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Excess properties of diethyl carbonate + ketone binary mixtures at variable temperatures: Application of PFP theory to excess volumes

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ABSTRACT

Measurements of densities ρ, viscosities η, and refractive indices n_D have been carried out for binary mixtures of diethyl carbonate (DEC) with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone over the entire composition range at the temperatures (303.15, 308.15 and 313.15) K and at atmospheric pressure. From these experimental data, the excess volumes V^E, deviation in viscosity $\Delta\eta$ and deviation in molar refraction ΔR have been calculated. The Redlich–Kister polynomial equation has been used to estimate the binary fitting parameters and the standard errors. The Prigogine–Flory–Patterson (PFP) theory and its applicability in predicting V^E at (303.15, 308.15 and 313.15) K has been tested. The experimental viscosities were analyzed on the basis of Lobe and Auslaender models. Further different mixing rules have been applied to predict the refractive index values of the studied mixtures.

1. Introduction

The molecular interaction studies of esters of carbonic acid hold considerable interest due to their applications in industries for the synthesis of many chemicals, in pharmaceutical and in agricultural chemistry. Diethyl carbonate (DEC) is a solvent of both extraction and reaction used in many industries: pharmaceuticals, agrochemicals, and hydrocarbon refinery. It can make dyeing uniformity and increase fading against sunshine. DEC is used as paint remover in the paint industry. In the plastic process it is the solvent used as solvent of plasticizer directly. In the pharmaceutical industry it is the basic ingredient used to synthesize intermediate phenobarbital. Thus DEC has an extensive market developing prospect.

Mixtures containing DEC + alcohols, and alkanes have been studied by Rodriguez et al. [1–4] for investigating density, viscosity, refractive index, and speed of sound at several temperatures. Pal et al. [5–7] have studied excess molar volumes, viscosities, and refractive indices of DEC with diethylene glycol dimethyl ether and triethylene glycol dimethyl ether. Pardo et al. [8–10] studied excess molar volumes, excess molar heat capacities and speed of sound for DEC + n-heptane, DEC + n-dodecane, or n-tetradecane and DEC + cyclohexane mixtures. Francesconi and Comelli [11] studied excess enthalpies and excess molar volumes for DEC + n-alkanol mixtures at 298.15 K. Ottani et al. [12] studied densities, viscosities, and refractive indices of poly (ethylene glycols) + DEC mixtures at 313.15 K. Likewise Rivas et al. [13] studied permittivity and density of DEC + dodecane at (298.15 to 328.15) K. Yang et al. [14] have determined density and viscosity for mixtures of DEC + alcohols at (293.15 to 363.15) K. However there are only a few studies on binary mixtures of DEC + ketones [15–18] reported in literature.

In view of the increasing importance of DEC, and the lack of extensive knowledge about its behavior with ketones, it has created in us an interest to undertake this present research. In continuation of our earlier work [19–22], in this paper we report density, viscosity, and refractive index data for the binary mixtures of DEC with acetophenone, cyclopentanone, cyclohexanone, or 3-pentanone at (303.15, 308.15 and 313.15) K over the entire composition range. From the experimental data, the excess volume, deviation in viscosity and deviation in molar refraction have been calculated. The main aim of this present investigation is to i) test the applicability of Prigogine–Flory–Patterson (PFP) theory [26–30] to the binary mixtures reported in this work, ii) study the correlating ability of the viscosity models proposed by Lobe [31], and Auslaender [32] and iii) study the predictive ability of various mixing rules of refractive indices.

2. Experimental

2.1. Materials

Diethyl carbonate, acetophenone (Sigma-Aldrich), cyclopentanone, cyclohexanone and 3-pentanone (all Merck) with mass fraction purities greater than 99.0% were used. These chemicals were stored over 0.4 nm molecular sieves to reduce water content, and distilled just before use. The purity of these chemicals was ascertained by gas chromatographic analysis (GC-8610) and the analysis of purity was found to be >99.8%.

