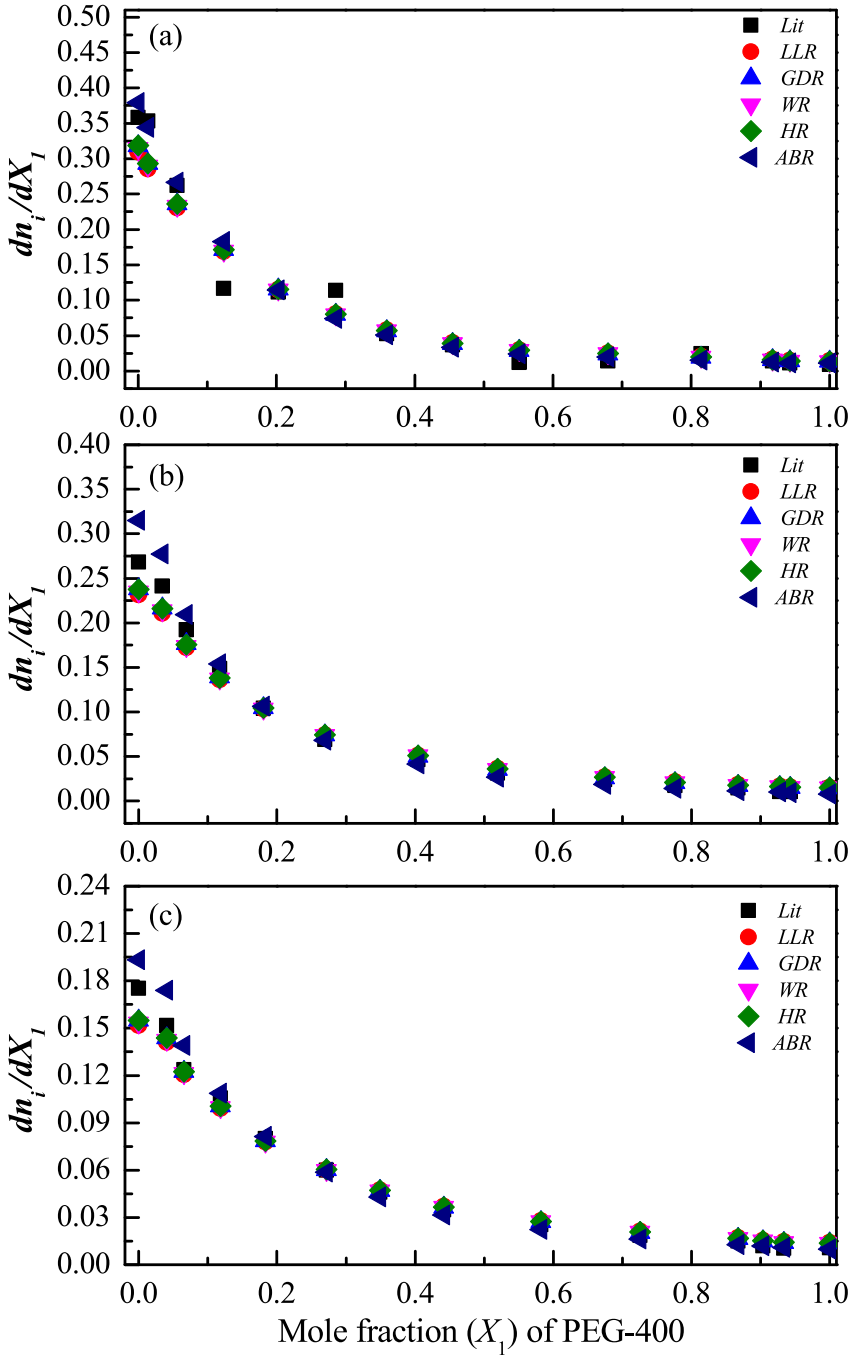

Fig. 5. Comparison of dn_i/dX_1 (i = Lit, LLR, GDR, WR, HR, and ABR) *values for (a) PEG-400 + 1,3 Dioxolane (b) PEG-400 + Oxolane (c) PEG-400 + Oxane at various mole fractions* (X_1) *of PEG-400 in polymer mixture.*

standard experimental limits (generally 0.05). A similar trend is evident in Fig. 3 for the binary mixtures of PEG-400 and cyclic ethers.

