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Research Article

REFRACTIVE INDICES FOR BINARY MIXTURES OF PROPYLENE CARBOANTE

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ABSTRACT

Refractive indices (n), excess refractive indices (Δn), molar volume (Vm), molar refraction (R) and excess molar refraction (ΔR) are presented for the binary mixtures of propylene carbonate (PC) (1) with tetrahydrofuran (THF), 1,4-dioxane, acetylacetone and acetone (2) at 298.15, 303.15 and 308.15 K over the entire mole fraction range. The excess refractive index (Δn) values have been fitted to Redlich-Kister equation at 298.15 K and standard deviations have been calculated.

Keywords*:* Refractive index; propylene carbonate; excess refractive index; molar refraction

INTRODUCTION

The studies on molecular interaction of liquid-liquid mixtures are gaining a lot of importance in these days. Refractive index, excess refractive index etc. are used to explain the nature of solute-solvent interactions. The refractive index along with density values of mixtures are used to test the accuracy of available refractive index mixing relationships in predicting binary refractive index data.

In continuation to our research work on thermodynamic properties of liquid-liquid mixtures of PC with polar, nonpolar, applicable solvents[1-5], we represent here refractive indices (n), excess refractive indices (Δn), molar volume (Vm), molar refraction (R) and excess molar refraction (ΔR) values for the binary mixtures of PC (1) with THF, 1, 4-dioxane, acetylacetone and acetone (2) at 298.15, 303.15 and 308.15 K over the entire mole fraction range. The excess refractive index values (Δn) have been fitted to Redlich-Kister equation at 298.15 K and standard deviations have been calculated. The results obtained are discussed in terms of intermolecular interactions present amongst the components.

MATERIAL AND METHODS

PC (Merck, > 99%) was refluxed over anhydrous calcium carbonate and distilled at atmospheric pressure[6]. 1, 4-dioxane (S. D. Fine Chem., Pvt. Ltd.), THF, acetylacetone and acetone (Spectrochem. Pvt. Ltd.) were distilled at atmospheric pressure. All the liquids were double distilled. The middle fraction collected of all the liquids was stored over 4 Å molecular sieves.

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles in order to minimize the evaporation losses. All measurements of mass were performed on a Mettler one pan balance which can be read up to the fifth decimal place with an accuracy of ±0.05 mg.

The refractive indices were measured with a thermostated Abbe refractometer (Focus AR-201 85010) using the sodium D line. The refractometer was calibrated by means of a glass test piece of known refractive index supplied by the manufacturer. The uncertainity in the refractive index measurement was ± $3x10^{-4}$.

For all the measurements, the temperature was controlled by circulating the water through an ultra thermostat Julabo F-25 (made in Germany) which has an accuracy of $\pm 0.02^0$C.

CONCLUSION

The refractive index (n) values were utilized to calculate excess refractive indices (Δn) using the following equation,

$$\Delta n = n_m - x_1 n_1 - x_2 n_2 \quad (1)$$

Molar refraction (R) for the binary mixtures was calculated using Lorentz-Lorentz equation[7]

$$R = (n^2-1/n^2+2).V_m \quad (2)$$

Where V_m is the molar volume.

Excess molar refraction (ΔR) values give more information than Δn about the mixture phenomenon because it takes into account the electronic perturbation of molecular orbitals during the liquid mixture process[8] and *R* is also directly related to the dispersion forces.

The ΔR values were calculated for all the binary mixtures at all the above said temperatures using following equation

$$\Delta R = R_m - x_1R_1 - x_2R_2 \quad (3)$$

The calculated values of Δn were correlated by Redlich-Kister polynomial[9] at 298.15 K as shown in equation

$$Y^E = x_1x_2\Sigma\, a_i\,(x_1-x_2)^i \quad (4)$$

The coefficients in equation (4) were estimated by the least square fit method and the standard deviations were calculated by equation

$$\sigma = [\Sigma\,(Y^E_{expt} - Y^E_{cal})^2/(D-N)]^{0.5} \quad (5)$$

Where D and N are the number of data points and parameters respectively. Regression results for Δn values of all the binary mixtures at 298.15 K are as shown in Table 2.

