J. Chem. Eng. Data **2008,** *53,* 603–606 **603**

Phase Equilibria in Binary Mixtures of Water with Cyclic Alkylene Carbonates

Yury Chernyak*

Huntsman Corporation, 8600 Gosling Road, The Woodlands, Texas 77381

Vapor–liquid equilibrium (P,T,x) of water/ethylene carbonate was measured at T = (312.91 to 383.13) K by the ebulliometric method. Liquid–liquid equilibria of water/propylene carbonate and water/butylene carbonate systems were measured at atmospheric pressure and T = (280.65 to 293.15) K using analytical sampling techniques. The experimental results were correlated with a NRTL model.

Introduction

One of the primary industrial uses of cyclic alkylene carbonates is in cleaners and degreasers. Their advantage over traditional solvents is due to their low volatility, excellent compatibility, and solubility properties. The objective of this work was an experimental study of phase equilibria in binary systems of water with ethylene carbonate (EC, CAS No. 96-49-1), propylene carbonate (PC, CAS No. 108-32-7), and butylene carbonate (BC, CAS No. 4437-85-8). The water/EC system was completely miscible, while water/PC and water/BC exhibited partial immiscibility in the range of experimental parameters. No publicly available data on water/EC and water/BC phase equilibrium were found. Liquid–liquid equilibrium data on the water/PC system presented here and its corresponding thermodynamic model were found in good agreement with some LLE data, as well as with VLE and heat of mixing data reported in the literature.

Experimental Section

The samples of alkylene carbonates were obtained from Huntsman (JEFFSOL grade, Conroe, TX) and used without further purification. The purity was above 99.9 mass % for EC and PC and above 99.7 mass % for BC. More details on the samples' purity analysis are given in our earlier work.[1]

Experimental vapor–liquid equilibrium data (P,T,x) were developed using a Washburn-type ebulliometer. The apparatus and experimental procedure were described in detail elsewhere.[1] The experimental method was based on boiling temperature measurements of mixtures of known total composition at a preset pressure. The composition of a liquid phase, x, was assumed to be the same as a mixture's total composition. Measurements were performed at those composition ranges where the effect of liquid holdup in the vapor phase resulted in less than 0.1 % error of liquid phase composition. Temperature and pressure were measured with an accuracy of 0.025 K and 0.03 kPa, respectively. The overall uncertainty of the reported herein P,T,x data was estimated to be better than 2 % in the range from 1 to 10 kPa and 1 % at pressures over 10 kPa.

Table 1. Estimated Uncertainties of Liquid–Liquid Equilibrium Measurements

	($x_{1,\text{exptl}} - x_1$), mole fraction	
phase	water (1)/PC (2)	water (1)/BC (2)
Composition Analysis Technique: Density Measurements		
carbonate-rich	0.018	0.030
water-rich	0.003	0.001
Composition Analysis Technique: Karl Fischer Titration		
carbonate-rich	0.015	0.030
water-rich	0.0025	0.001

Table 2. Pure Components T_c, P_c, and Wagner Vapor Pressure Parameters[a]

parameter	EC	PC	BC	water
Critical Properties				
T_c/K	805.0	782.6	778.5	647.3
P_c/bar	61.4	50.7	44.4	221.1
Coefficients of Equation 2				
A	1.9256	−9.7095	−5.6078	−7.7760
B	−19.8576	5.1640	−4.8868	1.4788
C	21.4518	−7.1776	6.7442	−2.7877
D	−35.3071	0	−23.7328	−1.2492

[a] As reported earlier by Chernyak and Clements.[1]

Measurements of liquid–liquid equilibrium were performed in a 250 mL three-neck glass flask immersed in a thermostatted liquid bath and equipped with a mechanical stirrer. The two liquid phase system was agitated by the stirrer for approximately 2 h. Then, the system was allowed to equilibrate for another 16 h. Approximately 10 mL samples of each liquid phase were simultaneously withdrawn with the aid of a syringe and analyzed. Two different analytical techniques were utilized for the sample analysis. The main method of composition analysis employed in this study was based on the samples' density measurements using vibrating tube densimeter DMA4500 from Anton Paar GmbH. Karl Fischer titration for water was used as an additional analytical technique to ensure the absence of unexpected systematic errors in this work. During the course of a run, the temperature of the bath maintained constant to within 0.05 K. The temperature was measured with an accuracy of 0.1 K. The results on experimental uncertainty estimation for both methods are given in Table 1.

