(16) Michels, A.; Wassenaar, T.; Wolkers, G. J.; Prins, Chr.; Klundert, L. v. d. J. Chem. Eng. Data 1966, 11, 449.
(17) Rathjen, W.; Straub, J. Proc. Symp. Thermophys. Prop., 7th 1977, 839.
(18) Booth, H. S.; Swinehart, C. F. J. Am. Chem. Soc. 1935, 57, 1337.
(19) Benning, A. F.; McHarness, R. C. Ind. Eng. Chem. 1939, 31, 912.
(20) Zander, M. Proc. Symp. Thermophys. Prop., 4th 1968, 114.
(21) Kletskii, A. V. "Thermophysical Properties of Freon-22"; Israel Program for Scientific Translations: Jerusalem, 1971.
(22) Hirata, M.; Nagahama, K.; Saito, J.; Wakamatsu, N. Prepr. 8th Autumn Meeting Soc. Chem. Eng., Jpn. 1974, 444.

Solubility of Carbon Monoxide in 1,4-Dioxane

Ewald Veleckis* and David S. Hacker[†]

Argonne National Laboratory, Argonne, Illinois 60439

The solubility of CO in 1,4-dioxane was determined as a function of pressure (7–70 atm) and temperature (80–173 °C). Solubility data can be represented by the equation $x_2 = (2.025 \times 10^{-3} - 0.4974T^{-1})P_2 + [-2.574 \times 10^{-6} + (7.351 \times 10^{-4})T^{-1}]P_2^2$, where x_2 and P_2 are the mole fraction and the partial pressure of CO (in atmospheres), respectively, and T is the Kelvin temperature. The results, analyzed in terms of the Krichevsky–Ilinskaya equation, showed that the partial molar volume of CO was independent of pressure and that the isobaric Henry's law was obeyed in the ranges studied. The temperature dependence of the Henry's law constant may be expressed by $\ln H_{2,1} = 5.688 + 594.6T^{-1}$ where $H_{2,1}$ is in atm (mole fraction of CO)$^{-1}$. Comparisons with other solvents showed that, on the basis of CO dissolution characteristics, 1,4-dioxane can be classified better with polar than with nonpolar solvents.

Introduction

The solubility of hydrogen and carbon monoxide in organic solvents is of interest in certain applications of the Fischer–Tropsch (FT) catalytic synthesis of hydrocarbons, where an optimum solvent must be selected to serve as a suspending medium for the slurried catalyst (1). Reliable solubility data on these two gases at the conditions of the synthesis (~1000 psi, ~250 °C) are sparse. For example, in the case of CO, a recent compilation (2) cites solubility data for only 16 solvents, most data being taken at moderate temperatures and pressures. The present study was undertaken to investigate P–C–T relationships for solutions of CO in 1,4-dioxane, one of the solvents used in the slurried FT catalysis. A survey of the literature revealed no previous work on this system.

Experimental Section

Chemicals. Carbon monoxide (99.99+%) was supplied by the Matheson Co., Inc., and was used without any further compression and purification; 1,4-dioxane (spectrophotometric grade, 99+%) was purchased from the Aldrich Chemical Co. Prior to introduction into the autoclave, the liquid was degassed according to a procedure suggested by Battino et al. (3): the vigorously agitated liquid was subjected to a series of brief exposures to vacuum until all air was extracted as indicated on a vacuum gauge connected to the liquid container via a cryogenic trap.

Apparatus and Procedure. The solubility of CO in 1,4-dioxane was measured in a 2-L stainless-steel autoclave (Autoclave Engineers, Erie, PA, Model AFP-2005) equipped with (1)

a magnetically driven stirrer; (2) a pressure transducer (Validyne Engineering Corp., Northridge, CA, Model P-10, 1250 psi range), calibrated against a dead-weight standard; (3) a chromel–alumel thermocouple, calibrated against a platinum resistance thermometer; (4) inlets for the gas and liquid; and (5) a 0.062-in.-i.d. liquid-sampling tube that extended to a point located near the bottom of the autoclave. The autoclave was heated with a jacket-type furnace. Temperature of the liquid sample in the autoclave could be controlled to within ±0.5 °C.