Figures 2 and 3 also reveal that for all binary mixtures with $X_1 > 0.5$ (mole fraction PEG-200 or PEG-400), the deviations (Δn) of all the mixing rules from literature values are almost negligible. It points out that these mixtures exhibit almost ideal behavior in higher concentration region ($X_1 > 0.5$). It is further evident from Fig. 2 that the deviation in PEG-200 + Oxolane is higher than PEG-200 + 1,3-Dioxolane and PEG 200 + Oxane. A similar trend has been observed in the case of PEG-400 + Oxolane w.r.t. other binary mixtures of PEG-400 and cyclic ethers [Fig. 3]. The small positive deviations reported by these relations can be accounted for by the volume contraction due to intermolecular interactions among polar molecules on mixing the constituents [15]. The average percentage deviations of the refractive indices for the six binary mixtures of PEG and cyclic ethers at 303.15 K are reported in Table 5. Based on the above discussion and very low values of average percentage deviation of refractive index (Table 5), it is pointed out that all the five theoretical mixing rules perform well over the given concentration range of these binary mixtures. Thereby, these relations are capable to predict the refractive indices for the entire concentration range of these mixtures.

The concentration derivatives of the refractive index (dn_i/dX_1) for all six binary polymer mixtures are calculated. The obtained values of dn_i/dX_1 are plotted against mole fraction (X_1) of PEG-200 and PEG-400. In the expression dn_i/dX_1, i = Lit, LLR, GDR, WR, HR, and ABR. All these abbreviations have the same meaning as reported earlier. The obtained graphs are presented in Figs. 4 and 5, respectively. These graphs reveal a good agreement

Table 6. Deviation in refractive index (Δn_{Lit}), and reduced free volume ($\Delta(V/R_m)$) values for PEG 200(1) + 1,3 Dioxolane(2), PEG 200(1) + Oxolane(2) and PEG-200(1) + Oxane(2) at 303.15 K.

PEG-200 + 1,3 Dioxolane			PEG-200 + Oxolane			PEG-200 + Oxane		
X_1	Δn_{Lit}	$\Delta(V/R_m)$	X_1	Δn_{Lit}	$\Delta(V/R_m)$	X_1	Δn_{Lit}	$\Delta(V/R_m)$
0	0.0000	0.0000	0	0.0000	0.0000	0	0.0000	0.0000
0.0141	0.0002	−0.0019	0.0471	0.0158	−0.1340	0.0568	0.0001	−0.0013
0.0565	−0.0001	−0.0001	0.0884	0.0148	−0.1238	0.1041	0.0001	−0.0018
0.124	0.0001	−0.0030	0.1622	0.0145	−0.1176	0.1912	0.0002	−0.0029
0.2029	0.0002	−0.0042	0.2191	0.0160	−0.1266	0.289	0.0005	−0.0050
0.2859	0.0003	−0.0051	0.3201	0.0150	−0.1160	0.379	0.0005	−0.0050
0.3599	0.0005	−0.0064	0.4394	0.0123	−0.0924	0.572	0.0006	−0.0047
0.4548	0.0006	−0.0064	0.5854	0.0092	−0.0677	0.6305	0.0005	−0.0043
0.5515	0.0005	−0.0056	0.7046	0.0088	−0.0633	0.679	0.0006	−0.0048
0.6794	0.0006	−0.0057	0.8261	0.0078	−0.0550	0.7954	0.0005	−0.0042
0.8142	0.0004	−0.0036	0.8799	0.0085	−0.0592	0.9006	0.0000	−0.0004
0.9175	0.0003	−0.0022	0.95	0.0071	−0.0488	0.9292	0.0001	−0.0011
0.9424	0.0002	−0.0018	0.953	0.0073	−0.0503	0.9631	0.0001	−0.0010
1	0.0000	0.0000	1	0.0000	0.0000	1	0.0000	0.0000

Table 7. Deviation in refractive index (Δn_{Lit}) and reduced free volume ($\Delta(V/R_m)$) values for PEG-400(1) + 1,3 Dioxolane(2), PEG-400(1) + Oxolane(2) and PEG-400(1) + Oxane(2) at 303.15 K.

