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Excess Enthalpy and *T*–*x* Data of Aromatic–Propylene Carbonate Mixtures

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Boiling temperatures of binary mixtures containing propylene carbonate and an aromatic compound (benzene, toluene, *p*-xylene) were measured at pressures of 100 and 200 mmHg. Excess enthalpy data for these systems were also measured at 25 °C. Both data are used to obtain the activity coefficients.

Introduction

In the last few years alkylene carbonates were claimed in the scientific literature to have good properties as solvents for a variety of extractions of industrial interest (*1–4*).

The purpose of our experimental investigations is to analyze the solvent properties of propylene carbonate in the extraction of aromatic compounds from normal paraffins and other hydrocarbons.

To this end the determination of the thermodynamic behavior of these mixtures, in particular fluid-phase equilibrium properties, is needed. In this paper, we report *T*–*x* data of the mixtures propylene carbonate–aromatic to obtain the activity coefficients; excess enthalpy data were also measured to have information on the temperature dependence of the excess free energy.

Experimental Section

A couple of Swietoslawsky ebulliometers, with the condensers connected together, were used for the measurement of the boiling points of pure propylene carbonate and of its mixtures with aromatic compounds.

One of the ebulliometers was filled with redistilled water used as a reference substance and the pressure was determined via its boiling point. The required value of *P* was adjusted by an ejector connected to the pressure line through a dead volume and a valve. The estimated precision in pressure measurements was ±1 mmHg.

The temperature was detected by a Lauda Pt resistance digital thermometer with a display having a ±0.01 °C resolution. The estimated uncertainty in the equilibrium temperature was ±0.05 °C.

Table I. Boiling Temperatures of Mixtures Propylene Carbonate (1)–Benzene (2) at 100 and 200 mmHg

press. = 100 mmHg		press. = 200 mmHg	
x_1	T, °C	x_1	T, °C
0.013	26.03	0.013	42.32
0.107	27.21	0.107	43.75
0.189	28.04	0.189	44.70
0.281	29.04	0.281	45.91
0.341	29.83	0.341	46.77
0.403	30.83	0.403	47.88
0.482	32.44	0.482	49.79
0.518	33.20	0.518	50.61
0.569	34.77	0.569	52.45
0.617	36.20	0.617	54.10
0.670	38.30	0.670	56.61
0.712	40.46	0.712	59.08
0.750	43.08	0.750	62.13
0.785	46.22	0.785	65.85
0.802	48.34	0.802	68.64
0.838	54.10	0.838	75.62
0.870	59.75	0.870	83.94
0.895	64.73	0.895	89.21

The composition of liquid mixtures was measured by a Bausch and Lomb precision refractometer at the end of each experimental run. The experimental precision of the equilibrium mixture composition measurements was assumed to be ±0.001 mole fraction.

Heat of mixing data were obtained at 25 °C with a LKB 10700/2 microcalorimeter.

The aromatic compounds used were pure-grade products of Carlo Erba with a purity claimed of 99.5% for benzene and toluene and of 99% for *p*-xylene. Propylene carbonate, 99% pure, was a Merck product. No further purification was carried out.

Several equilibrium runs for each system were carried out twice to check the reproducibility of the method. In all cases differences observed in the temperature measurement were in the range of the experimental uncertainties (<0.05 °C).

Discussion

Boiling temperatures of the three systems are reported in

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Table II. Boiling Temperatures of Mixtures Propylene Carbonate (1)-Toluene (2) at 100 and 200 mmHg

press. = 100 mmHg		press. = 200 mmHg	
x_1	T, °C	x_1	T, °C
0.045	52.80	0.010	69.71
0.121	53.50	0.045	70.36
0.218	54.35	0.090	71.05
0.307	55.27	0.148	71.74
0.396	56.15	0.198	72.25
0.457	57.08	0.285	73.07
0.529	58.43	0.378	74.28
0.587	59.75	0.476	75.85
0.646	61.57	0.513	77.02
0.677	62.65	0.587	78.89
0.707	64.00	0.626	80.03
0.742	65.87	0.670	81.94
0.768	68.03	0.737	85.98
0.798	70.53	0.770	88.97
0.827	74.07	0.797	91.80
0.855	78.61	0.818	95.02
0.877	82.88	0.841	98.02
0.893	86.42	0.860	102.32
		0.872	105.34
		0.885	107.22
		0.889	108.61
		0.892	108.85
		0.907	114.06