The values of refractive indices (n), molar volume (Vm) and molar refraction (R) for the binary mixtures of PC with THF, 1, 4-dioxane, acetylacetone and acetone at 298.15, 303.15 and 308.15 K are represented in Table 1. From Table it can be noticed that, the n values increase with increasing mole fraction of PC and decrease with increasing temperature for all mixtures.

Figure 1 shows the graphical variation of excess refractive index (Δn) values for the binary mixtures of PC (1) with THF, 1, 4-dioxane, acetylacetone and acetone (2) at 298.15 K. The Δn values are complete negative for THF, 1, 4-dioxane and acetone mixtures. The negative values are increasing with increasing temperatures. For acetylacetone mixtures, positive values are observed up to 0.7 mole fraction of PC and then becoming slightly negative towards the end. These values follow the order, acetylacetone > acetone > THF > 1, 4-dioxane.

Figure 2 shows the graphical variation of excess molar refraction (ΔR) values for the binary mixtures at 298.15 K. The ΔR values are negative for binary mixtures of PC with THF, 1, 4-dioxane and acetone. The acetylacetone mixture shows positive values of ΔR. The ΔR values follow the order, acetylacetone > acetone > 1, 4-dioxane > THF. The values for acetone didn't follow a smooth trend.

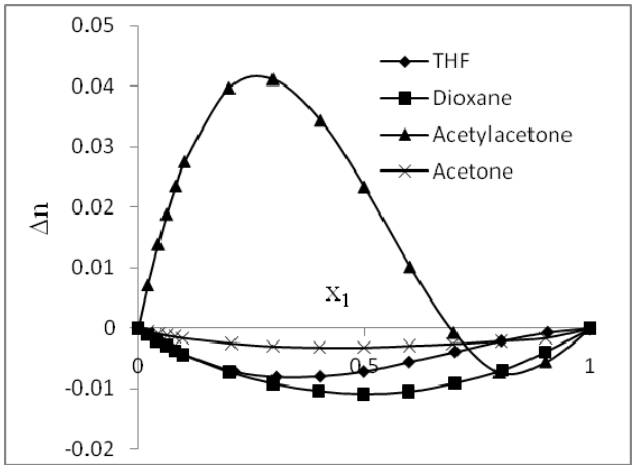

Fig. 1: It shows variation of excess refractive indices (n) for binary mixtures of PC (1) + THF, 1, 4-dioxane, acetylacetone and acetone at 298.15 K

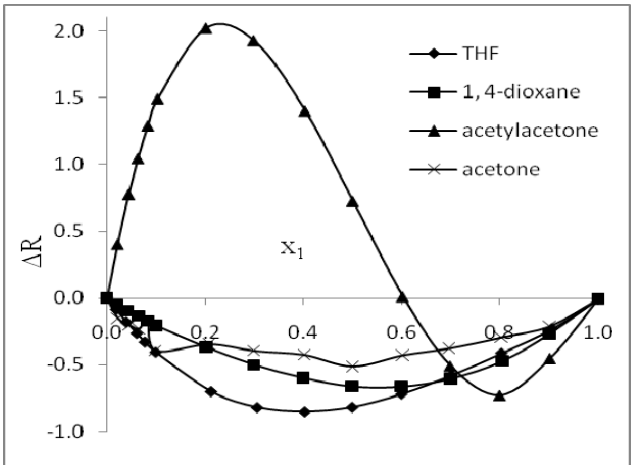

FIg. 2: It shows variation of excess molar refraction (R) for binary mixtures of PC (1) + THF, 1, 4-dioxane, acetylacetone and acetone at 298.15 K

Table 1: It shows refractive index (n), molar volume (Vm) and molar refraction (R) values for binary mixtures of PC (1) with THF, 1, 4-dioxane, acetylacetone and acetone (2) at 298.15, 303.15 and 308.15 K.

