Isobaric Phase Equilibria of Diethyl Carbonate with Five Alcohols at 101.3 kPa

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Isobaric vapor−liquid equilibria (VLE) have been experimentally determined for the binary systems methanol + diethyl carbonate (DEC), ethanol + DEC, 1-propanol + DEC, 1-butanol + DEC, and DEC + 1-pentanol at 101.3 kPa. In the binary systems, the results indicate a strong positive deviation from ideality and a single minimum temperature azeotrope corresponding to the binaries 1-butanol and 1-pentanol with DEC. The results were tested for thermodynamic consistency and were satisfactorily correlated with the Wilson and UNIQUAC equations. Our interaction parameters in the ASOG and UNIFAC methods, for the carbonate group (−OCOO−) and alcohols (−OH), were used to predict our experimental VLE data.

1. Introduction

This work has several useful purposes, the first of which is to better define the thermodynamic properties of mixtures of dialkyl carbonates with other components. There is also a strong interest in applications[1] to storage batteries based on intercalation of lithium and bromine in graphite, that can be recharged thermally at relatively low temperatures. In this paper, we have continued our earlier work on the determination of thermodynamic properties of dialkyl carbonate;[2−10] we present experimental data of isobaric vapor−liquid equilibria for the binary systems methanol + diethyl carbonate (DEC), ethanol + DEC, 1-propanol + DEC, 1-butanol + DEC, and DEC + 1-pentanol at 101.3 kPa and compare them with literature data[11] for these binary systems.

The experimental results will be compared with those correlated through the equations of Wilson[12] and UNIQUAC.[13] The interaction parameters of the functional group (−OCOO−) with (CH_3−) and with (OH−) in the ASOG[14] method and of (−OCOO−) with (CH_3−) and with (CH_3OH) and (OH−) in the UNIFAC[15] method have been determined previously[8,10] using our experimental isobaric VLE data. ASOG and UNIFAC group contribution methods will be employed to predict these binary systems.

2. Experimental Section

Chemicals. Methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol were supplied by Merck, and DEC was supplied by Fluka. Their mass fraction purities were >99.8 mass %, >99.9 mass %, >99.8 mass %, >99.8 mass %, >99.0 mass %, and >99.5 mass %, respectively. They were degassed ultrasonically and dried over molecular sieves (supplied by Aldrich) type 3 Å for methanol and 4 Å for the rest of the components and kept in an inert argon atmosphere with a maximum content in water of 2×10^{-6} by mass fraction. Chromatographic tests of the solvents showed purities which complied with purchaser specifications. The maximum water contents of the liquids were determined using a Metrohm 737 KF coulometer. The corresponding obtained values of water in mass percent were 0.11 for methanol, 0.13 for ethanol, 0.07 for 1-propanol, 0.14 for 1-butanol, and 0.28 for 1-pentanol, and an unknown quantity for DEC. The chemical purities were compared with recent published density and refractive index values in Table 1.

Table 1. Comparison of Density ρ and Refractive Index n_D at 298.15 K and the Boiling Points of the Pure Components with Literature Data

	ρ/g·cm^{-3}		n_D		T_{bp}/K	
component	expt	lit.	expt	lit.	expt	lit.
DEC	0.9691	0.969 24[a]	1.382 40	1.382 87[c]	399.32	399.95[c]
		0.969 00[b]		1.382 70[b]		
		0.969 26[c]		1.382 40[g]		
methanol	0.7866	0.786 64[c,d]	1.326 45	1.326 52[c,d]	337.83	337.70[c]
ethanol	0.7850	0.785 09[d]	1.359 22	1.359 22[e]	351.49	351.44[c]
1-propanol	0.7995	0.799 50[f]	1.383 07	1.383 20[f]	370.30	370.30[c]
1-butanol	0.8059	0.805 75[c]	1.397 02	1.397 41[c]	390.91	390.88[c]
1-pentanol	0.8109	0.810 80[c]	1.382 40	1.382 40[g]	411.11	411.13[c]

[a] Francesconi and Comelli.[23] [b] Pal et al.[24] [c] Riddick et al.[25] [d] Das et al.[26] [e] Arce et al.[27] [f] Ortega.[28] [g] Cocero et al.[29] [h] García de la Fuente et al.[30]

Apparatus and Procedure. A glass Fischer LABODEST VLE apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic recirculating still, equipped with a Cottrell circulation pump. This pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature-sensing element. The equilibrium temperature was measured with a digital Yokogawa model 7563 thermometer with an accuracy of ±0.01 K. The apparatus is equipped with a glass temperature probe PT 100 with an accuracy of ±0.01 K. For the pressure measurement, a digital pressure controller Ruska model 7218 with an accuracy of ±0.001 kPa was used. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. Then, samples of liquid and condensate were taken for analysis. The composition analyses of both samples were determined using an Anton-Paar DSA-48 digital vibrating tube densimeter with an accuracy of ±0.0001 g·cm^{-3}. The concentrations of the liquid and vapor phases at equilib-

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Table 2. Vapor−Liquid Equilibrium Data for the Methanol (1) + DEC (2) System at 101.3 kPa

