Physical Properties and Liquid−Liquid Equilibrium of the Ternary Mixture (Dimethyl Carbonate + Methanol + Hexane) at 298.15 K

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The density, refractive index, and speed of sound of the mixtures dimethyl carbonate + hexane and dimethyl carbonate + methanol + hexane have been measured at 298.15 K and atmospheric pressure, over the miscibility composition range. These results are used to calculate excess molar volumes, deviations of refractive index, and deviations in isentropic compressibility. The calculated quantities are further fitted to the Redlich−Kister and Cibulka equations to estimate the binary and ternary fitting parameters and root-mean-square deviations from the regression lines. Values of derived and excess properties were estimated and compared by different methods. Excess partial molar volumes at infinite dilution are also calculated. The liquid−liquid equilibrium of the ternary mixture dimethyl carbonate + methanol + hexane at 298.15 K has been measured. The UNIQUAC equation was used to correlate the experimental data, and the root-mean-square deviations are shown.

1. Introduction

As a continuation of the thermodynamic study of the mixture containing dimethyl carbonate and methanol,[1] the ternary mixture dimethyl carbonate + methanol + hexane and the binary mixture dimethyl carbonate + hexane have been studied in this work. Densities, refractive indices, and speeds of sound of the binary and ternary mixtures, at 298.15 K and atmospheric pressure, have been measured. The results were used to calculate excess molar volumes and deviations of refractive index over the miscibility composition range for the mixtures. Experimental values of binary and ternary mixtures were correlated by Redlich−Kister[2] and Cibulka[3] equations, respectively. The root-mean-square deviations are shown. Literature data are not available to compare with the experimental values.

Excess molar volumes, changes of refractive index on mixing, and deviations in isentropic compressibility were compared with the results obtained by applying several equations developed in a previous paper,[4] that predict excess and derived properties from the Redlich−Kister fitting parameters of binary systems. Their root-mean-square deviations are shown. By means of the calculated Redlich−Kister correlation parameters, the partial excess molar volumes corresponding to limiting values are being evaluated as a function of mole fraction.

The liquid−liquid equilibrium of the ternary mixture dimethyl carbonate + methanol + hexane due to a region of immiscibility was present when the physical properties were studied. The experimental tie lines were used to obtain, by applying the UNIQUAC equation, the binodal curve. No experimental data of liquid−liquid equilibrium related with the above ternary were found in the literature.

2. Experimental Section

Methanol was supplied by Merck, and dimethyl carbonate and hexane were supplied by Fluka. The pure components were degassed ultrasonically and dried over molecular sieves Type 3 Å and 4 Å (supplied by Aldrich) and kept in an inert argon atmosphere as soon as the bottles were opened. Chromatography (GLC) then gave mass fraction purities as >99 mass % for dimethyl carbonate, >99.8 mass % for methanol, and >99.5 mass % for hexane. The maximum water contents of the liquids were determined using a Metrohm 737 KF coulometer. The corresponding obtained values were 1.1×10^{-2} mass % for methanol and unappreciated quantities for the rest of the liquids. The densities and refractive indices of the pure solvents were compared with recently published values in Table 1.

Table 1. Comparison of Data with Literature Data for Pure Liquids at 298.15 K

	ρ/(g·cm^{-3})		n_D	
component	exptl	lit.	exptl	lit.
dimethyl carbonate	1.0635	1.063 50[a] 1.063 20[b]	1.366 40	1.366 70[a,b]
methanol	0.7866	0.786 64[c,d]	1.326 45	1.326 52[c,d]
hexane	0.6548	0.654 84[c,d]	1.372 26	1.372 26[c,d]

[a] García et al.[8] [b] Pal et al.[9] [c] Das et al.[10] [d] Riddick et al.[11]

The mixtures were prepared from known masses of the pure liquids, by syringing into stoppered bottles to prevent evaporation and reducing possible errors in mole fraction calculations. A Mettler AT-261 Delta Range balance was used with a precision of $\pm 10^{-5}$ g. The density and the speed of sound of the pure liquids and mixtures were measured with an Anton Paar DSA-48 vibration tube densimeter and sound analyzer with a precision of $\pm 10^{-4}$ g·cm^{-3} and ±1 m·s^{-1}, respectively. The refractive index was measured by the automatic refractometer ABBEMAT-HP Dr Kernchen with a precision of $\pm 10.^{-5}$ Before this kind of measurements, these instruments were calibrated with Millipore quality water and ambient air, respectively, in accordance with the instructions.