Propylene carbonate (1) + THF (2)									
x_1	**n**	**V_m**	**R**	**n**	**V_m**	**R**	**n**	**V_m**	**R**
	T= 298.15 K			**T = 303.15 K**			**T = 308.15 K**		
0.0000	1.4049	81.76	20.04	1.4026	82.29	20.06	1.4008	82.80	20.11
0.0188	1.4043	81.63	19.98	1.4022	82.15	20.01	1.4005	82.66	20.06
0.0393	1.4036	81.51	19.92	1.4017	82.02	19.96	1.4001	82.52	20.01
0.0603	1.4031	81.39	19.87	1.4013	81.90	19.91	1.3999	82.39	19.97
0.0770	1.4027	81.31	19.83	1.4011	81.81	19.88	1.3997	82.30	19.94
0.0988	1.4023	81.21	19.79	1.4009	81.71	19.85	1.3996	82.19	19.91
0.2117	1.4014	80.93	19.68	1.4005	81.41	19.76	1.3996	81.86	19.83
0.3057	1.4021	80.95	19.71	1.4013	81.40	19.79	1.4006	81.83	19.86
0.4024	1.4039	81.15	19.84	1.4030	81.58	19.91	1.4024	81.99	19.98
0.4992	1.4064	81.50	20.04	1.4053	81.91	20.09	1.4048	82.31	20.16
0.5997	1.4097	81.99	20.30	1.4084	82.40	20.34	1.4077	82.78	20.41
0.7015	1.4132	82.62	20.61	1.4118	83.00	20.64	1.4109	83.38	20.70
0.8033	1.4168	83.32	20.94	1.4152	83.71	20.97	1.4140	84.08	21.01
0.9064	1.4200	84.16	21.30	1.4183	84.50	21.31	1.4170	84.88	21.34
1.0000	1.4223	85.25	21.68	1.4205	85.61	21.69	1.4191	86.00	21.72

Continue...

Propylene carbonate (1) + 1, 4-dioxane (2)									
x_1	**n**	**V_m**	**R**	**n**	**V_m**	**R**	**n**	**V_m**	**R**
	T= 298.15 K			**T = 303.15 K**			**T = 308.15 K**		
0.0000	1.4200	85.72	21.69	1.4174	86.21	21.70	1.4153	86.68	21.72
0.0213	1.4189	85.71	21.64	1.4166	86.20	21.66	1.4147	86.66	21.69
0.0410	1.4180	85.70	21.60	1.4159	86.18	21.62	1.4141	86.64	21.66
0.0636	1.4172	85.68	21.56	1.4152	86.16	21.58	1.4135	86.62	21.62
0.0823	1.4165	85.66	21.52	1.4146	86.14	21.55	1.4130	86.59	21.59
0.0999	1.4158	85.64	21.48	1.4141	86.11	21.52	1.4126	86.56	21.57
0.2020	1.4132	85.46	21.32	1.4115	85.92	21.36	1.4104	86.35	21.41
0.2990	1.4115	85.24	21.19	1.4099	85.67	21.22	1.4089	86.10	21.28
0.3991	1.4105	85.02	21.09	1.4090	85.43	21.12	1.4080	85.84	21.18
0.4991	1.4102	84.81	21.02	1.4089	85.21	21.06	1.4078	85.61	21.11
0.5987	1.4109	84.68	21.02	1.4096	85.06	21.06	1.4086	85.45	21.11
0.6996	1.4125	84.63	21.08	1.4113	85.00	21.12	1.4104	85.39	21.17
0.8049	1.4149	84.72	21.21	1.4139	85.08	21.26	1.4130	85.47	21.31
0.9003	1.4182	84.94	21.42	1.4171	85.31	21.46	1.4160	85.70	21.51
1.0000	1.4223	85.25	21.68	1.4205	85.61	21.69	1.4191	86.00	21.72

Continue...