T/K	x	y	γ_1	γ_2
392.43	0.0169	0.1955	2.078	0.985
386.24	0.0339	0.3425	2.133	0.983
382.17	0.0463	0.4232	2.157	0.990
377.77	0.0613	0.5029	2.193	0.996
373.28	0.0792	0.5730	2.204	1.010
368.84	0.1004	0.6399	2.218	1.014
365.99	0.1166	0.6798	2.215	1.014
362.68	0.1399	0.7203	2.171	1.024
359.23	0.1692	0.7597	2.114	1.034
356.86	0.1971	0.7841	2.025	1.051
355.05	0.2237	0.8018	1.937	1.069
352.99	0.2585	0.8222	1.843	1.087
351.59	0.2908	0.8363	1.748	1.106
350.97	0.3118	0.8424	1.677	1.125
350.27	0.3376	0.8505	1.602	1.140
349.42	0.3603	0.8587	1.561	1.154
348.57	0.3926	0.8668	1.489	1.187
347.78	0.4297	0.8747	1.412	1.227
347.30	0.4556	0.8793	1.361	1.263
346.59	0.4830	0.8868	1.328	1.285
346.00	0.5164	0.8926	1.276	1.335
344.90	0.5606	0.9036	1.238	1.380
344.24	0.5970	0.9103	1.199	1.440
343.56	0.6349	0.9168	1.164	1.518
342.98	0.6681	0.9227	1.137	1.591
341.97	0.7222	0.9335	1.104	1.708
340.96	0.7741	0.9436	1.080	1.860
340.28	0.8082	0.9513	1.069	1.948
339.70	0.8492	0.9608	1.050	2.048
339.30	0.8790	0.9666	1.036	2.215
339.07	0.9048	0.9712	1.020	2.452
338.87	0.9181	0.9753	1.017	2.466
338.58	0.9387	0.9798	1.010	2.725
338.17	0.9624	0.9870	1.008	2.906
337.98	0.9837	0.9940	1.000	3.164

Table 3. Vapor−Liquid Equilibrium Data for the Ethanol (1) + DEC (2) System at 101.3 kPa

T/K	x	y	γ_1	γ_2
396.02	0.0157	0.1093	1.634	0.984
392.45	0.0315	0.2018	1.657	0.991
389.31	0.0464	0.2756	1.680	1.001
385.53	0.0671	0.3658	1.723	1.002
382.53	0.0851	0.4344	1.766	0.999
379.44	0.1061	0.4949	1.775	1.006
375.88	0.1341	0.5635	1.789	1.006
372.96	0.1615	0.6169	1.786	1.004
370.00	0.1951	0.6659	1.760	1.008
368.25	0.2195	0.6924	1.726	1.016
366.50	0.2472	0.7219	1.695	1.012
365.20	0.2725	0.7409	1.650	1.021
363.65	0.3070	0.7658	1.598	1.024
362.36	0.3425	0.7855	1.537	1.035
361.24	0.3796	0.8026	1.474	1.052
360.27	0.4168	0.8175	1.416	1.072
359.45	0.4524	0.8303	1.364	1.094
358.73	0.4836	0.8414	1.328	1.114
358.45	0.5018	0.8462	1.300	1.132
357.67	0.5395	0.8587	1.262	1.158
357.25	0.5633	0.8658	1.237	1.179
356.47	0.6074	0.8787	1.199	1.220
355.82	0.6464	0.8901	1.168	1.259
355.12	0.6905	0.9018	1.137	1.320
354.57	0.7282	0.9123	1.114	1.371
353.78	0.7895	0.9267	1.075	1.525
353.46	0.8222	0.9350	1.054	1.622
353.15	0.8528	0.9425	1.036	1.755
352.84	0.8828	0.9484	1.019	1.999
352.50	0.9112	0.9576	1.010	2.200
352.32	0.9331	0.9660	1.001	2.357
352.10	0.9541	0.9745	0.996	2.602
351.91	0.9649	0.9800	0.998	2.691
351.73	0.9861	0.9918	0.995	2.803

Table 4. Vapor−Liquid Equilibrium Data for the 1-Propanol (1) + DEC (2) System at 101.3 kPa

T/K	x	y	γ_1	γ_2
397.64	0.0200	0.0719	1.460	0.984
395.99	0.0352	0.1216	1.474	0.991
394.22	0.0532	0.1762	1.491	0.995
392.87	0.0679	0.2184	1.509	0.996
390.65	0.0940	0.2832	1.514	1.002
387.95	0.1304	0.3628	1.523	1.005
384.92	0.1764	0.4427	1.516	1.016
382.59	0.2218	0.5057	1.487	1.024
380.55	0.2718	0.5599	1.438	1.039
379.29	0.3101	0.5943	1.396	1.052
378.54	0.3366	0.6148	1.365	1.064
377.70	0.3690	0.6393	1.333	1.076
376.69	0.4195	0.6701	1.273	1.105
376.06	0.4525	0.6893	1.241	1.126
375.39	0.4871	0.7113	1.218	1.142
374.74	0.5355	0.7335	1.169	1.189
374.22	0.5731	0.7520	1.140	1.225
373.68	0.6089	0.7723	1.123	1.250
373.30	0.6447	0.7874	1.096	1.301
372.80	0.6867	0.8085	1.076	1.352
372.18	0.7361	0.8373	1.063	1.392
371.76	0.7764	0.8563	1.046	1.472
371.38	0.8234	0.8811	1.029	1.563
371.07	0.8641	0.9048	1.018	1.644
370.66	0.9065	0.9300	1.013	1.782
370.45	0.9458	0.9537	1.003	2.047
370.37	0.9729	0.9749	1.000	2.235
370.35	0.9887	0.9894	0.999	2.247

rium were determined on the basis of density−composition curves obtained previously for each of the binary mixtures. The root-mean-square deviation in the mole fraction was usually <0.001. The refractive indices have been measured in an automatic refractometer ABBEMAT-HP Dr. Kerncher with an accuracy of ±0.000 01 unit.