PEG-400 + 1,3 Dioxolane			PEG-400 + Oxolane			PEG-400 + Oxane		
X_1	Δn_{Lit}	$\Delta(V/R_m)$	X_1	Δn_{Lit}	$\Delta(V/R_m)$	X_1	Δn_{Lit}	$\Delta(V/R_m)$
0	0.0000	0.0000	0	0.0000	0.0000	0	0.0000	0.0000
0.0187	0.0008	−0.0077	0.0343	0.0010	−0.0098	0.0405	0.0008	−0.0073
0.0474	0.0031	−0.0284	0.0688	0.0017	−0.0159	0.0655	0.0007	−0.0066
0.1026	0.0015	−0.0154	0.1171	0.0023	−0.0210	0.1183	0.0011	−0.0098
0.1865	−0.0054	0.0381	0.1806	0.0027	−0.0243	0.1836	0.0013	−0.0114
0.2794	0.0015	−0.0152	0.2695	0.0021	−0.0191	0.2716	0.0013	−0.0114
0.3361	0.0012	−0.0123	0.4046	0.0017	−0.0157	0.3489	0.0012	−0.0108
0.5284	0.0008	−0.0082	0.5197	0.0011	−0.0105	0.4415	0.0011	−0.0095
0.6065	0.0007	−0.0069	0.6744	0.0008	−0.0070	0.5822	0.0009	−0.0076
0.6612	−0.0010	0.0055	0.7762	0.0006	−0.0053	0.726	0.0006	−0.0049
0.786	0.0005	−0.0041	0.8676	0.0002	−0.0021	0.8677	0.0004	−0.0029
0.9215	0.0002	−0.0016	0.9283	0.0002	−0.0013	0.9037	0.0003	−0.0025
0.9672	0.0001	−0.0011	0.9433	0.0000	−0.0004	0.9336	0.0002	−0.0015
1	0.0000	0.0000	1	0.0000	0.0000	1	0.0000	0.0000

with the corresponding plots of the literature values. However, a closed examination of Fig. 4(c) points out that in the PEG-200 + Oxane binary system, at a lower mole fraction of PEG-200, dn_{ABR}/dX_1 value deviates from the corresponding literature value. It is likely due to the preponderance of cohesive interactions among the molecules of individual liquids over the intermolecular interactions prevalent in the constituents of the binary mixtures. Furthermore, for the three binary systems: PEG-400 + cyclic ethers [Fig. 5], a similar trend of variation for dn_{ABR}/dX_1 versus X_1 is observed in the low-concentration region of the polymer. However, the overall trend of these variations support and supplement the conclusion arrived at earlier.

Brocos and co-workers [6] reported that refractive index deviation of computed value from respective experimental ones and pointed out that understanding the nature of intermolecular interactions among constituents of a mixture; volume fraction property is more useful than mole fraction. The same research group [6] has also pointed out that intermolecular interactions could be easily interpreted in terms of the sign-reversal measurement of deviation in reduced free volume. Considering the above suggestion, Δn_{Lit} and $\Delta(V/R_m)$ are computed and the obtained results are reported in Tables 6 and 7. These results indicate that, in general, Δn_{Lit} values are positive over the entire concentration range for all the six binary polymer mixtures. This trend of variation of Δn_{Lit} values indicates the presence of associative interactions among constituent molecules of the binary mixtures [20]. The negative values of reduced free volume $\Delta(V/R_m)$ for all the systems supplements these results. It is well known that PEG-200 (Dipole moment = 3.18 D), PEG-400 (Dipole moment = 3.50 D), and Oxolane (Dipole moment = 1.63 D) are polar molecules and 1,3 Dioxolane and Oxane contain polar covalent -C-O- bonds. So, dipole–dipole interactions and hydrogen bonding among the constituting molecules of the binary mixtures are expected.