Approximately 1 L of degassed 1,4-dioxane was introduced into the previously evacuated autoclave, which was then pressurized with CO and heated to the desired temperature. The mixture was equilibrated while a steady stirring rate of 250 rpm was maintained. The attainment of the equilibrium was judged to be complete when the pressure remained constant for a period of at least 1 h. The time to reach equilibrium ranged from 1 h at 173 °C to 10 h at 80 °C.

The saturated liquid was sampled by withdrawing a small quantity from the autoclave, via a metering valve, at the rate of ~8 mL min^{-1}. The initial portion of the sample (~6 mL) was always discarded by directing the liquid flow into a special container. The sample itself (8–12 mL) was collected in a previously evacuated buret system. Upon entering the burets, the gas flashed out of solution and produced two distinguishable phases, which were then compressed to atmospheric pressure, mercury being used as the leveling fluid. All gas–liquid–mercury interfaces were recorded with the aid of a cathetometer. The quantities of the separated gas and liquid phases were calculated from their respective volumes, buret-system temperature, barometric pressure, and density of 1,4-dioxane ($d_{20°C}$ = 1.0337 g cm^{-3} (4)). After the measurements, gas pressure in the autoclave was changed to a new value and the buret system was cleared in preparation for the next sampling.

The buret system used in the sample analysis was similar to one described by Wiebe et al. (5, 6). It comprised two calibrated, connected burets (50- and 100-mL capacity) enclosed in a thermostated water jacket. Gas volumes in the burets could be individually varied by controlling the mercury levels. Volume measurements were precise to within ±0.2 mL.

Stirring of the liquid during sampling was necessary to maintain a uniform temperature distribution. Samples taken at different stirring rates (250–500 rpm) showed no variation in the quantity of the dissolved CO. Slight reduction in the autoclave pressure caused by the sample removal was assumed to have no effect on the CO concentration because the response time of the solution toward changes in pressure was comparatively slow. For example, at 96 °C and 70-atm pressure, >2 h would have been required to compensate for a 1.5-atm pressure deficit encountered during a typical sampling operation.

The transducer used for measuring autoclave pressures was located outside the heated zone and was connected to the autoclave via a 30-in.-long, 0.062-in.-i.d. tube. Some question

[†] Present address: Amoco Chemicals Corp., Naperville, IL 60566.

Table I. Fugacity and Solubility of CO in 1,4-Dioxane at Experimental Temperatures (t) and Pressures (P)^a

P, atm	$f°_2$,^{b} atm	x_2	P, atm	$f°_2$,^{b} atm	x_2
		$t = 79.6$ °C; $P°_1 = 0.49$ atm			
7.20	6.71	0.004 18	39.76	39.41	0.023 87
14.04	13.56	0.008 43	46.62	46.33	0.027 61
23.61	23.16	0.014 28	54.11	53.91	0.032 16
25.33	24.89	0.015 55	60.97	60.87	0.035 49
30.57	30.15	0.018 36	68.82	68.86	0.041 02
32.48	32.08	0.019 71			
		$t = 96.5$ °C; $P°_1 = 0.86$ atm			
6.51	5.64	0.003 78	38.70	38.08	0.024 58
13.03	12.18	0.008 09	46.42	45.91	0.029 24
17.26	16.43	0.010 96	52.80	52.41	0.033 45
23.35	22.57	0.015 19	60.60	60.38	0.037 78
30.78	30.06	0.019 52	67.30	67.26	0.042 39
		$t = 113.7$ °C; $P°_1 = 1.44$ atm			
8.56	7.12	0.005 10	43.12	42.07	0.029 29
10.65	9.22	0.006 53	48.82	47.90	0.033 77
13.99	12.58	0.009 04	55.70	54.95	0.038 09
21.39	20.04	0.014 37	62.31	61.76	0.041 72
28.77	27.49	0.019 07	63.64	63.13	0.042 50
35.36	34.17	0.023 78			
		$t = 138.2$ °C; $P°_1 = 2.75$ atm			
11.24	8.49	0.006 72	41.94	39.64	0.030 29
13.72	10.99	0.008 65	49.33	47.22	0.036 12
21.72	19.07	0.014 70	56.35	54.46	0.041 01
27.62	25.04	0.019 23	63.02	61.36	0.045 97
34.78	32.31	0.025 02	70.20	68.84	0.051 05
		$t = 173.4$ °C; $P°_1 = 6.05$ atm			
13.69	7.65	0.006 99	41.94	36.31	0.031 91
20.65	14.67	0.013 18	48.66	43.22	0.038 43
27.71	21.81	0.019 18	55.64	50.42	0.043 67
34.93	29.14	0.025 59	63.30	58.38	0.050 39