3. Results and Discussion

The temperature T and the liquid-phase and vapor-phase mole fractions x_i and y_i for the binary systems methanol + DEC, ethanol + DEC, 1-propanol + DEC, 1-butanol + DEC, and DEC + 1-pentanol at 101.3 kPa are presented in Tables 2−6, and they are plotted in Figures 1 and 2. Figure 3 shows the activity coefficients γ_i that were calculated from the equation

$$\ln \gamma_i = \ln\frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)}{RT} + \frac{P}{2RT}\sum_{j=1}^{n}\sum_{k=1}^{n} y_i y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where δ_{ji} and δ_{jk} are defined by

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

$$\delta_{jk} = 2B_{jk} - B_{jj} - B_{kk} \quad (3)$$

where T and P are the boiling point and the total pressure, respectively, V_i^{L} is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, P_i° is the saturation pressure, and δ_{ij} is related to the cross second virial coefficient. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell[16] using the molecular parameters suggested by Prausnitz et al.[17] Critical properties of all components were taken from DIPPR.[18] The experimental vapor pressures of DEC were determined experimentally and were presented in a previous paper.[9]

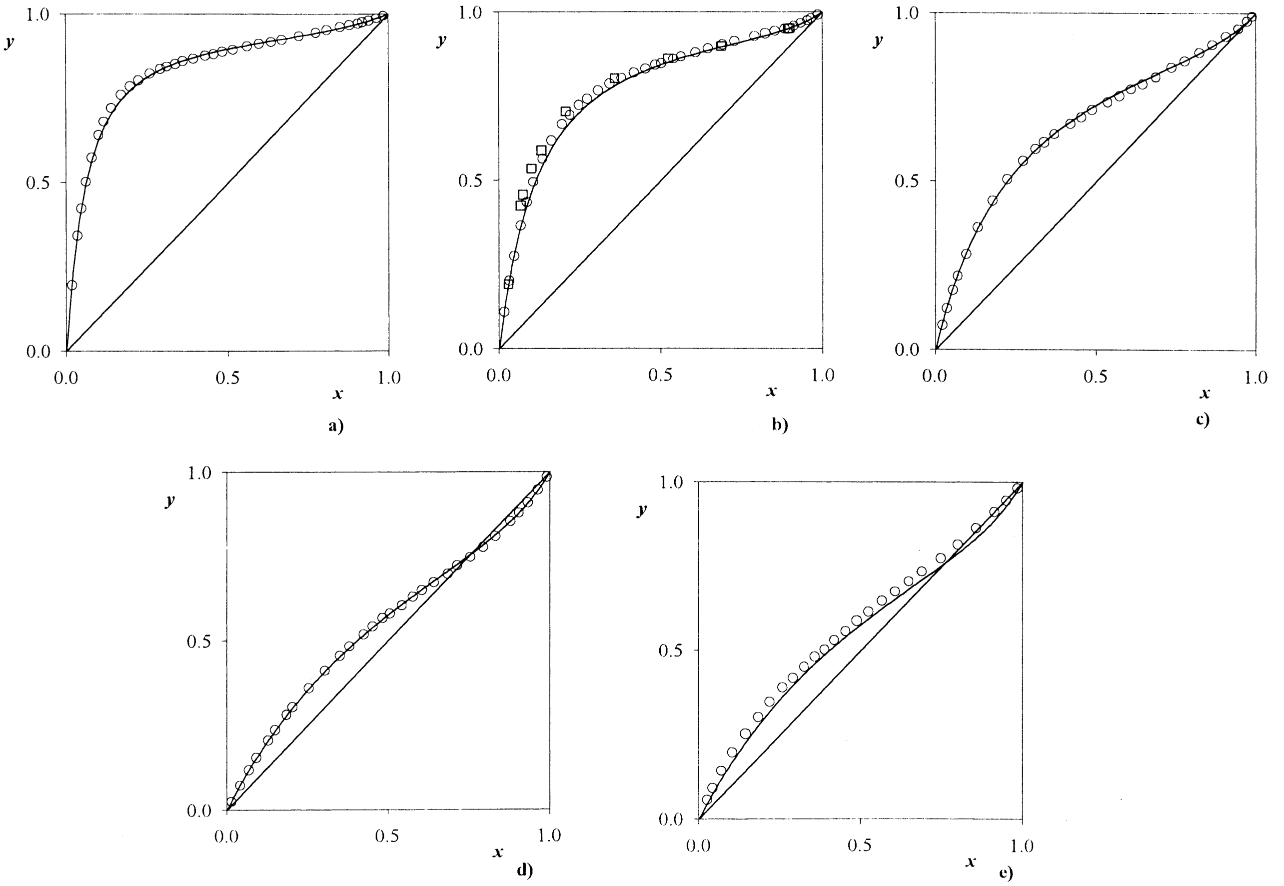

Figure 1. Experimental $x-y$ data for the binary systems at 101.3 kPa: (○) this work; (□) Luo et al.;[11] (—) correlated model; (a) methanol (1) + DEC (2), Wilson; (b) ethanol (1) + DEC (2), Wilson; (c) 1-propanol (1) + DEC (2), Wilson; (d) 1-butanol (1) + DEC (2), UNIQUAC; (e) DEC (1) + 1-pentanol (2), UNIQUAC