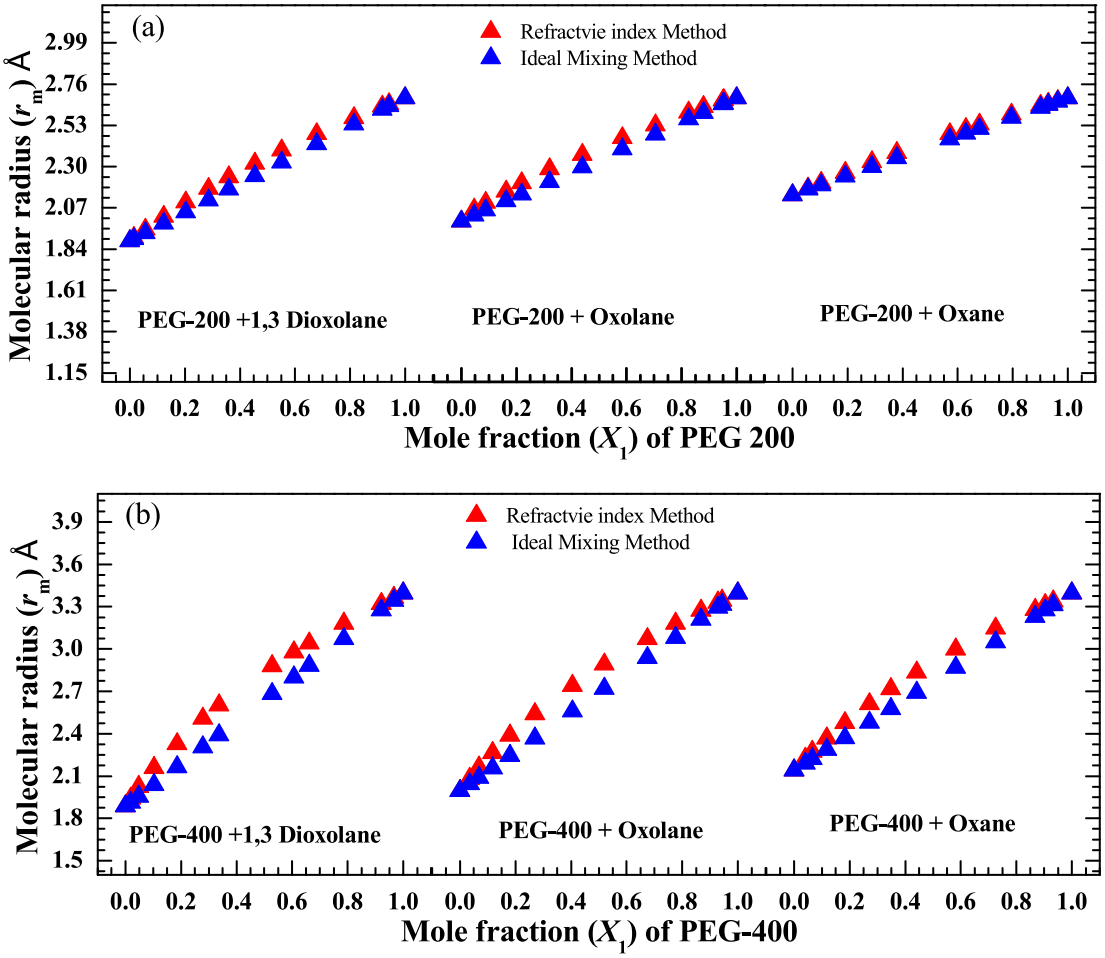

Fig. 6. Molecular radius(r_m) of (a) PEG-200 + 1,3 Dioxolane, PEG-200 + Oxolane, and PEG-200 + Oxane (b) PEG-400 + 1,3 Dioxolane, PEG-400 + Oxolane, and PEG-400 + Oxane at various mole fractions of PEG.

The molecular radius at various mole fractions of the six binary mixtures, under study, is computed using the refractive index method [Eq. (9)] and the ideal mixing method [Eq. (11)]. These results are reported in Fig. 6. The close look of Fig. 6 reveals that there is a good agreement between the refractive index and the ideal mixing methods for all the binary mixtures studied here. This deduction supports the additive nature of r_m with respect to the mole fraction of pure components [20]. The gradual linear increase in r_m values with the increase in mole fraction of PEG in all the six binary mixtures is as expected. It is due to the replacement of small-sized molecules of solvents (e.g., 1, 3 Dioxolane, $r_m = 188.6$ pm; Oxolane, $r_m = 199.6$ pm; and Oxane, $r_m = 214.1$ pm) by relatively big-sized molecules of the solute (PEG-200, $r_m = 268.4$ pm and PEG-400, $r_m = 339.5$pm), with the rise in mole fraction (X_1) of PEG in the respective binary mixtures. Figure 6 also indicates that the magnitude of r_m is slightly higher in the binary mixtures of PEG-400 and cyclic ethers as compared to PEG-200 and cyclic ethers. It is likely because of the addition of bigger-sized molecules of PEG-400 (containing an average of 8.7 oxyethylene groups) as compared to the small-sized PEG-200 molecules (containing an average of 4.13 oxyethylene groups). The overall increase in the r_m values for all these systems also suggests the possibility of weak dispersive interactions. However, the preponderance of dipole–dipole interactions and hydrogen bonding among the constituting molecules of the binary mixtures cannot be ruled out [37,38].