Data Reduction. The procedure of data reduction was based on the activity coefficient approach with the NRTL equation[2] representing the liquid phase and the ideal-gas equation of state representing the vapor phase.

The basic thermodynamic expression for vapor–liquid equilibrium calculations was

---

* To whom correspondence should be addressed. E-mail: yury_chernyak@huntsman.com.

10.1021/je700689w CCC: $40.75

$$y_iP = x_i\gamma_iP_i \tag{1}$$

where x_i and y_i are liquid and vapor mole fractions of the mixture component i; γ_i is the activity coefficient of the component i in the liquid phase; P is the total pressure; and P_i is the vapor pressure of the component i at the system temperature.

The vapor pressure of pure components was calculated from the Wagner equation

$$\ln(P/P_c) = (1/T_r)(A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^3 + D(1-T_r)^6) \tag{2}$$

where P is pressure; P_c is critical pressure; T_r is reduced temperature; $T_r = T/T_c$; T is temperature; T_c is critical temperature; and A, B, C, and D are coefficients.

The liquid phase activity coefficient, γ, was given by

$$\ln\gamma_1 = x_2^2\left[\frac{\tau_{21}G_{21}^2}{(x_1 + x_2G_{21})^2} + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{3}$$

$$\ln\gamma_2 = x_1^2\left[\frac{\tau_{12}G_{12}^2}{(x_2 + x_1G_{12})^2} + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$$

$$G_{12} = \exp(-\alpha\tau_{12})$$

$$G_{21} = \exp(-\alpha\tau_{21})$$

$$\tau_{12} = a_{12} + b_{12}/T$$

$$\tau_{21} = a_{21} + b_{21}/T$$

where α is the nonrandomness parameter and a_{21}, a_{21}, b_{12}, and b_{21} are parameters obtained by fitting experimental data using the minimization function, F, expressed by

$$F = \frac{1}{N}\sum_{k=1}^{N}\left(\frac{P_{k,\mathrm{exptl}} - P_{k,\mathrm{calcd}}}{P_{k,\mathrm{exptl}}}\right)^2 \tag{4}$$

where N is the number of data points and $P_{k,\mathrm{exptl}}$ and $P_{k,\mathrm{calcd}}$ are the experimental and calculated pressures.

The basic equation for liquid–liquid equilibrium calculations was

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta, \quad \sum x_i^\alpha = 1, \quad \sum x_i^\beta = 1 \tag{5}$$

where superscripts α and β correspond to separate liquid phases.

The selection of physically significant solutions of eq 5 was based on the procedure of Mettelin and Verhoeye.[3] The NRTL parameters τ_{12} and τ_{21} (eq 3) were calculated from experimental LLE data at each temperature and then correlated with temperature to develop parameters a_{21}, a_{21}, b_{12}, and b_{21}.

Results and Discussion

No measurements of pure component vapor pressures were performed in this work. Wagner vapor pressure parameters of carbonates were taken from our earlier work.[1] The summary on pure component parameters used in the reduction of phase equilibrium data is given in Table 2. The NRTL parameters for all five mixtures are summarized in Table 3.

Table 3. NRTL Equation Parameters

NRTL parameter/J·mol^{-1}	water/EC	water/PC	water/BC
a_{12}	1.6017	3.1815	4.9631
a_{21}	−4.0518	−3.5890	−2.3085
b_{12}	158.52	−87.12	−39.81
b_{21}	1602.50	1492.20	1037.63
α	0.47	0.40	0.30