Table 5. Vapor−Liquid Equilibrium Data for the 1-Butanol (1) + DEC (2) System at 101.3 kPa

T/K	x	y	γ_1	γ_2
398.97	0.0135	0.0239	1.371	0.992
398.17	0.0409	0.0715	1.384	0.992
397.2	0.0682	0.1170	1.403	0.997
396.45	0.0910	0.1535	1.413	1.001
395.45	0.1277	0.2056	1.393	1.006
394.86	0.1498	0.2357	1.388	1.010
394.14	0.1844	0.2809	1.375	1.011
393.73	0.2033	0.3028	1.363	1.016
392.88	0.2537	0.3589	1.330	1.022
392.15	0.3038	0.4114	1.304	1.028
391.59	0.3502	0.4547	1.273	1.037
391.30	0.3807	0.4827	1.255	1.041
390.87	0.4250	0.5184	1.225	1.058
390.59	0.4519	0.5407	1.213	1.067
390.35	0.4835	0.5657	1.195	1.079
390.24	0.5065	0.5797	1.173	1.097
390.03	0.5422	0.6035	1.149	1.123
389.88	0.5767	0.6294	1.132	1.140
389.73	0.6047	0.6480	1.117	1.165
389.60	0.6411	0.6717	1.097	1.202
389.52	0.6837	0.6967	1.069	1.264
389.48	0.7136	0.7212	1.062	1.286
389.47	0.7542	0.7465	1.040	1.363
389.52	0.7930	0.7762	1.026	1.428
389.67	0.8316	0.8081	1.013	1.500
389.85	0.8784	0.8521	1.005	1.594
390.05	0.9043	0.8784	1.000	1.656
390.22	0.9314	0.9079	0.997	1.743
390.50	0.9632	0.9466	0.996	1.871
390.77	0.9901	0.9846	0.998	2.000

Table 6. Vapor−Liquid Equilibrium Data for the DEC (1) + 1-Pentanol (2) System at 101.3 kPa

T/K	x	y	γ_1	γ_2
410.19	0.0244	0.0566	1.739	0.998
409.57	0.0422	0.0914	1.646	0.999
408.71	0.0689	0.1424	1.607	0.997
407.69	0.1017	0.1974	1.549	1.000
406.71	0.1427	0.2521	1.446	1.008
405.87	0.1818	0.3010	1.384	1.015
405.12	0.2176	0.3467	1.358	1.018
404.45	0.2570	0.3893	1.314	1.024
404.00	0.2892	0.4171	1.265	1.038
403.54	0.3254	0.4506	1.229	1.047
403.09	0.3575	0.4812	1.209	1.054
402.80	0.3885	0.5019	1.169	1.074
402.42	0.4165	0.5297	1.163	1.077
402.06	0.4530	0.5561	1.133	1.097
401.70	0.4870	0.5869	1.123	1.103
401.37	0.5232	0.6136	1.103	1.122
401.02	0.5640	0.6461	1.087	1.138
400.67	0.6056	0.6749	1.067	1.170
400.36	0.6481	0.7043	1.050	1.206
400.06	0.6886	0.7332	1.036	1.243
399.75	0.7457	0.7726	1.017	1.311
399.52	0.7989	0.8140	1.006	1.367
399.28	0.8555	0.8627	1.002	1.417
399.18	0.9128	0.9102	0.994	1.543
399.20	0.9491	0.9451	0.992	1.614
399.29	0.9847	0.9818	0.991	1.780

The results reported in these tables indicate that the binary systems 1-butanol + DEC and DEC + 1-pentanol exhibit a minimum boiling azeotrope. Azeotropic compositions have been obtained by determining the x_1 values that make the function $(x_1 - y_1) = f(x_1)$ equal to zero. The corresponding azeotropic temperatures were computed from a cubic polynomial equation $T = f\ (x_1)$, whose coefficients were obtained by fitting the experimental results around the azeotropic point, using the x_1 values