Table III. Boiling Temperatures of Mixtures Propylene Carbonate (1)-p-Xylene (2) at 100 and 200 mmHg

press. = 100 mmHg		press. = 200 mmHg	
x_1	T, °C	x_1	T, °C
0.009	75.98	0.009	94.70
0.123	77.38	0.054	95.50
0.194	77.95	0.139	96.55
0.361	79.28	0.211	97.24
0.413	79.72	0.305	98.06
0.521	81.02	0.397	99.04
0.585	81.95	0.460	99.77
0.642	83.35	0.528	100.79
0.687	84.82	0.549	101.26
0.712	85.65	0.582	101.92
0.761	88.48	0.608	102.53
0.800	91.35	0.633	103.30
0.830	94.23	0.669	104.62
0.850	96.75	0.700	106.00
0.882	102.15	0.728	107.50
0.890	104.25	0.749	108.64
0.905	106.75	0.776	110.75
		0.797	112.49
		0.812	113.79
		0.833	116.96
		0.867	122.04
		0.887	126.00
		0.912	132.08

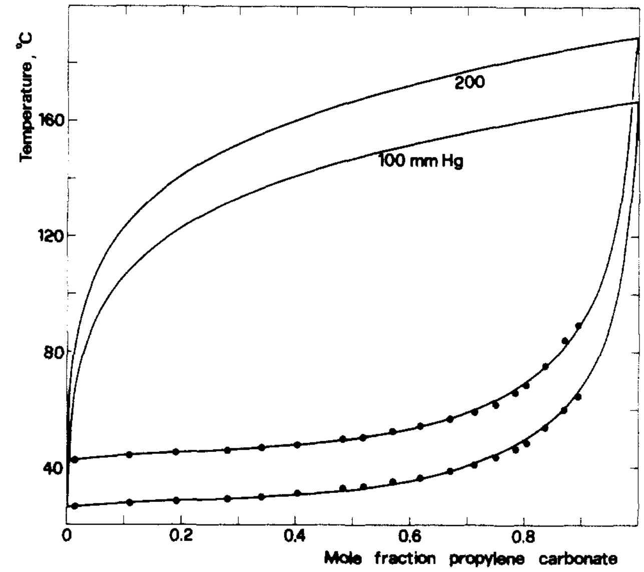

Figure 1. Vapor-liquid equilibria of mixtures propylene carbonate-benzene at 100 and 200 mmHg.

Tables I-III. Excess enthalpy data are reported in Table IV. Data reduction was carried out by means of Barker's method (*5*), which is based, at low pressures, on the following equilibrium equation:

$$P = \gamma_1 x_1 p_{s1} + \gamma_2 x_2 p_{s2} \qquad (1)$$

We used the NRTL equation (*6*) to calculate the activity coefficients. Vapor pressures of pure compounds were calculated by means of Antoine's equation with the values of parameters reported in Table V. For the propylene carbonate the parameters were obtained by the least-squares method applied to our data and literature data (*7*).

Two procedures were adopted to obtain the parameters of the NRTL equation from the data. In the first procedure the NRTL equation was assumed to correctly represent the temperature dependence of activity coefficients and the validity of this assumption was tested by comparing the NRTL excess enthalpy with the experimental data. In the second procedure the temperature dependence of activity coefficients, calculated from heat of mixing data, was included in eq 1:

$$P = \gamma_1^{T_0} x_1 p_{s1} \exp\left[\frac{\bar{H}_1 - H_1}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] + \gamma_2^{T_0} x_2 p_{s2} \exp\left[\frac{\bar{H}_2 - H_2}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \qquad (2)$$

In this equation, partial molar excess enthalpies were obtained by fitting heat of mixing data by means of the following empirical equation:

$$H^E = A x_1 x_2 \qquad (3)$$

Table IV. Excess Enthalpy Data at 25 °C for Mixtures Propylene Carbonate (1)-Benzene, Propylene Carbonate-Toluene, and Propylene Carbonate-p-Xylene

propylene carbonate-benzene		propylene carbonate-toluene		propylene carbonate-p-xylene	
x_1	H^E, cal/mol	x_1	H^E, cal/mol	x_1	H^E, cal/mol
0.156	35.6	0.200	76.9	0.145	82.5
0.285	65.4	0.280	89.9	0.245	115.8
0.323	66.5	0.421	101.1	0.300	136.1
0.529	73.1	0.465	104.5	0.452	157.6
0.529	74.0	0.532	103.5	0.464	155.6
0.540	82.8	0.593	94.9	0.478	152.3
0.590	80.0	0.658	90.2	0.525	155.4
0.690	80.0	0.749	72.1	0.554	154.8
0.817	55.0	0.821	59.5	0.577	156.0
0.909	36.0			0.688	131.5
0.965	13.5			0.744	118.7
				0.908	55.7

Table V. Parameters of Antoine's Equation[a]

	A	B	C
propylene carbonate	18.8817	6284.73	
benzene (*8*)	15.9008	2788.51	−52.36
toluene (*8*)	16.0137	3096.52	−53.67
p-xylene (*8*)	16.0963	3346.65	−57.84

[a] $\ln p_S = A - B/(T + C)$; p_S in mmHg, T in Kelvin.