Table 4. Results of Vapor–Liquid Equilibrium (*P*,*T*,*x*) Measurements for the Water (1)/Ethylene Carbonate (2) System

x_1	$y_{1,\mathrm{calcd}}$	T K	P_{exptl} kPa	P_{calcd} kPa	$(P_{\mathrm{exptl}} - P_{\mathrm{calcd}})$ kPa
0.400	0.9989	314.23	6.58	6.57	0.01
0.400	0.9986	319.95	8.73	8.74	−0.01
0.400	0.9984	325.63	11.43	11.45	−0.02
0.400	0.9979	333.13	16.16	16.05	0.11
0.400	0.9975	340.17	21.60	21.65	−0.05
0.400	0.9969	347.39	28.82	28.95	−0.13
0.400	0.9964	353.95	37.42	37.18	0.24
0.400	0.9959	360.15	46.75	46.58	0.17
0.400	0.9953	365.87	57.24	56.83	0.41
0.400	0.9947	372.15	70.03	70.03	0.00
0.400	0.9941	378.02	84.38	84.42	−0.04
0.400	0.9935	383.13	98.73	98.72	0.01
0.600	0.9991	312.99	6.61	6.63	−0.02
0.600	0.9989	318.53	8.85	8.83	0.02
0.600	0.9987	323.90	11.50	11.52	−0.02
0.600	0.9984	331.35	16.36	16.39	−0.04
0.600	0.9981	337.81	21.89	21.91	−0.02
0.600	0.9978	344.39	29.05	29.05	0.00
0.600	0.9975	350.47	37.28	37.26	0.02
0.600	0.9972	356.26	46.74	46.77	−0.03
0.600	0.9969	361.65	57.44	57.33	0.12
0.600	0.9965	367.27	70.14	70.32	−0.18
0.600	0.9962	372.69	85.13	85.01	0.12
0.600	0.9959	377.48	99.97	99.95	0.01
0.800	0.9992	312.91	6.74	6.74	0.00
0.800	0.9990	319.29	9.41	9.40	0.01
0.800	0.9988	324.66	12.30	12.29	0.02
0.800	0.9985	332.14	17.63	17.55	0.08
0.800	0.9983	338.09	23.11	23.00	0.11
0.800	0.9981	344.45	30.43	30.34	0.09
0.800	0.9978	351.27	40.39	40.31	0.08
0.800	0.9976	356.72	50.23	50.13	0.09
0.800	0.9974	361.61	60.72	60.56	0.15
0.800	0.9972	366.88	73.88	73.76	0.12
0.800	0.9970	372.12	89.27	89.16	0.11
0.800	0.9969	375.15	99.37	99.20	0.17

Table 5. Results of Liquid–Liquid Equilibrium Measurements for the Water (1)/Propylene Carbonate (2) System

	carbonate phase			water phase		
T/K	x_1^α	$x_{1,\mathrm{calcd}}^\alpha$	$x_1^\alpha - x_{1,\mathrm{calcd}}^\alpha$	x_1^β	$x_{1,\mathrm{calcd}}^\beta$	$x_1^\beta - x_{1,\mathrm{calcd}}^\beta$
Composition Analysis Technique: Density Measurements						
283.15	0.2426	0.2461	−0.0035	0.9575	0.9575	0.0000
288.15	0.2673	0.2700	−0.0027	0.9561	0.9575	−0.0014
293.15	0.2908	0.2930	−0.0022	0.9539	0.9574	−0.0035
Composition Analysis Technique: Karl Fischer Titration						
282.95	0.2530	0.2451	0.0079	0.9603	0.9575	0.0028
287.95	0.2680	0.2690	−0.0010	0.9591	0.9575	0.0016

Water/Ethylene Carbonate. *P*,*T*,*x* measurements of the water/EC system were performed from (312.91 to 383.13) K at liquid phase compositions 0.4, 0.6, and 0.8. Table 4 provides the results of *P*,*T*,*x* measurements for the water/EC system. Values of vapor mole fraction y_1 and pressures P_{calcd} in Table 4 were calculated from the NRTL model. The deviations of experimental data from the model, $(P_{\mathrm{exptl}} - P_{\mathrm{calcd}})$, did not exceed 0.4 kPa and were less than 0.15 kPa for the majority of data points.