The experimental technique for the calculation of the liquid−liquid equilibrium is described in a previous paper.[5]

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Table 2. Density, ρ, Refractive Index, n_D, Excess Molar Volume, V_m^E, and Speed of Sound, u, for Binary Mixtures at 298.15 K

x_1	ρ/(g·cm^{-3})	n_D	u/(m·s^{-1})	V_m^E/(cm^3·mol^{-1})
Dimethyl Carbonate (1) + Hexane (3)				
0	0.6548	1.372 26	1078	0
0.0820	0.6745	1.370 41	1071	0.477
0.1269	0.6863	1.369 59	1068	0.633
0.2131	0.7105	1.368 37	1066	0.849
0.3197	0.7437	1.367 39	1067	0.942
0.3787	0.7636	1.366 97	1069	0.947
0.4712	0.7972	1.366 53	1075	0.901
0.5121	0.8132	1.366 35	1079	0.843
0.6067	0.8524	1.366 18	1091	0.727
0.6987	0.8943	1.366 02	1107	0.577
0.8420	0.9677	1.366 09	1142	0.337
0.9248	1.0157	1.366 27	1168	0.170
0.9615	1.0385	1.366 35	1182	0.088
1	1.0635	1.366 40	1196	0

The accuracy estimated in mole fraction for the equilibrium data was 3×10^{-3} in the hexane rich region (phase I) and 2×10^{-3} in the methanol rich region (phase II).

3. Results and Discussion

Density, refractive index, speed of sound, excess molar volume, change of refractive index on mixing, isentropic compressibility (determined by means of the Laplace equation, $\kappa_S = \rho^{-1}u^{-2}$), and deviation in isentropic compressibility of the binary and ternary mixtures are reported in Tables 2 and 3, respectively. In previous papers the physical properties of dimethyl carbonate + methanol[4] and methanol + hexane[5] have been measured. Excess molar volumes, changes of refractive indices on mixing, and deviations in isentropic compressibility for binary and ternary mixtures were derived, respectively, from eqs 1−3.

$$V_m^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{\circ -1}) \tag{1}$$

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di}^{\circ} \tag{2}$$

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{N} x_i \kappa_{S,i} \tag{3}$$

In these equations, ρ and n_D are the density and refractive index of the mixture, ρ_i° and n_{Di}° are the density and refractive index of pure components, κ_S is the isentropic compressibility of the mixture, and $\kappa_{S,i}$ is the isentropic compressibility of the pure component.

The binary values were fitted to a Redlich−Kister type equation:

$$\Delta Q = x_i x_j \sum_{p=0}^{M} B_p(x_i - x_j)^p \tag{4}$$

where ΔQ_{ij} is the excess property, x is the mole fraction, B_p is the fitting parameter, and M is the degree of the polynomic expansion. For ternary mixtures the corresponding equation is

$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + x_1 x_2(1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \tag{5}$$

where ΔQ_{12}, ΔQ_{13}, and ΔQ_{23} are the parameters representing the binary interactions in accordance with the Redlich−Kister expression. The degree of this equation was optimized by applying the F-test.[6] The correlation parameters calculated using eqs 4 and 5 are listed in Table 4, together with the root-mean-square deviations (σ). This deviation is calculated by applying the following expression:

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \tag{6}$$

where property values and the number of experimental data are represented by z and n_{DAT}, respectively.