Table VI. NRTL Parameters for the Three Systems Obtained with Two Different Procedures[a] and Parameter A of Eq 3[b]

	first procedure		second procedure[c]		
	$g_{12} - g_{22}$	$g_{12} - g_{11}$	$g_{12} - g_{22}$	$g_{12} - g_{11}$	A
propylene carbonate-benzene	−279	1493	−230	1378	323
propylene carbonate-toluene	−38	1376	22	1192	415
propylene carbonate-*p*-xylene	237	1266	300	1068	629

[a] See the text. [b] The value of α in the NRTL equation was assumed to be 0.3. All values in the table are in cal/mol. [c] T_0 = 25 °C.

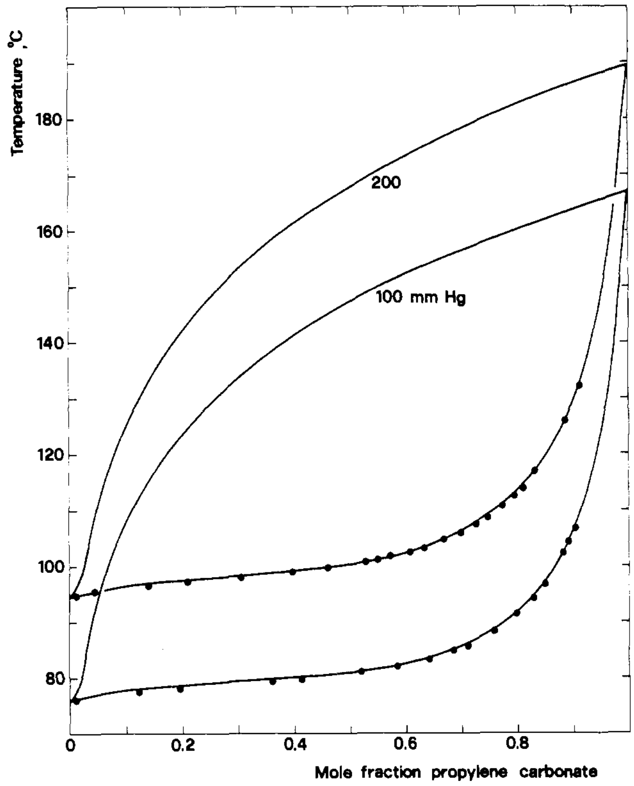

Figure 2. Vapor–liquid equilibria of mixtures propylene carbonate–*p*-xylene at 100 and 200 mmHg.

The values of A are reported in Table VI together with the NRTL parameters. The latter ones were obtained for both procedures minimizing the objective function $\sum_{i=1}^{n} [P_{i,\mathrm{exptl}} - P_{i,\mathrm{calcd}}]^2$. Both sets of data at 100 and 200 mmHg were used in data reduction.

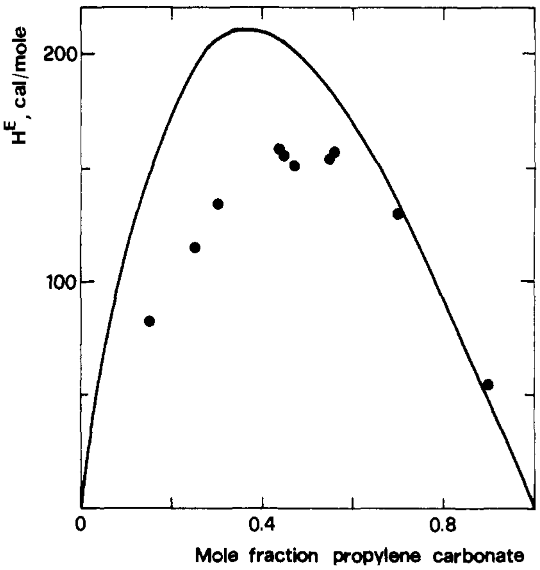

Figure 3. Heats of mixing of mixtures propylene carbonate–*p*-xylene at 25 °C calculated with NRTL parameters $g_{12} - g_{22}$ and $g_{12} - g_{11}$ independent of temperature.

Activity coefficients obtained with the different procedures do not much deviate from each other and in the scale of Figures 1 and 2 no difference can be noted in the representation of T–x curves and the prediction of vapor curves.

Heats of mixing calculated with the first procedure are shown in Figure 3 for the *p*-xylene–propylene carbonate system. Maximum deviations from the experimental data are of the order of 50%; the result is not very bad if one considers the uncertainties related to this kind of procedure (*9*).

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Registry No. Propylene carbonate, 108-32-7; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3.

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