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Table 1
Mole fraction (x_1), densities (ρ), excess volumes (V^E), dynamic viscosities (η), refractive indices (n_D) for the binary mixtures.

x_1	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}	η/mPa s	n_D
Diethyl carbonate (1) + acetophenone (2)				
T = 303.15 K				
0.0000	1.0199		1.518	1.5294
0.0972	1.0153	−0.130	1.413	1.5151
0.1515	1.0126	−0.190	1.358	1.5072
0.2512	1.0075	−0.280	1.260	1.4928
0.3615	1.0015	−0.328	1.155	1.4766
0.4921	0.9943	−0.365	1.040	1.4572
0.5705	0.9899	−0.364	0.977	1.4455
0.6654	0.9842	−0.330	0.906	1.4311
0.7584	0.9786	−0.281	0.843	1.4169
0.8932	0.9699	−0.125	0.760	1.3964
0.9425	0.9667	−0.075	0.732	1.3890
1.0000	0.9630		0.701	1.3801
Diethyl carbonate (1) + acetophenone (2)				
T = 308.15 K				
0.0000	1.0169		1.378	1.5270
0.0972	1.0121	−0.138	1.286	1.5127
0.1515	1.0092	−0.198	1.237	1.5049
0.2512	1.0039	−0.285	1.150	1.4905
0.3615	0.9977	−0.345	1.059	1.4743
0.4921	0.9902	−0.385	0.958	1.4550
0.5705	0.9855	−0.385	0.902	1.4434
0.6654	0.9796	−0.343	0.839	1.4292
0.7584	0.9737	−0.288	0.783	1.4151
0.8932	0.9647	−0.136	0.708	1.3948
0.9425	0.9614	−0.080	0.683	1.3874
1.0000	0.9575		0.656	1.3787
Diethyl carbonate (1) + acetophenone (2)				
T = 313.15 K				
0.0000	1.0135		1.291	1.5250
0.0972	1.0085	−0.145	1.205	1.5107
0.1515	1.0055	−0.205	1.159	1.5028
0.2512	1.0000	−0.300	1.079	1.4884
0.3615	0.9937	−0.375	0.995	1.4723
0.4921	0.9858	−0.400	0.901	1.4530
0.5705	0.9810	−0.400	0.850	1.4414
0.6654	0.9749	−0.375	0.791	1.4274
0.7584	0.9687	−0.302	0.738	1.4135
0.8932	0.9594	−0.147	0.669	1.3934
0.9425	0.9561	−0.093	0.646	1.3861
1.0000	0.9520		0.621	1.3775
Diethyl carbonate (1) + cyclopentanone (2)				
T = 303.15 K				
0.0000	0.9385		0.999	1.4335
0.0876	0.9417	−0.030	0.958	1.4275
0.1356	0.9433	−0.050	0.937	1.4245
0.2458	0.9469	−0.090	0.891	1.4178
0.3359	0.9497	−0.120	0.859	1.4126
0.4228	0.9520	−0.134	0.830	1.4078
0.5415	0.9548	−0.135	0.797	1.4015
0.6475	0.9571	−0.127	0.770	1.3962
0.7513	0.9590	−0.095	0.747	1.3912
0.8664	0.9610	−0.055	0.725	1.3858
0.9352	0.9620	−0.025	0.713	1.3828
1.0000	0.9630		0.701	1.3801
Diethyl carbonate (1) + cyclopentanone (2)				
T = 308.15 K				
0.0000	0.9339		0.927	1.4310
0.0876	0.9371	−0.050	0.893	1.4255
0.1356	0.9389	−0.080	0.873	1.4226
0.2458	0.9426	−0.151	0.833	1.4162
0.3359	0.9454	−0.198	0.803	1.4112
0.4228	0.9477	−0.218	0.776	1.4065
0.5415	0.9504	−0.217	0.745	1.4003
0.6475	0.9525	−0.200	0.722	1.3950
0.7513	0.9542	−0.155	0.701	1.3900
0.8664	0.9558	−0.090	0.681	1.3846
0.9352	0.9567	−0.040	0.668	1.3815
1.0000	0.9575		0.656	1.3787

