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Supplementary Material Available: Table I listing unsmoothed solubility data for naphthalene in water, organic solvents, and solvent mixtures at 25 °C (9 pages). Ordering information is given on any current masthead page.

Thermodynamics of Binary Mixtures Containing Organic Carbonates. 3. Isothermal Vapor–Liquid Equilibria for Diethyl Carbonate + Cyclohexane, + Benzene, or + Tetrachloromethane†

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Vapor and liquid equilibrium phase compositions were determined at 298.65 K for binary systems containing diethyl carbonate and cyclohexane, benzene, or tetrachloromethane. The diethyl carbonate + cyclohexane system shows large positive deviations from Raoult's law. By contrast, the diethyl carbonate + benzene or + tetrachloromethane systems are almost ideal.

Introduction

In part 1 of this series (*2*) we reported excess enthalpies for dimethyl carbonate + some *n*-alkanes, + cyclohexane, + methylcyclohexane, + benzene, + toluene, and + tetrachloromethane. In part 2, the isothermal vapor–liquid equilibrium (VLE) for dimethyl carbonate + cyclohexane, + benzene, or + tetrachloromethane (*3*) were reported. In this paper isothermal VLE data are presented for the binary systems diethyl carbonate (1) + cyclohexane (2), + benzene (2), or + tetrachloromethane (2) at 298.65 K. Excess enthalpies for these systems have been published previously (*4*). All these data will serve for estimating interaction parameters for group contribution activity coefficient models. No VLE data are available for diethyl carbonate with any of the above-mentioned solvents.

Experimental Section

***Materials*.** All the chemicals used were from Fluka. Diethyl carbonate (puriss p.a., >99.5%) was used without further purification after gas chromatographic analysis failed to show any significant impurities. Source, purity, purification, and physical constants of cyclohexane, benzene, and tetrachloromethane were found to be the same as in our previous paper (*2*). The density and refractive index at 298.15 K, $\rho = 969.4$ kg m^{-3} and $n_D = 1.3824$, were in good agreement with literature values (*5*, *6*). Prior to the actual measurements, the liquids were dried over a molecular sieve (Union Carbide Type 4A from Fluka).

***Apparatus and Procedure*.** A detailed description of the experimental equipment and operating procedure can be found in our previous papers (*3*, *7*).

The equilibrium temperature, *T*, was measured accurate to 0.05 K with a certified PROTON mercury thermometer (Model BER-MAN) previously calibrated with a Hewlett-Packard, Model 2804A, quartz thermometer.

The composition of the vapor phase was determined by use of a Hewlett-Packard, Model 5980, gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard, Model 3390, electronic integrator. The column, 200 cm long and $^1/_4$ in. in diameter, was packed with Carbowax 1500 and was operated isothermally within the range from 80 to 130 °C depending on the nature of the analyzed materials. The chromatograph was calibrated with synthetic mixtures. The mole fraction of the vapor phase, *y*, accurate to within 0.0002 for

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† This paper is a contribution to the TOM Project (*1*).

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Table I. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i for the System Diethyl Carbonate (1) + Cyclohexane (2) at 298.65 K

x_1	y_1	P/kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.110	0.038	12.56	2.901	1.019	0.9905	0.9937
0.204	0.059	11.98	2.381	1.064	0.9909	0.9940
0.293	0.073	11.49	1.916	1.132	0.9913	0.9942
0.410	0.089	10.88	1.582	1.263	0.9917	0.9945
0.495	0.096	10.41	1.352	1.400	0.9921	0.9948
0.598	0.114	9.71	1.241	1.610	0.9926	0.9951
0.700	0.135	8.77	1.135	1.903	0.9933	0.9956
0.811	0.172	7.21	1.027	2.380	0.9945	0.9964
0.892	0.251	5.44	1.030	2.846	0.9958	0.9973
0.947	0.376	3.73	0.997	3.314	0.9971	0.9981

Table II. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i for the System Diethyl Carbonate (1) + Benzene (2) at 298.65 K

x_1	y_1	P/kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.140	0.020	10.86	1.039	0.9549	0.9920	0.9953
0.227	0.037	9.69	1.059	0.9319	0.9928	0.9958
0.321	0.056	8.68	1.016	0.9321	0.9936	0.9962
0.409	0.080	7.86	1.032	0.9453	0.9942	0.9966
0.525	0.122	6.74	1.053	0.9636	0.9950	0.9971
0.621	0.170	5.68	1.046	0.9625	0.9957	0.9975
0.714	0.238	4.57	1.025	0.9424	0.9965	0.9980
0.788	0.320	3.71	1.013	0.9199	0.9972	0.9984
0.896	0.516	2.57	0.996	0.9251	0.9980	0.9989
0.957	0.739	1.96	1.019	0.9206	0.9985	0.9992