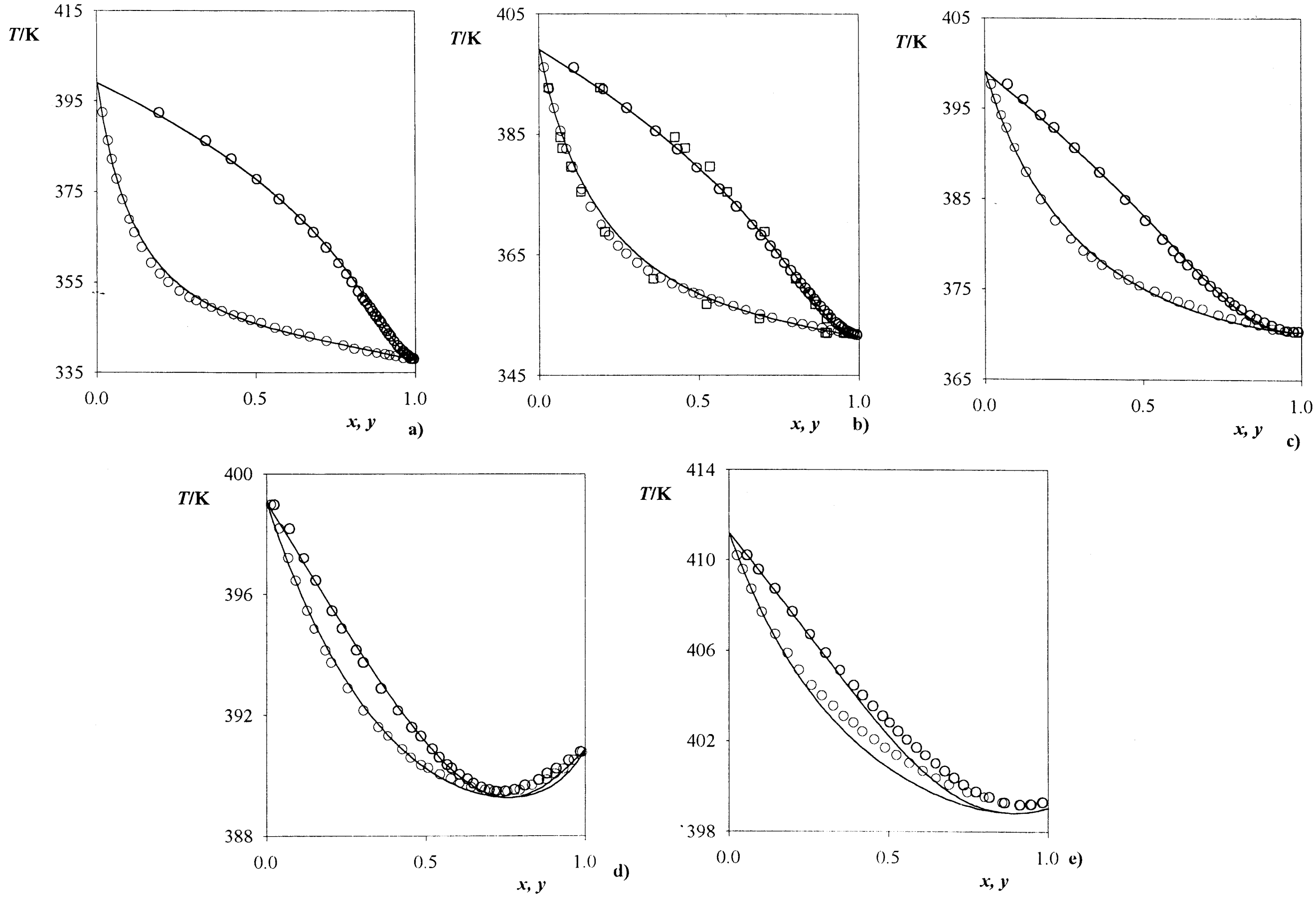

Figure 2. Boiling temperature diagram (*T*) for the binary systems at 101.3 kPa: (○) this work; (□) Luo et al.;[11] (—) correlated model; (a) methanol (1) + DEC (2), Wilson; (b) ethanol (1) + DEC (2), Wilson; (c) 1-propanol (1) + DEC (2), Wilson; (d) 1-butanol (1) + DEC (2), UNIQUAC; (e) DEC (1) + 1-pentanol (2), UNIQUAC.

Table 7. Consistency Test for the Binary Mixtures

system	ΔP^a/kPa	Δy^b
methanol + DEC	0.0027	0.005
ethanol + DEC	0.0016	0.007
1-propanol + DEC	0.0011	0.004
1-butanol + DEC	0.00003	0.003
DEC + 1-pentanol	0.00003	0.006

[a] ΔP = deviation between P_{exp} and P_{calc}. [b] Δy = deviation between y_{exp} and y_{calc}.

determined previously. The liquid composition and boiling temperature of the azeotropes for the binary mixtures 1-butanol + DEC and DEC + 1-pentanol are 0.7337 and 389.48 and 0.8975 and 399.21, respectively. The VLE data were found to be thermodynamically consistent by the point-to-point method of Van Ness et al.[19] and modified by Fredeslund et al.,[20] and the results are reported in Table 7.

***Correlation and Prediction*.** The parameters of the Wilson and UNIQUAC equations were optimized by minimizing the objective function

$$\mathrm{OF} = \sum_{j=1}^{np}\sum_{i=1}^{nc}\left[\frac{\gamma_{ij}^{\text{exp}} - \gamma_{ij}^{\text{cal}}}{\gamma_{ij}^{\text{exp}}}\right]^2 \qquad (4)$$

Table 8 gives the correlating parameters and the root-mean-square deviations for both the boiling point and the vapor-phase mole fraction. Inspection of the results shows that both models are suitable to correlate the binary data. Figures 1 and 2 show the temperature, the liquid-phase and vapor-phase mole fractions, the correlated line corresponding to the best model for each binary system, and the literature data. The correlating parameters for the binary systems were calculated using the Thermath program that had been extended by Castier[21] to determine the model