Table 3. Density, ρ, Refractive Index, n_D, Excess Molar Volume, V_m^E, and Speed of Sound, u, for Ternary Mixture at 298.15 K

x_1	x_2	ρ/(g·cm^{-3})	n_D	u/(m·s^{-1})	V_m^E/(cm^3·mol^{-1})
Dimethyl Carbonate (1) + Methanol (2) + Hexane (3)					
0.0489	0.0527	0.6683	1.370 12	1067	0.441
0.0498	0.9054	0.7929	1.334 57	1089	0.120
0.1041	0.1069	0.6864	1.367 95	1061	0.699
0.1064	0.2026	0.6947	1.366 21	1060	0.653
0.1065	0.3362	0.7080	1.362 95	1060	0.539
0.1031	0.4102	0.7154	1.360 92	1060	0.486
0.1042	0.5242	0.7318	1.356 75	1060	0.454
0.0804	0.6614	0.7437	1.350 54	1058	0.420
0.0761	0.7189	0.7536	1.347 29	1060	0.396
0.0950	0.8024	0.7914	1.341 37	1077	0.238
0.2840	0.0977	0.7430	1.365 95	1063	0.950
0.2135	0.2186	0.7333	1.364 28	1060	0.789
0.1995	0.3022	0.7395	1.362 42	1062	0.676
0.1635	0.4984	0.7562	1.356 71	1063	0.477
0.1747	0.5584	0.7747	1.354 18	1066	0.429
0.1350	0.6829	0.7825	1.348 58	1068	0.341
0.2067	0.6977	0.8384	1.346 80	1092	0.189
0.2387	0.1307	0.7313	1.365 78	1061	0.905
0.2612	0.2139	0.7507	1.363 82	1063	0.810
0.2592	0.3319	0.7697	1.360 80	1066	0.644
0.2742	0.4213	0.7959	1.357 91	1072	0.504
0.2920	0.5113	0.8306	1.354 59	1082	0.353
0.2620	0.6384	0.8561	1.349 30	1097	0.183
0.3610	0.1118	0.7733	1.365 15	1068	0.921
0.3544	0.2373	0.7935	1.362 62	1072	0.737
0.3503	0.3336	0.8133	1.360 0	1077	0.574
0.2961	0.5451	0.8445	1.352 92	1088	0.287
0.3803	0.5576	0.9096	1.352 10	1121	0.089
0.4327	0.1680	0.8138	1.363 52	1078	0.749
0.4545	0.2173	0.8355	1.362 50	1086	0.645
0.4985	0.2611	0.8707	1.361 13	1098	0.477
0.4603	0.4347	0.9115	1.356 46	1117	0.183
0.5797	0.0905	0.8625	1.364 67	1095	0.666
0.5797	0.1975	0.8943	1.362 54	1108	0.468
0.6001	0.3236	0.9572	1.359 40	1142	0.123
0.6903	0.1054	0.9232	1.364 28	1122	0.433
0.6737	0.2209	0.9589	1.362 04	1143	0.209
0.7966	0.1091	0.9864	1.364 29	1157	0.202
0.8916	0.0551	1.0210	1.365 47	1175	0.112
0.5099	0.1005	0.8329	1.364 50	1084	0.766
0.3608	0.4111	0.8404	1.357 60	1086	0.411
0.0606	0.1562	0.6772	1.367 83	1061	0.546
0.0483	0.8575	0.7732	1.338 45	1073	0.243
0.0515	0.3456	0.6892	1.364 20	1062	0.398
0.0477	0.6986	0.7320	1.349 32	1056	0.431

The fitted curves, as well as excess values at 298.15 K for the binary mixture, are shown in Figure 1. Excess molar volumes are positive in the entire composition range. The binary mixture dimethyl carbonate with hexane is miscible in the entire composition range.

Figure 2 exhibits the excess properties for the ternary mixture dimethyl carbonate + methanol + hexane. Excess molar volumes are positive over most of the composition diagram, except when they are close to the binary mixture dimethyl carbonate + methanol, where a change in sign occurs.