Table III. Experimental x-y Data and Calculated Values of P, γ_i, and ϕ_i for the System Diethyl Carbonate (1) + Tetrachloromethane (2) at 298.65 K

x_1	y_1	P/kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.0747	0.0080	14.52	1.0390	1.000	0.9890	0.9927
0.2093	0.0261	12.69	1.0587	1.006	0.9904	0.9937
0.2981	0.0380	11.49	0.9811	1.014	0.9913	0.9943
0.3918	0.0564	10.23	0.9865	1.022	0.9922	0.9949
0.5029	0.0844	8.69	0.9787	1.032	0.9934	0.9957
0.6028	0.1208	7.27	0.9784	1.038	0.9944	0.9964
0.7075	0.1810	5.74	0.9867	1.037	0.9956	0.9971
0.7937	0.2583	4.45	0.9753	1.034	0.9966	0.9978
0.8891	0.4306	3.04	0.9928	1.099	0.9876	0.9985
0.9258	0.5407	2.51	0.9889	1.006	0.9989	0.9988

the diethyl carbonate + tetrachloromethane system and to within 0.001 for the other systems, was calculated from the peak-area ratio of the samples.

Results and Discussion

Tables I–III present the experimental x-y VLE data for the systems diethyl carbonate (1) + cyclohexane (2), + benzene (2), or + tetrachloromethane (2) at 298.65 K, together with the calculated values of total vapor pressures, P, liquid-phase activity coefficients, γ_1 and γ_2, and vapor-phase fugacity coefficients, ϕ_1 and ϕ_2.

Inasmuch as the method does not provide experimental data for the total vapor pressures, these values of P, as well as the activity coefficients, γ_i, and the fugacity coefficients, ϕ_i, were derived from the x-y-T data and from the vapor pressures of the pure components, P_i°, by means of an iterative procedure described elsewhere (*8*).

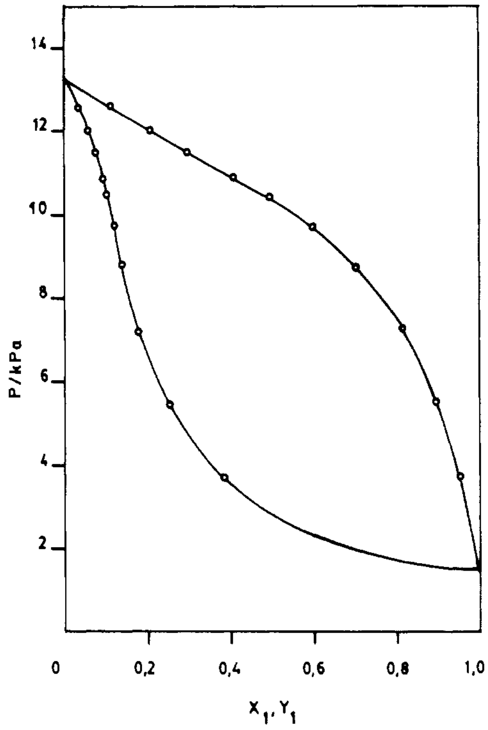

Figure 1. P-x-y phase equilibrium diagram for diethyl carbonate (1) + cyclohexane (2) at 298.65 K: (O) experimental; (—) fit of the Wilson equation.

The vapor pressures of the pure components at 298.65 K (Table IV) were calculated from the Antoine coefficients reported in the literature (*9–11*).

Similar results were obtained when vapor-phase nonidealities were calculated from the Peng–Robinson (*12*) equation of state or from the virial equation of state truncated after the second term, with the second virial coefficients obtained by the method of Hayden and O'Connell (*13*). The values used for the critical constants, T_i^c and P_i^c, the acentric factors, ω_i, the dipole moments, μ_i, the coefficients a_{ii} and b_{ii} for the Peng–Robinson equation and the second molar virial coefficients, B_{ij}, are given in Table IV. The values for diethyl carbonate were obtained from literature or estimated by prediction methods (*14*). The binary interaction coefficients in the Peng–Robinson equation were set as zero for all the systems. The vapor-phase fugacity coefficients in Tables I–III were calculated by the Peng–Robinson equation.

Diethyl carbonate + benzene and diethyl carbonate + tetrachloromethane are nearly ideal mixtures. Diethyl carbonate + cyclohexane presents large positive deviations from Raoult's law. The experimental data were found to be thermodynamically consistent, as checked by using the Redlich–Kister area test (*15*). The data were fitted to the van Laar (*16*), Mato (*17*), Wilson (*18*), NRTL (*19*), and LEMF (*20*) equations by a nonlinear regression method as described previously (*3*).

The model parameters are shown in Table V along with the average absolute deviations in vapor-phase composition. The different correlating equations yield nearly the same deviations in vapor-phase composition.