Table 8. Parameters and Root-Mean-Square Deviations between Experimental and Calculated Values for the Binary Systems at 101.3 kPa

model	parameters[a]				Δ(*T*)/K	Δ(*y*)
			Methanol + DEC			
Wilson	$\lambda_{11} - \lambda_{12}$	999.86	$\lambda_{21} - \lambda_{22}$	−132.25	0.82	0.0065
UNIQUAC	$u_{11} - u_{12}$	−127.86	$u_{21} - u_{22}$	803.51	0.90	0.0079
			Ethanol + DEC			
Wilson	$\lambda_{11} - \lambda_{12}$	442.66	$\lambda_{21} - \lambda_{22}$	395.97	0.83	0.0111
UNIQUAC	$u_{11} - u_{12}$	44.45	$u_{21} - u_{22}$	262.51	0.97	0.0125
			1-Propanol + DEC			
Wilson	$\lambda_{11} - \lambda_{12}$	228.50	$\lambda_{21} - \lambda_{22}$	442.96	0.39	0.0059
UNIQUAC	$u_{11} - u_{12}$	129.91	$u_{21} - u_{22}$	57.71	0.42	0.0065
			1-Butanol + DEC			
Wilson	$\lambda_{11} - \lambda_{12}$	20.04	$\lambda_{21} - \lambda_{22}$	581.69	0.29	0.0028
UNIQUAC	$u_{11} - u_{12}$	299.62	$u_{21} - u_{22}$	−139.54	0.19	0.0033
			DEC + 1-Pentanol			
Wilson	$\lambda_{11} - \lambda_{12}$	147.35	$\lambda_{21} - \lambda_{22}$	300.85	0.55	0.0037
UNIQUAC	$u_{11} - u_{12}$	165.26	$u_{21} - u_{22}$	−46.90	0.55	0.0035

[a] $\lambda_{ij} - \lambda_{ii}$ and $u_{ij} - u_{jj}$ are in units of cal·mol^{-1}.

Table 9. ASOG Interaction Parameters

	OH		OCOO	
	m_{kl}	n_{kl}	m_{kl}	n_{kl}
OH	0	0	1.0435	−960.96
OCOO	−0.5276	134.18	0	0