Table 1 (*continued*)

x_1	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}	η/mPa s	n_D
Diethyl carbonate (1) + cyclopentanone (2)				
T = 313.15 K				
0.0000	0.9290		0.865	1.4290
0.0876	0.9324	−0.075	0.835	1.4238
0.1356	0.9343	−0.125	0.819	1.4211
0.2458	0.9382	−0.225	0.783	1.4150
0.3359	0.9411	−0.288	0.757	1.4102
0.4228	0.9434	−0.320	0.733	1.4056
0.5415	0.9460	−0.321	0.705	1.3994
0.6475	0.9480	−0.295	0.683	1.3941
0.7513	0.9495	−0.240	0.664	1.3890
0.8664	0.9509	−0.150	0.644	1.3836
0.9352	0.9515	−0.080	0.632	1.3804
1.0000	0.9520		0.621	1.3775
Diethyl carbonate (1) + cyclohexanone (2)				
T = 303.15 K				
0.0000	0.9377		1.816	1.4465
0.0898	0.9405	−0.020	1.626	1.4397
0.1505	0.9423	−0.030	1.498	1.4353
0.2556	0.9453	−0.045	1.321	1.4278
0.3587	0.9482	−0.055	1.156	1.4207
0.4619	0.9509	−0.061	1.028	1.4138
0.5665	0.9535	−0.061	0.911	1.4069
0.6701	0.9560	−0.054	0.825	1.4002
0.7601	0.9580	−0.043	0.768	1.3945
0.8945	0.9608	−0.019	0.719	1.3863
0.9487	0.9619	−0.007	0.708	1.3831
1.0000	0.9630		0.701	1.3801
Diethyl carbonate (1) + cyclohexanone (2)				
T = 308.15 K				
0.0000	0.9328		1.657	1.4440
0.0898	0.9358	−0.050	1.479	1.4376
0.1505	0.9377	−0.080	1.370	1.4334
0.2556	0.9409	−0.120	1.202	1.4262
0.3587	0.9439	−0.150	1.056	1.4193
0.4619	0.9466	−0.169	0.937	1.4125
0.5665	0.9492	−0.172	0.837	1.4057
0.6701	0.9514	−0.148	0.759	1.3990
0.7601	0.9531	−0.110	0.711	1.3933
0.8945	0.9556	−0.045	0.669	1.3850
0.9487	0.9566	−0.020	0.658	1.3817
1.0000	0.9575		0.656	1.3787
Diethyl carbonate (1) + cyclohexanone (2)				
T = 313.15 K				
0.0000	0.9282		1.542	1.4420
0.0898	0.9313	−0.075	1.375	1.4359
0.1505	0.9334	−0.125	1.274	1.4319
0.2556	0.9367	−0.195	1.116	1.4249
0.3587	0.9397	−0.250	0.981	1.4182
0.4619	0.9426	−0.298	0.873	1.4116
0.5665	0.9450	−0.300	0.784	1.4049
0.6701	0.9470	−0.255	0.714	1.3982
0.7601	0.9484	−0.185	0.668	1.3923
0.8945	0.9505	−0.082	0.626	1.3839
0.9487	0.9513	−0.040	0.617	1.3806
1.0000	0.9520		0.621	1.3775
Diethyl carbonate (1) + 3-pentanone (2)				
T = 303.15 K				
0.0000	0.8057		0.429	1.3879
0.0893	0.8214	0.030	0.452	1.3875
0.1498	0.8317	0.055	0.468	1.3872
0.2601	0.8501	0.100	0.496	1.3868
0.3555	0.8656	0.135	0.521	1.3864
0.4667	0.8833	0.157	0.550	1.3859
0.5689	0.8992	0.157	0.578	1.3851
0.6701	0.9147	0.140	0.606	1.3839
0.7565	0.9277	0.102	0.631	1.3828
0.8858	0.9468	0.045	0.668	1.3813
0.9501	0.9560	0.020	0.686	1.3807
1.0000	0.9630		0.701	1.3801