The space-filling ability assumes that the molecules are incompressible hard spheres having uniform radii [39]. The variation of the space-filling factor (r_f) with change in the mole fraction (X_1) of PEG for all the systems under investigation is plotted in Fig. 7. The packing efficiency difference for these binary mixtures is reflected via different shapes of the space-filling ability curves in the higher concentration region of PEG. The slight change in the shape of the curve in the high-concentration region of the PEG indicates structural rearrangement. The space-filling ability for the PEG-400 + cyclic ethers is slightly higher than that of the PEG-200 + cyclic ethers in the higher concentration region of these binary systems. The isotherms (r_f) versus X_1 for these mixtures become slightly convex-shaped in the high mole fraction region (i.e., above $X_1 \sim 0.5$). The space-filling ability becomes maximum in this region. It indicates the dominance of relatively strong dipole–dipole interactions in this region. On further increasing the mole fraction of PEG, structural rearrangement occurs among the constituent molecules. So the space-filling ability rises again. However, for the PEG-200 + cyclic ethers mixtures, these isotherms are slightly less convex as compared to the corresponding graphs of PEG-400+cyclic ethers. It is as

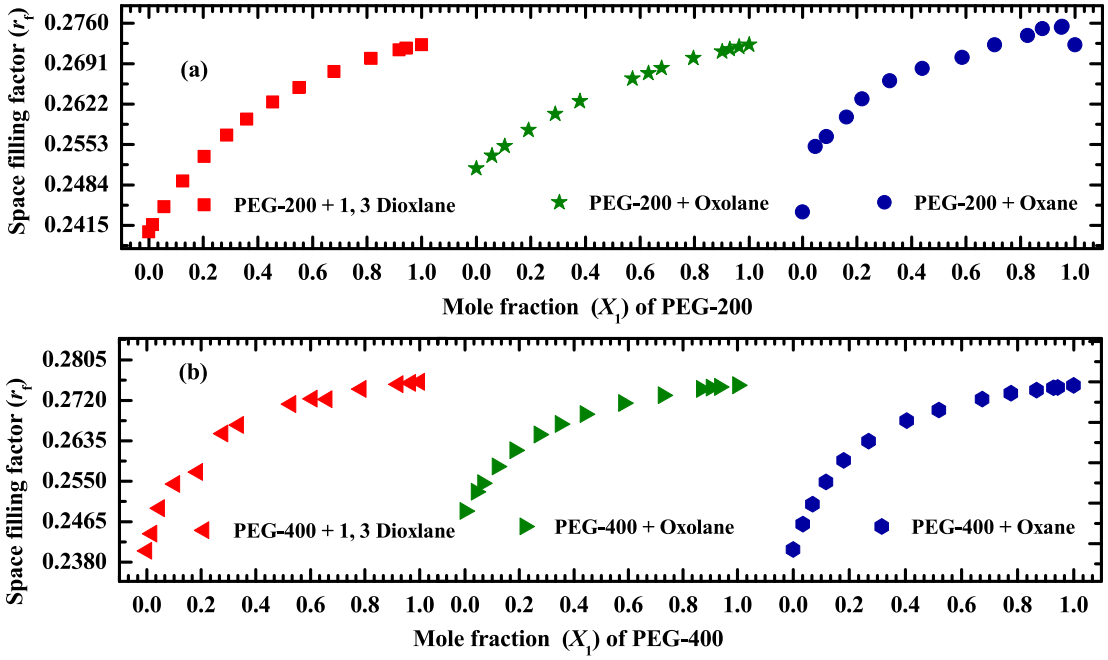

Fig. 7. Space-filling factor (r_f) of (a) PEG-200 + 1,3 Dioxolane, PEG-200 + Oxolane, and PEG-200 + Oxane (b) PEG-400 + 1,3 Dioxolane, PEG-400 + Oxolane, and PEG-400 + Oxane at various mole fractions of PEG.

expected as PEG-200 (Dipole moment = 3.18 D) is slightly less polar as compared to PEG-400 (Dipole moment = 3.50 D).

4. Conclusions

The relative efficacy of five refractive index mixing rules to predict refractive indices for six binary polymer mixtures has been established. Using the reduced free volume and the deviation of computed refractive indices from their corresponding literature data, the nature and strength of intermolecular interactions among the constituents of these binary mixtures have been determined. It is identified that the dipole−dipole interactions and hydrogen bonding type of associative interactions exist in these mixtures. Furthermore, the molecular radius for these binary mixtures is predicted using the refractive index and ideal mixing methods. The variation of molecular radius, with a change in the mole fraction of PEG, supplements and supports the existence of weak associative intermolecular interactions among the constituents of these systems.

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