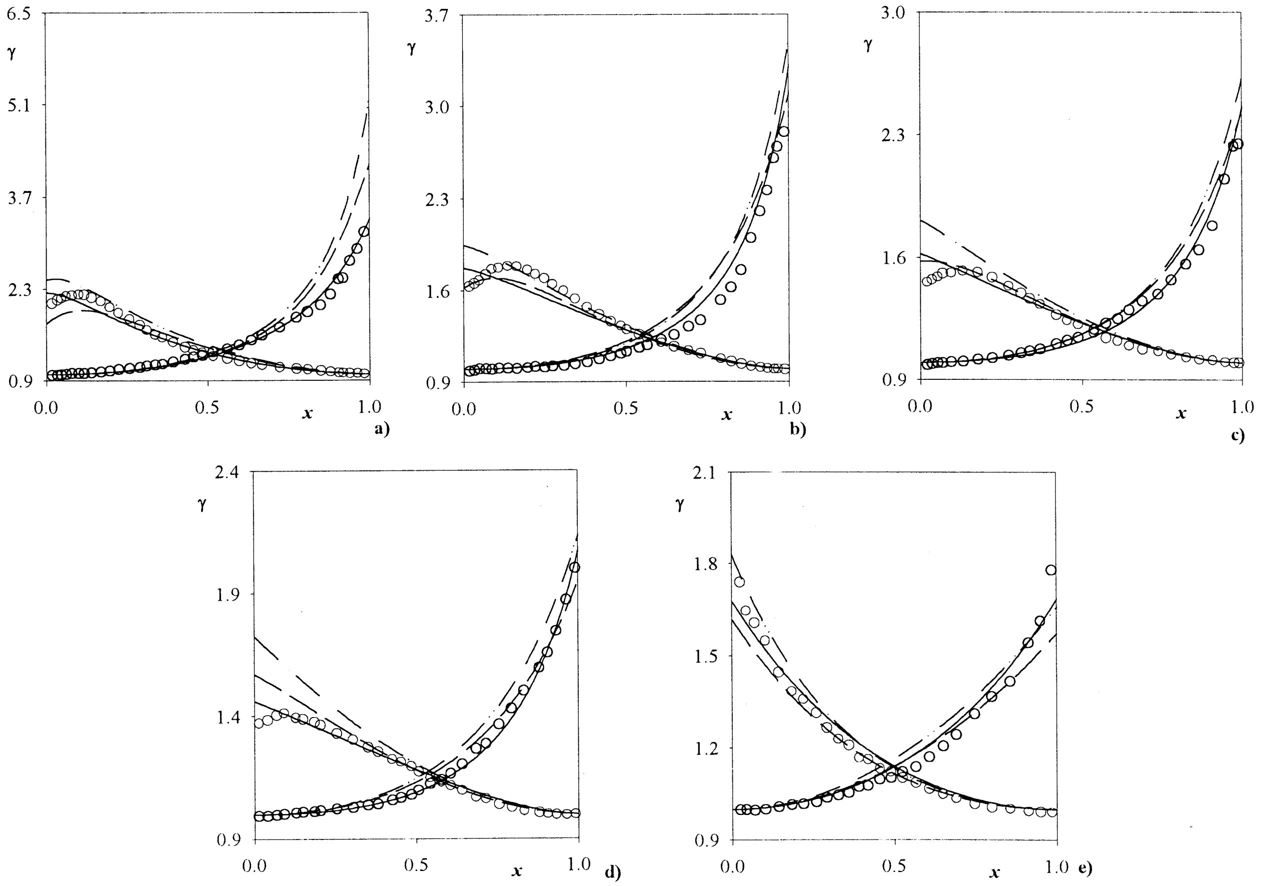

Figure 3. Activity coefficient (γ) plot for binary systems at 101.3 kPa: (○) this work; (—) correlated equation for several mixtures and the corresponding fitting curves using the (– – –) ASOG and (– .. – .. –) UNIFAC methods for the binary systems: (a) methanol (1) + DEC (2); (b) ethanol (1) + DEC (2); (c) 1-propanol (1) + DEC (2); (d) 1-butanol (1) + DEC (2); (e) DEC (1) + 1-pentanol (2)

Table 10. UNIFAC Interaction Parameters

	CH_3OH	OH	OCOO
CH_3OH	0	249.10	334.87
OH	−137.10	0	380.19
OCOO	184.75	83.04	0

Table 11. Root-Mean-Square Deviations of Boiling Points $\sigma(T)$ and Vapor-Phase Mole Fraction $\sigma(y)$ Resulting from the Prediction of VLE Using ASOG and UNIFAC Methods

method	$\sigma(y)$	$\sigma(T)$/K
	Methanol + DEC	
ASOG	0.0151	1.2940
UNIFAC	0.0142	1.6049
	Ethanol + DEC	
ASOG	0.0119	0.5495
UNIFAC	0.0108	0.5904
	1-Propanol + DEC	
ASOG	0.0045	0.4218
UNIFAC	0.0117	0.8525
	1-Butanol + DEC	
ASOG	0.0067	0.4248
UNIFAC	0.0111	0.8777
	DEC + 1-Pentanol	
ASOG	0.0051	0.2635
UNIFAC	0.0059	0.7422

parameters for the Wilson and UNIQUAC excess Gibbs free energy models from vapor−liquid equilibrium data. This computer program is capable of generating code that can be readily interfaced with the INTBIS/INTLIB package modified by Schnepper and Stadtherr.[22]

Table 12. Root-Mean-Square Deviations of Pressure $\sigma(P)$ and Vapor-Phase Mole Fraction $\sigma(y)$ Resulting from the Prediction of VLE Using ASOG and UNIFAC Methods for Published Data[a]

system	isobaric VLE/method	$\sigma(T)$/°C	$\sigma(y)$
ethanol + DEC	P = 101.13 kPa/ASOG	1.26	0.0429
ethanol + DEC	P = 101.13 kPa/UNIFAC	0.62	0.0289

[a] Luo et al.[11]

By using the VLE data of the binary systems dimethyl carbonate and DEC with alkanes and with linear alcohols, the interaction parameters of (−OCOO−) with (CH_3−) and with (OH−) in the ASOG method and of (−OCOO−) with (CH_3−) and with (CH_3OH) and (OH−) in the UNIFAC method were calculated previously.[8,10] They are summarized in Tables 9 and 10.

ASOG and UNIFAC group contribution methods have been employed to predict the VLE of the binary systems. The volume R_k and surface area Q_k parameters were obtained from the literaure.[11]

Figure 3 displays the comparison of the calculated and the experimental activity coefficients for the binary systems with a very good agreement achieved. Table 11 presents the root-mean-square deviation between experimental and predicted values of the boiling points and the vapor-phase mole fractions for the binary systems. Published data[11] for binary systems have been used to verify the new parameters for both methods. The results, in terms of root-mean-square deviations, are shown in Table 12.

Group contribution methods have been employed to predict the VLE of the binary systems under study. The root-mean-square deviations of the temperature and the composition of the vapor phase indicate that ASOG and UNIFAC methods give similar predictions for methanol and ethanol with DEC; however, for linear alcohols from C_3 to C_5 the ASOG method gives smaller deviations between experimental and calculated values. For literature data (Luo et al.[11]) the UNIFAC method gives smaller deviations.

Literature Cited

(1) Sharma, P. K.; Narayanan, S.; Hickey, G. S. NASA's Jet Propulsion Laboratory. U.S. Patent No. 6,042,964.

(2) Rodríguez, A.; Canosa, J.; Tojo, J. Physical Properties of the Ternary Mixture Dimethyl Carbonate + Methanol + Benzene and Its Corresponding Binaries at 298.15 K. *J. Chem. Eng. Data*. **1999**, *44*, 1298−1303.

(3) Rodríguez, A.; Canosa, J.; Tojo, J. Density, refractive index on mixing, and speed of sound of the ternary mixtures (dimethyl carbonate or diethyl carbonate + methanol + toluene) and the corresponding binaries at T = 298.15 K. *J. Chem. Thermodyn*. **2001**, *33*, 1−14.

(4) Rodríguez, A.; Canosa, J.; Tojo, J. Physical Properties and Liquid−Liquid Equilibrium of the Ternary Mixture (Dimethyl Carbonate+Methanol+Hexane) at 298.15 K. *J. Chem. Eng. Data*. **2001**, *46*, 184−187.