Table 4. Parameters and Root-Mean-Square Deviations σ

		Dimethyl Carbonate (1) + Hexane (3)			
$V_m^E/(cm^3 \cdot mol^{-1})$	$B_0 = 3.436$	$B_1 = -2.174$	$B_2 = 1.221$		$\sigma = 0.008$
Δn_D	$B_0 = -0.0117$	$B_1 = 0.0048$	$B_2 = -0.0027$	$B_3 = 0.0016$	$\sigma = 0.00002$
$\Delta\kappa_S/(TPa^{-1})$	$B_0 = 316.86$	$B_1 = -108.89$	$B_2 = 8.495$	$B_3 = -31.39$	$\sigma = 0.3$
		Dimethyl Carbonate (1) + Methanol (2) + Hexane (3)			
$V_m^E/(cm^3 \cdot mol^{-1})$	$C_1 = 10.109$	$C_2 = -7.103$	$C_3 = -14.482$		$\sigma = 0.004$
Δn_D	$C_1 = -0.0680$	$C_2 = 0.0610$	$C_3 = -0.0341$		$\sigma = 0.00014$
$\Delta\kappa_S/(TPa^{-1})$	$C_1 = 981.5$	$C_2 = -1127.1$	$C_3 = -80.9$		$\sigma = 0.6$

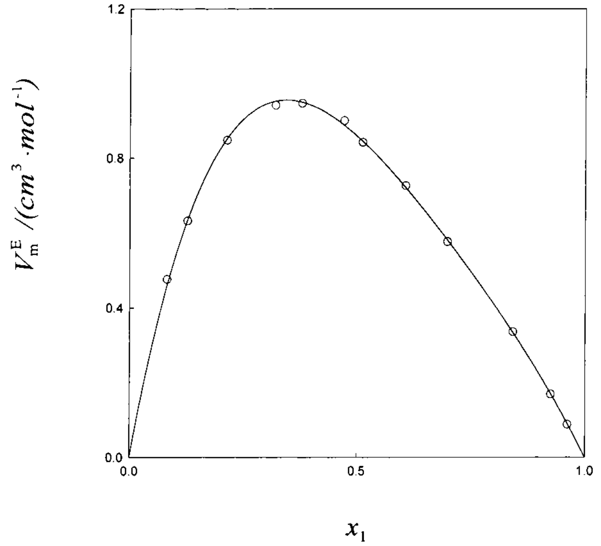

Figure 1. Curves of excess molar volumes $V_m^E/(cm^3 \cdot mol^{-1})$ from the Redlich–Kister equation, eq 4, at 298.15 K for dimethyl carbonate (1) + hexane (2): (○) experimental values; (—) fitted curves.

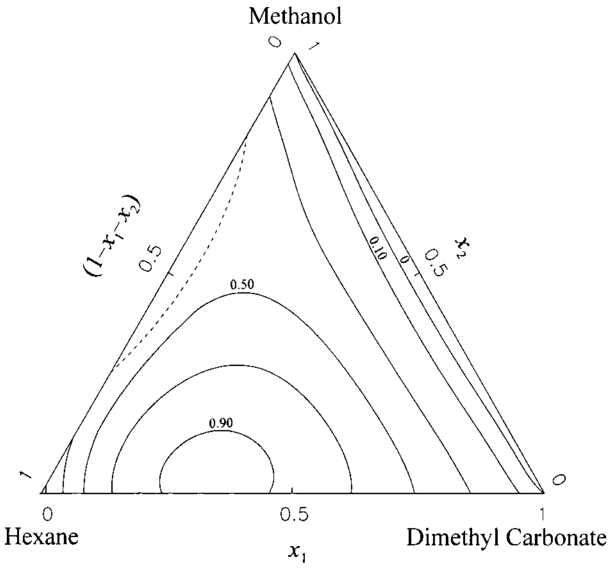

Figure 2. Curves of constant excess molar volumes $V_m^E/(cm^3 \cdot mol^{-1})$ from the Cibulka equation, eq 5, at 298.15 K for dimethyl carbonate (1) + methanol (2) + hexane (3) and (- - -) binodal curve obtained by the UNIQUAC equation.