^{a} $P°_1$ is calculated from the equation given in ref 7.
^{b} Calculated from eq 3.

might arise as to whether the pressures recorded by the transducer are representative of those found in the autoclave. This issue was resolved by extrapolating the isothermal total pressure vs. CO concentration data (shown in Table I) to zero CO content. Within the experimental error, in all cases, the resulting values were identical with the vapor pressures of 1,4-dioxane (7) at the same temperature thereby confirming the transducer readings. It is possible that the solvent had condensed in the transducer and in the narrow connecting tube and thus acted as a transmitting fluid for the autoclave pressure.

Results and Discussion

Results reported in this paper consist of 50 measurements of the solubility of CO in 1,4-dioxane carried out isothermally at five temperatures between 80 and 173 °C and for CO pressures up to 70 atm. The low temperature limit was dictated by the rapidly diminishing rates at which the equilibrium conditions in the autoclave could be established; below 80 °C the rates were deemed to be too slow. The high temperature limitation was necessary because of the high vapor pressure of 1,4-dioxane (>10 atm at >200 °C (7)) and increasing nonideality of 1,4-dioxane near its critical temperature ($t_c = 315$ °C (7)).

Solubility data are listed in Table I and are shown in Figure 1 as x_2 vs. P_2 isotherms. The data were fitted by the method of least squares to an equation of the form

$$x_2 = \alpha P_2 + \beta P_2^2 \qquad (1)$$

where x_2 is the mole fraction of CO dissolved in 1,4-dioxane, P_2 is the partial pressure of CO, and the parameters α and β are expressed as functions of temperature by $\alpha = 2.025 \times 10^{-3} - 0.4974T^{-1}$ atm^{-1} and $\beta = -2.574 \times 10^{-6} + (7.351 \times$
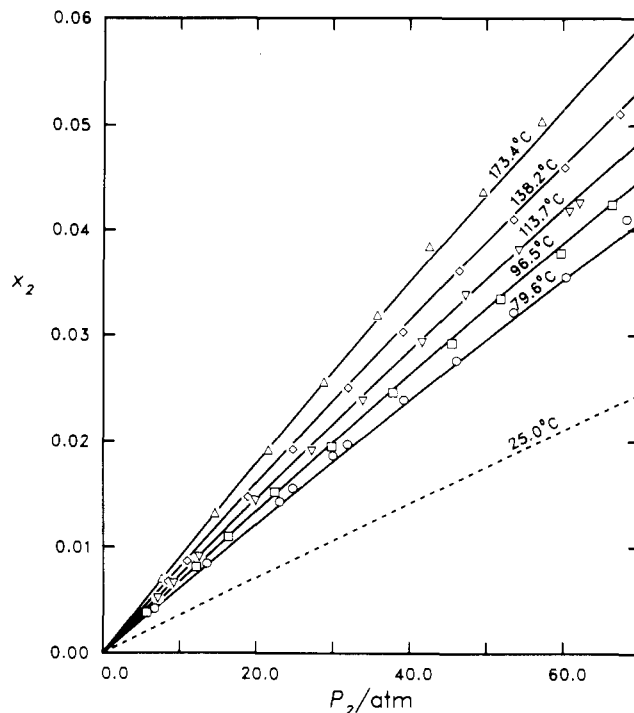

Figure 1. Isotherms representing the solubility of CO in 1,4-dioxane as a function of CO pressure. The lines were drawn according to eq 1.