(5) Rodríguez, A.; Canosa, J.; Tojo, J. Physical Properties of Binary Mixtures (Dimethyl carbonate+alcohols) at several temperatures. *J. Chem. Eng. Data*. **2001**, *46*, 1476−1486.

(6) Rodríguez, A.; Canosa, J.; Tojo, J. Liquid−liquid Equilibrium and Physical Properties of Ternary Mixture (Dimethyl Carbonate + Methanol + Cyclohexane) at 298.15 K. *J. Chem. Eng. Data*. **2001**, *46*, 846−850.

(7) Rodríguez, A.; Canosa, J.; Tojo, J. Density, Refractive Index, and Speed of Sound of Binary Mixtures (Diethyl carbonate+Alcohols) at several temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1506−1515.

(8) Rodríguez, A.; Canosa, J.; Tojo, J. Isobaric vapor-liquid equilibria of dimethyl carbonate with alkanes and cyclohexane at 101.3 kPa. *Fluid Phase Equilib*. **2002**, *198*, 95−109.

(9) Rodríguez, A.; Canosa, J.; Tojo, J. Isobaric vapor-liquid equilibria of diethyl carbonate with alkanes at 101.3 kPa. *J. Chem. Eng. Data*., in press.

(10) Rodríguez, A.; Canosa, J.; Tojo, J. Vapour−liquid equilibria of dimethyl carbonate with linear alcohols and estimation of interaction parameters for UNIFAC and ASOG methods. *Fluid Phase Equilib*. **2002**, *201*, 187−201.

(11) Luo, H.-P.; Xiao, W.-D.; Zhu, K.-H. Isobaric Vapor-Liquid Equilibria of Alkyl Carbonates with Alcohols. *Fluid Phase Equilib*. **2000**, *175*, 91−105.

(12) Wilson, G. M. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc*. **1964**, *86*, 127−131.

(13) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess energy of partly or completely miscible systems. *AIChE J*. **1975**, *21*, 116−128.

(14) Kojima, K.; Tochigi, K. *Prediction of vapor-liquid equilibria by the ASOG method*; Kodansha: Tokyo, 1979.

(15) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J*. **1975**, *21*, 1086−1099.

(16) Hayden, J.; O'Connell, J. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev*. **1975**, *14*, 209−216.

(17) Praustnitz, J.; Anderson, T.; Grens, E.; Eckert, C.; Hsieh, R.; O'Connell, J. Computer calculations for multicomponent vapor-liquid and liquid−liquid equilibria. Prentice Hall: Englewood Cliffs, NJ, 1980.

(18) Daubert, T. E.; Danner, R. P. *Data compilation tables of properties of pure compounds*; AICHE: New York, 2000.

(19) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor liquid equilibrium. I. Appraisal of data reduction methods. *AIChE J*. **1973**, *19*, 238−244.

(20) Fredeslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-liquid Equilibria using UNIFAC*; Elsevier: Amsterdam, 1977.

(21) Castier, M. Automatic implementation of thermodynamic models using computer algebra. *Comput. Chem. Eng*. **1999**, *23*, 1229−1236.

(22) Schnepper, C. A.; Stadtherr, M. A. Robust process simulation interval methods. *Comput. Chem. Eng*. **1996**, *20*, 187−192.

(23) Francesconi, R.; Comelli, F. Excess Molar Enthalpies, Densities, and Excess Molar Volumes of Diethyl Carbonate in Binary Mixtures with seven *n*-Alkanols at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 45−48.

(24) Pal, A.; Dass, G.; Kumar, A. Excess Molar Volumes, Viscosities, and Refractive Indices of Triethylene Glycol Dimethyl Ether with Dimethyl Carbonate, Diethyl Carbonate, and Propylene Carbonate at 298.15 K. *J. Chem. Eng. Data*. **1998**, *43*, 738−741.

(25) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Techniques of Chemistry*, 4th ed.; Wiley: New York, 1986; Vol. II.

(26) Das, A.; Frenkel, M.; Gadalla, N. M.; Marsh, K.; Wilhoit, R. C. *TRC Thermodynamic Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994.

(27) Arce, A.; Martínez-Ageitos, J.; Mendoza, J.; Soto, A. Densities, Refractive Indices, and Excess Molar Volumes of Water + Methanol + 2-Methoxy-2-methylpropane at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 647−649.

(28) Ortega, J.; Susial, P. Excess molar volumes of mixtures containing methyl alkanoates (acetate, propanoate, and butanoate) with normal alkanols (from ethanol to pentan-1-ol). *Can. J. Chem*. **1989**, *67*, 1120−1124.

(29) Cocero, M. J.; Mato, F.; García, J. C. Thermodynamics of Binary Mixtures Containing Organic Carbonates + Cyclohexane + Benzene, + Tetrachloromethane. *J. Chem. Eng. Data*. **1989**, *34*, 443−445.

(30) Garcia de la Fuente, I.; Gonzalez, J. A.; Cobos, J. C.; Casanova, C. Excess molar volumes of diethyl carbonate with hydrocarbons or tetrachloromethane at 25 °C. *J. Solution Chem*. **1995**, *24*, 827−835.

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