Table IV. Pure Component Vapor Pressures, P_i° (*9–11*) at 298.65 K, Critical Temperatures, T_i^c (*14*), Critical Pressures, P_i^c (*14*), Acentric Factors, ω_i (*14*), Coefficients a_{ii} and b_{ii} for the Peng–Robinson Equation, Molecular Dipole Moments, μ_i (*21*), and Second Molar Virial Coefficients, B_{ii} and B_{ij}

component	P_i^0/kPa	T_i^c/K	P_i^c/kPa	ω_i	a_{ii}/J m^3 mol^{-2}	$b_{ii}/10^{-5}$ m^3 mol^{-1}	μ_i/D	$-B_{ii}/10^{-6}$ m^3 mol^{-1}	$-B_{ij}/10^{-6}$ m^3 mol^{-1}
diethyl carbonate (1)	1.482	569.0	3465	0.557	5.122	10.62	0.82	3200	
cyclohexane (2)	13.310	553.5	4070	0.212	3.329	8.80	0	1900	2000
benzene (2)	12.985	562.2	4890	0.212	2.877	7.43	0	1500	2200
tetrachloromethane (2)	15.567	556.4	4560	0.193	2.976	7.89	0	1700	2100

Table V. Parameters A_{12} and A_{21} in the Activity Coefficient Models at 298.65 K for Diethyl Carbonate (1) + Cyclohexane (2) System and Average Absolute Deviations in Vapor-Phase Mole Fractions $\Delta(y_1)$

	A_{12}	A_{21}	$\Delta(y_1)$
van Laar (*16*)	1.3486	1.3090	0.0020
Mato (*17*)	1.3086	1.3090	0.0020
Wilson (*18*)[a]	1947	2171	0.0015
NRTL (*19*) (α_{12} = 0.47)[a]	1891	2170	0.0015
LEMF (20)[a]	1371	1233	0.0016

[a] Parameters A_{12} and A_{21} in J mol^{-1}.

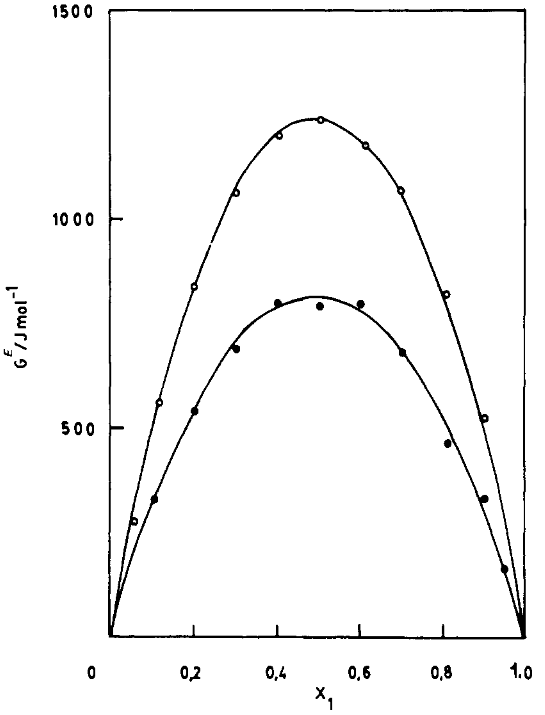

Figure 2. Molar excess Gibbs energy of diethyl carbonate (1) + cyclohexane (2) (●) and dimethyl carbonate (1) + cyclohexane (2) (○) mixtures at 298.65 and 298.15 K, respectively: (●, ○) experimental; (—) calculated from the Wilson parameters.

The P-x-y phase equilibrium diagram is shown in Figure 1. Figure 2 compares the molar excess Gibbs energies, $G^E = RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2]$, of dimethyl and diethyl carbonate + cyclohexane. As can be seen, $G^E(x_1{=}0.5)$ decreases from 1242 J mol^{-1} for dimethyl carbonate (*3*) to 812 J mol^{-1} for diethyl carbonate (this work). This fact is in accord with the values reported for the excess molar enthalpies, $H^E(x_1{=}0.5)$ at 298.15 K, which are 1947 J mol^{-1} for dimethyl carbonate + cyclohexane (*2*) and 1320 J mol^{-1} for diethyl carbonate + cyclohexane (*4*). Therefore, both G^E and H^E decrease by ca. 33% in going from dimethyl to diethyl carbonate.

On the other hand, the almost ideal behavior found in this work for diethyl carbonate + benzene or + tetrachloromethane agrees with the excess molar enthalpies reported (*4*) for these systems, where the curves of H^E vs x_1 have a sigmoid shape and exhibit very small values of H^E, ranging from -10 to 17 J mol^{-1} for benzene and from -6 to 25 J mol^{-1} for tetrachloromethane.

A quantitative treatment in terms of DISQUAC (*1*), an extended quasi-chemical group contribution method, of these vapor-liquid equilibria and H^E results and of additional measurements on dialkyl carbonates + n-alkanes will be presented in a forthcoming paper.

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Glossary

a, b	parameters in the Peng-Robinson equation
A	parameters in the excess Gibbs energy, J mol^{-1}, for Wilson, NRTL, and LEMF equations
B	second molar virial coefficient, m^3 mol^{-1}
G	molar Gibbs energy, J mol^{-1}
P	total vapor pressure, kPa
T	temperature, K
x	liquid mole fraction
y	vapor mole fraction

Greek Letters

γ	activity coefficient in the liquid
ϕ	fugacity coefficient in the vapor
μ	dipole moment, D
ω	acentric factor

Subscripts

i	property of component i (i = 1, 2)

Superscripts

c	critical-point property
E	excess property
o	pure component property

Registry No. Diethyl carbonate, 105-58-8; cyclohexane, 110-82-7; benzene, 71-43-2; tetrachloromethane, 56-23-5.

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