$10^{-4})T^{-1}$ atm^{-2}. Isotherms calculated from eq 1 at the experimental temperatures are compared with the solubility data in Figure 1. The calculated isotherm at 25 °C is included for comparison.

Solubility results were analyzed in terms of the Krichevsky–Ilinskaya equation (8, 9), which relates the fugacity of the solute to temperature, pressure, and composition of solution, i.e.

$$\ln \frac{f_2}{x_2} = \ln H_{2,1} + \frac{A}{RT}(x_1^2 - 1) + \frac{\bar{V}_2^\infty (P - P°_1)}{RT} \qquad (2)$$

where subscript 1 refers to the solvent (1,4-dioxane), subscript 2 refers to the solute (CO), f_2 is the solute fugacity, x is the mole fraction in the liquid phase, $H_{2,1}$ is the isobaric Henry's law constant dependent on temperature only, A is an empirical coefficient, $\bar{V}_2^\infty$ is the partial molar volume of the dissolved gas at infinite dilution, P is the total pressure, $P°_1$ is the vapor pressure of the solvent, R is the gas constant, and T is the Kelvin temperature. The last two terms in eq 2 account for deviations from Henry's law due to concentration and pressure, respectively.

In eq 2, f_2 refers to the fugacity of the gas in coexistence with the solvent vapor. Since in this study gas-phase compositions were not determined, f_2 was approximated by $f°_2$, the fugacity of pure CO. This assumption can be justified in view of the relatively low 1,4-dioxane concentration in the vapor phase, especially at low temperatures and high CO pressures. The values of the fugacity coefficient, $f°_2/P_2$, were then determined as a function of P_2 ($=P - P°_1$) using the virial equation of state (10), i.e.

$$RT \ln \frac{f°_2}{P_2} = BP_2 + \frac{C - B^2}{2RT} P_2^2 \qquad (3)$$

where B and C are the second and third virial coefficients, respectively, whose values for CO were obtained by interpolation of compiled data (10) which, in turn, were based on a paper by Michels et al. (11). Virial coefficients for CO estimated in this manner could be represented by the following empirical equations: $B = -118.7 + 0.5266T - (5.261 \times$

$10^{-4})T^2$ cm^3 mol^{-1} and C = 4225 − 12.18T + (1.208 × $10^{-2})T^2$ cm^6 mol^{-2}. For the temperature and pressure ranges used in this study, the fugacity coefficients assume values greater than unity. Fugacities of CO calculated from eq 3 are listed in Table I.

Equation 2 contains three temperature-dependent parameters: $H_{2,1}$, which is expected to be an exponential function of $1/T$; A, which can be assumed to be constant over the narrow temperature range of this study; and $\bar{V}_2^{\infty}$, which is usually expressed as a linear function of T. Introduction of these assumptions yields an expanded form of eq 2 containing five terms and five empirical parameters. These parameters were then evaluated by collectively fitting the data of Table I to the expanded eq 2 by the method of least squares. Owing to an appreciable scatter of the data points, however, the parameter representing the constant term of $\bar{V}_2^{\infty}$ had a value only half of the van der Waals covolume for CO, the latter being a measure of the volume occupied by the CO molecules themselves. To correct this discrepancy, an alternative fitting procedure was adopted. The two parameters associated with $\bar{V}_2^{\infty}$ were independently evaluated according to a treatment used for hydrogen by Orentlicher and Prausnitz (12), i.e.

$$\bar{V}_2^{\infty} = b_2 + FRT/\delta_1^2 \tag{4}$$

where b_2 = 39.85 cm^3 mol^{-1} (4) is the van der Waals covolume for CO, δ_1^2 = 100.0 cal cm^{-3} (13) is the square of the solubility parameter representing the internal pressure of 1,4-dioxane, and F is an empirical factor introduced to match the values of $\bar{V}_2^{\infty}$ with those available in the literature. In deriving eq 4, carbon monoxide is assumed to behave like a rigid-sphere gas.