Propylene carbonate (1) + acetylacetone (2)									
x_1	**n**	**V_m**	**R**	**n**	**V_m**	**R**	**n**	**V_m**	**R**
	T= 298.15 K			**T = 303.15 K**			**T = 308.15 K**		
0.0000	1.4016	102.99	25.05	1.3765	103.48	23.77	1.3518	103.92	22.46
0.0212	1.4091	102.65	25.38	1.3881	103.14	24.34	1.3680	103.60	23.32
0.0438	1.4163	102.26	25.68	1.3992	102.77	24.87	1.3836	103.23	24.11
0.0625	1.4217	101.93	25.89	1.4075	102.43	25.24	1.3952	102.91	24.68
0.0827	1.4268	101.55	26.06	1.4155	102.06	25.58	1.4065	102.54	25.21
0.1026	1.4312	101.16	26.20	1.4224	101.67	25.86	1.4163	102.16	25.66
0.2010	1.4455	99.07	26.39	1.4452	99.58	26.51	1.4492	100.09	26.86
0.2982	1.4489	96.85	25.97	1.4518	97.35	26.25	1.4599	97.84	26.79
0.4028	1.4442	94.43	25.09	1.4463	94.90	25.32	1.4540	95.37	25.83
0.5000	1.4352	92.28	24.09	1.4342	92.73	24.16	1.4388	93.16	24.49
0.6016	1.4242	90.23	23.03	1.4193	90.66	22.91	1.4193	91.06	23.01
0.6985	1.4153	88.55	22.19	1.4076	88.95	21.92	1.4035	89.33	21.82
0.7995	1.4108	87.15	21.63	1.4027	87.53	21.34	1.3964	87.90	21.14
0.9016	1.4147	86.16	21.56	1.4103	86.53	21.45	1.4056	86.90	21.33
1.0000	1.4223	85.25	21.68	1.4205	85.61	21.69	1.4191	86.00	21.72

Continue...

Propylene carbonate (1) + acetone (2)									
x_1	**n**	**V_m**	**R**	**n**	**V_m**	**R**	**n**	**V_m**	**R**
	T= 298.15 K			**T = 303.15 K**			**T = 308.15 K**		
0.0000	1.3562	74.00	16.18	1.3532	74.49	16.16	1.3506	75.03	16.17
0.0224	1.3572	73.70	16.15	1.3544	74.25	16.16	1.3519	74.78	16.17
0.0453	1.3583	73.84	16.23	1.3556	74.41	16.24	1.3533	74.94	16.26
0.0643	1.3593	74.01	16.30	1.3567	74.55	16.32	1.3544	75.06	16.33
0.0816	1.3602	74.54	16.46	1.3577	75.07	16.47	1.3555	75.58	16.49
0.0985	1.3611	73.78	16.33	1.3586	74.28	16.34	1.3565	74.78	16.36
0.2076	1.3674	75.53	16.98	1.3651	76.02	16.99	1.3632	76.51	17.02
0.2994	1.3730	76.51	17.43	1.3708	76.97	17.44	1.3690	77.44	17.47
0.4011	1.3795	77.63	17.96	1.3774	78.12	17.99	1.3757	78.50	18.00
0.4993	1.3860	78.39	18.41	1.3840	78.83	18.43	1.3824	79.24	18.46
0.6012	1.3930	79.85	19.06	1.3911	80.28	19.08	1.3896	80.69	19.11
0.6964	1.3996	81.06	19.63	1.3978	81.47	19.65	1.3964	81.89	19.69
0.8023	1.4071	82.44	20.30	1.4054	82.85	20.32	1.4041	83.24	20.36
0.9010	1.4142	83.71	20.93	1.4125	84.10	20.95	1.4113	84.49	20.99
1.0000	1.4223	85.25	21.68	1.4205	85.61	21.69	1.4191	86.00	21.72

Table 2: It shows Adjustable parameters a_i of the Redlich-Kister (Eq. (4)) and standard deviations σ, (Eq. (5)) of excess refractive indices (Δn) for the binary mixtures of PC (1) with THF, 1, 4-dioxane, acetylacetone, acetone (2) at 298.15 K.

a_0	**a_1**	**a_2**	**σ**
Propylene carbonate (1) + THF (2)			
-0.0285	0.0249	0.0002	0.0001
Propylene carbonate (1) + 1, 4-dioxane (2)			
-0.0432	0.0014	-0.0052	0.0001
Propylene carbonate (1) + acetylacetone (2)			
0.0920	-0.2422	0.0284	0.0001
Propylene carbonate (1) + acetone (2)			
-0.0124	0.0018	-0.0071	0.0001

The negative values of Δn are observed in the present case for all binary mixtures are indicative of interactions present in the mixtures. The positive values of ΔR indicate that the dispersion forces are higher in the mixtures than in the pure liquids[10] whereas negative values of ΔR indicate the presence of interactions amongst the mixture components. In the present case, the negative values of Δ*R* for all systems analyzed indicate the presence of interactions in the binary mixtures.

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