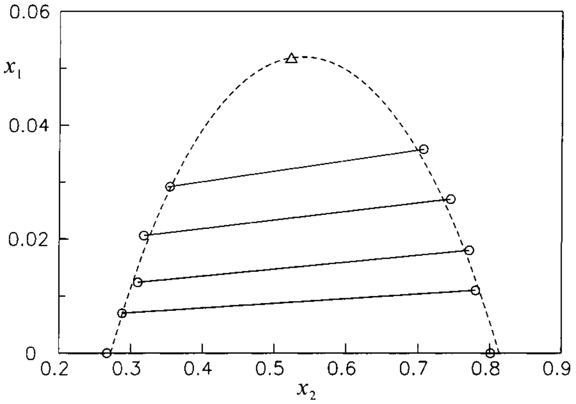

Figure 3. Experimental liquid–liquid equilibrium data of the ternary mixture dimethyl carbonate + methanol + hexane at 298.15 K: ○—○, experimental tie lines and the binodal curve modeling by UNIQUAC; (Δ) plait point extrapolated.

Table 5. Liquid–Liquid Equilibrium of the Ternary System at 298.15 K

x_1^I	x_2^I	x_1^{II}	x_2^{II}
0	0.267	0	0.801
0.007	0.288	0.011	0.780
0.012	0.310	0.018	0.771
0.021	0.318	0.027	0.745
0.029	0.354	0.036	0.711

Table 6. Correlating Parameters of the UNIQUAC Equation for the Ternary Mixture at 298.15 K and Root-Mean-Square Deviations σ

system	Δu_{ij}/ kJ·mol^{-1}	Δu_{ji}/ kJ·mol^{-1}
dimethyl carbonate (1) + methanol (2)	−20.273	−0.542
dimethyl carbonate (1) + hexane (3)	−20.340	0.647
methanol (2) + hexane (3)	4.534	0.092
$\sigma(x_{DMC}) = 0.008$	$\sigma(x_{MOH}) = 0.001$	

Table 7. Root-Mean-Square Deviations of the Experimental Results from the Prediction Results for Several Empirical Equations

	$\sigma(V_m^E/(cm^3 \cdot mol^{-1}))$	$\sigma(\Delta n_D)$	$\sigma(\Delta\kappa_S/(TPa^{-1}))$
Kohler	0.061	0.0013	30
Jacob–Fitzner	0.077	0.0013	31
Colinet	0.051	0.0013	29
Tsao–Smith[a]	0.087	0.0029	32
Tsao–Smith[b]	0.100	0.0003	18
Tsao–Smith[c]	0.111	0.0029	43
Scatchard[a]	0.043	0.0015	34
Scatchard[b]	0.061	0.0008	29
Scatchard[c]	0.104	0.0017	28
Toop[a]	0.049	0.0014	32
Toop[b]	0.055	0.0008	28
Toop[c]	0.104	0.0017	29

The liquid–liquid equilibrium for the ternary mixture has been determined at 298.15 K. Table 5 lists the liquid–liquid compositions of both phases and the root-mean-square deviations from the results of the UNIQUAC method at 298.15 K. Figure 3 shows the experimental tie lines, the binodal curve obtained by applying the UNIQUAC equation, and the extrapolated plait point at 298.15 K. The composition of this point is $x_{DMC} = 0.052$ and $x_{MOH} = 0.522$. In Table 6 the correlated parameters for the UNIQUAC equation and the root-mean-square deviations are shown.

Some predictive methods for ternary excess properties are based on additive binary contributions. In Table 7 the experimental and estimated excess values are compared and corresponding root-mean-square deviations are shown.

Table 8. Partial Excess Molar Volumes at Infinite Dilution of the Binary Mixtures at 298.15 K

system	($V_1^{E\infty}$/(cm^3·mol^{-1})	($V_2^{E\infty}$/(cm^3·mol^{-1})
dimethyl carbonate (1) + methanol (2)	−0.271	−0.232
dimethyl carbonate (1) + hexane (3)	6.830	2.483
methanol (2) + hexane (3)	4.598	3.724

In general for the ternary system the best estimations of excess molar volumes and changes of refractive index on mixing are given when applying symmetric equations. For deviations in isentropic compressibility, asymmetric equations obtain the bests results.

In Table 8, values of limiting pure partial excess molar volumes[7] at 298.15 K for the binary mixtures are shown.

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Registry Numbers Supplied by the Author: dimethyl carbonate, 616-38-6; methanol, 67-56-1; hexane, 107-83-5.

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