The factor F was calculated by substituting into eq 4 the value $\bar{V}_2^{\infty}$ = 52 cm^3 mol^{-1}, which has been estimated for CO at 25 °C by Gjaldbaek (14) on the basis of Horiuti's (15) dilatation experiments for solutions of CO in various solvents. The F value yielded by this approach for CO in 1,4-dioxane is 2.05, which compares with 2.2 reported for the solutions of hydrogen in normal hydrocarbons (12).

The remaining three parameters were then readjusted by using the same procedure to yield the following equation:

$$\ln \frac{f^{\circ}_2}{x_2} = 5.688 + \frac{594.6}{T} + \frac{211.2x_2(x_2 - 2)}{T} +$$
$$(4.963 × 10^{-4})P_2 + \frac{0.4856P_2}{T} \tag{5}$$

where the pressure dependence of x_2 can be calculated according to eq 1.

The plots generated by eq 5 are compared with the experimental data in Figure 2. Within the error limits, they can be represented by straight lines. The absence of curvature suggests (16) that the isobaric Henry's law is valid throughout the experimental temperature and pressure ranges and that the partial molar volume of CO is independent of pressure. The isobaric Henry's law constant, represented by the first two terms on the right-hand side of eq 5, makes by far the largest contribution. Thus, even at the highest CO pressure used in this study, these two terms still contribute >99% of the total value of ln (f°_2/x_2).

The partial molar entropy and enthalpy of CO at infinite dilution are given by $\Delta\bar{S}_2^{\infty}$ = −11.30 cal K^{-1} mol^{-1} and $\Delta\bar{H}_2^{\infty}$ = 1181 cal mol^{-1}. The values of $\bar{V}_2^{\infty}$, $H_{2,1}$, and A, calculated at the experimental temperatures and at 25 °C, are presented in Table II.

The Henry's law constant for solutions of CO in 1,4-dioxane at 25 °C ($H_{2,1}$ = 2170 atm) can be compared on the basis of the dielectric constant (ϵ = 2.21 for 1,4-dioxane) with those of other solvents for which CO solubility data at 25 °C are available (2): carbon tetrachloride ($H_{2,1}$ = 1141 atm, ϵ = 2.23),
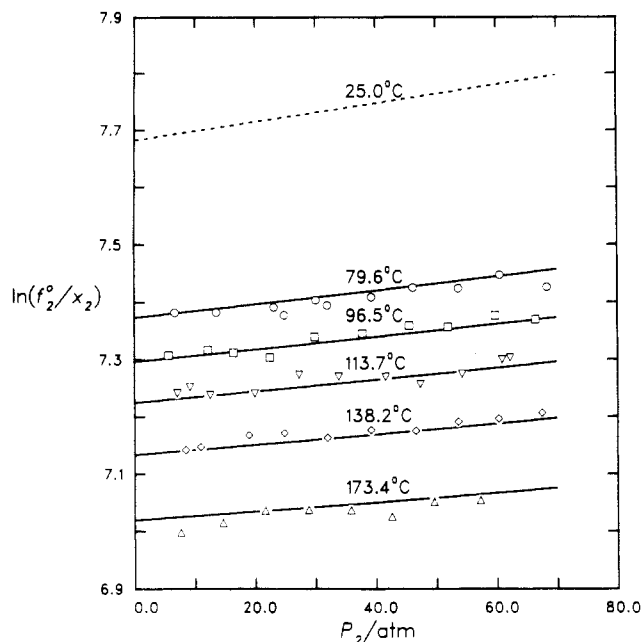

Figure 2. Variation of ln (f°_2/x_2) with P_2 in the system CO-1,4-dioxane. The lines were calculated by using eq 5.

Table II. Temperature Dependence of the Parameters $\bar{V}_2^{\infty}$, $H_{2,1}$, and A in the System CO-1,4-Dioxane

temp, °C	$\bar{V}_2^{\infty,a}$ cm^3 mol^{-1}	$H_{2,1},^b$ atm	A, L atm mol^{-1}
25.0	52.0	2170^c	17.33
79.6	54.2	1593	17.33
96.5	54.9	1475	17.33
113.7	55.6	1373	17.33
138.2	56.6	1253	17.33
173.4	58.0	1118	17.33

^{a} Calculated from eq 4: $V_2^{\times}$ = 39.85 + 0.04073T. ^{b} Calculated from ln $H_{2,1}$ = 5.688 + 594.6T^{-1}. ^{c} Extrapolated value.

toluene (1233, 2.44), benzene (1497, 2.27), chlorobenzene (1546, 2.23), ethanol (2065, 24.30), methanol (2659, 32.63), and nitrobenzene (2685, 24.30). The comparison shows that, on the basis of CO dissolution characteristics, 1,4-dioxane fits better with the polar solvents (e.g., ethanol) rather than the nonpolar solvents. Its low dielectric constant and the near-zero dipole moment, typical of nonpolar liquids, may be misleading because of the canceling effects of the two symmetrically placed oxygen atoms.

The $P-C-T$ relationships reported in this study can be helpful in evaluating the effects of suspending media on the hydrogen chain propagation in FT catalytic slurries, where large CO solubilities in the media are beneficial. In this respect, 1,4-dioxane compares favorably with the polar solvents under consideration in FT catalysis, e.g., ethanol, trifluoroethane, and dimethylformamide.

Acknowledgment

Literature Cited

(1) Haggin, J. Chem. Eng. News 1981, 59, 22–32.
(2) Wilhelm, E.; Battino, R. Chem. Rev. 1973, 73, 1–9.
(3) Battino, R.; Banzhof, M.; Bogan, M.; Wilhelm, E. Anal. Chem. 1971, 43, 806–7.
(4) Weast, R. C.; Astle, M. J. "Handbook of Chemistry and Physics", 63rd ed.; CRC Press: Boca Raton, FL, 1982.

(5) Wiebe, R.; Gaddy, V. L.; Heins, C. Ind. Eng. Chem. **1932**, 24, 823–5.
(6) Wiebe, R.; Gaddy, V. L.; Heins, C. J. Am. Chem. Soc. **1933**, 55, 947–53.
(7) Vinsor, C. G.; Martin, J. J. J. Chem. Eng. Data **1963**, 8, 74–5.
(8) Krichevsky, I. R.; Ilinskaya, A. Acta Physicochem. URSS **1945**, 20, 327–48.
(9) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(10) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Gases"; Clarendon Press: Oxford, 1969.
(11) Michels, A.; Lupton, J. M.; Wassenaar, T.; De Graaf, W. Physica **1952**, 18, 121–7.

(12) Orentlicher, M.; Prausnitz, J. M. Chem. Eng. Sci. **1964**, 19, 775–82.
(13) Hildebrand, J. H.; Scott, R. L. "Solubility of Non-Electrolytes"; Reinhold: New York, 1950.
(14) Gjaldbaek, J. C. Acta Chem. Scand. **1952**, 6, 623–33.
(15) Horiuti, J. Sci. Pap. Inst. Phys. Chem. Res. (Jpn.) **1931**, 17, 125–256.
(16) O'Sullivan, T. D.; Smith, N. O. J. Phys. Chem. **1970**, 74, 1460–6.

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

M. Cristina Annesini, Roberto De Santis,[†] Ireneo Kikic,[‡] and Luigi Marrelli*

Cattedra di Principi di Ingegneria Chimica, Università di Roma, 00184 Roma, Italy

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.

† Istituto di Chimica Applicata e Metallurgia, Università di Cagliari, Italy.
‡ Istituto di Chimica Applicata, Università di Trieste, Italy.

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