Water/Propylene Carbonate. Table 5 presents liquid–liquid equilibrium results for the water/PC mixture at temperatures from (283.15 to 293.15) K and ambient pressure. The deviations of our experimental data from the NRTL model, $(x_1 - x_{1,\mathrm{calcd}})$, were less than 0.008 and 0.0035 water mole fraction for the PC-rich and water-rich phase, respectively. Water/PC LLE data from several literature sources[4–7] were plotted in Figure 1 for comparison with our experimental results. A good agreement between our data and data of Lam and Benoit,[5] Hong et al.,[6] and Rajapakse et at.[7] was observed. However, PC solubility

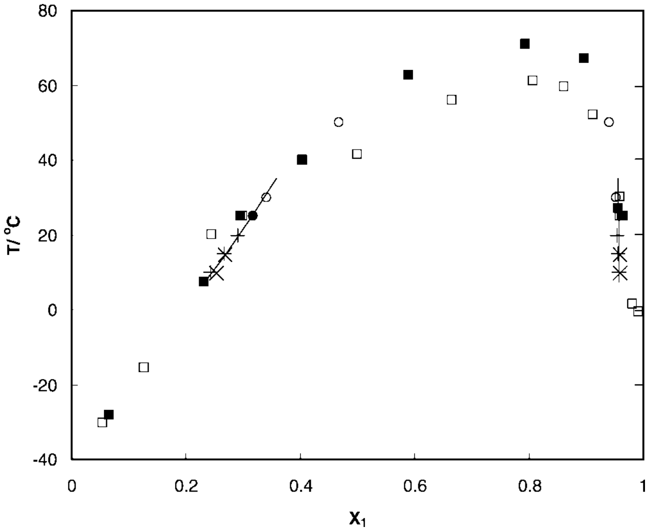

Figure 1. Water/propylene carbonate LLE data: +, ×, this work; ■, Catherall and Williamson;[4] •, Lam and Benoit;[5] □, Hong et al.;[6] ○, Rajapakse et al.;[7] —, calculated from the NRTL model.

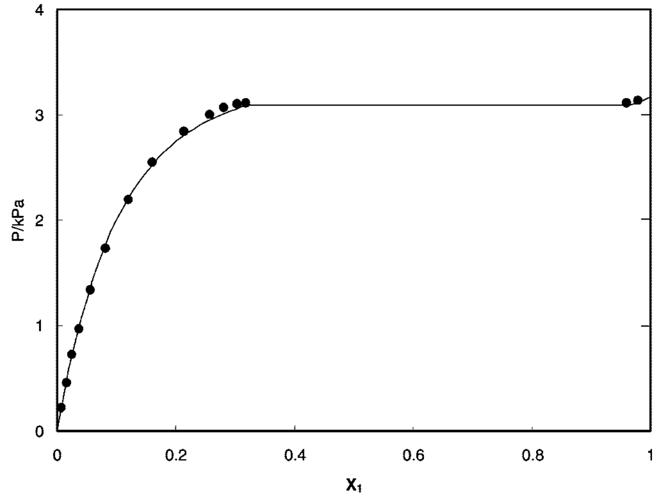

Figure 2. Water/propylene carbonate *Px* data at 25 °C: •, Lam and Benoit;[5] —, calculated from the NRTL model.

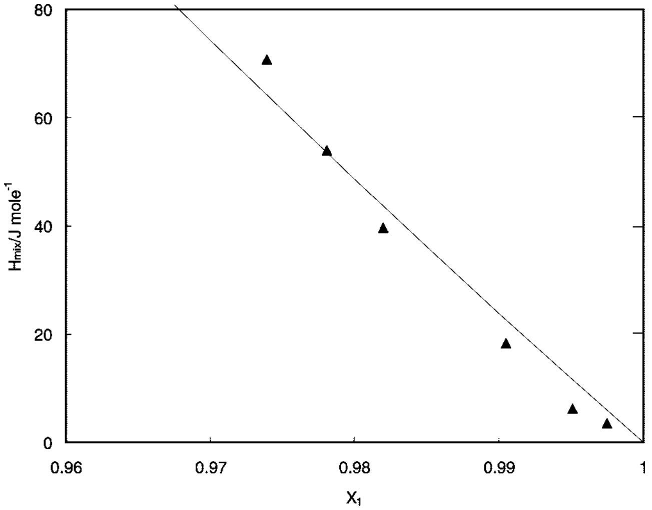

Figure 3. Water/propylene carbonate enthalpy of mixing data at 25 °C: ▲, Courtot-Coupez and L'Her;[8] —, calculated from the NRTL model.

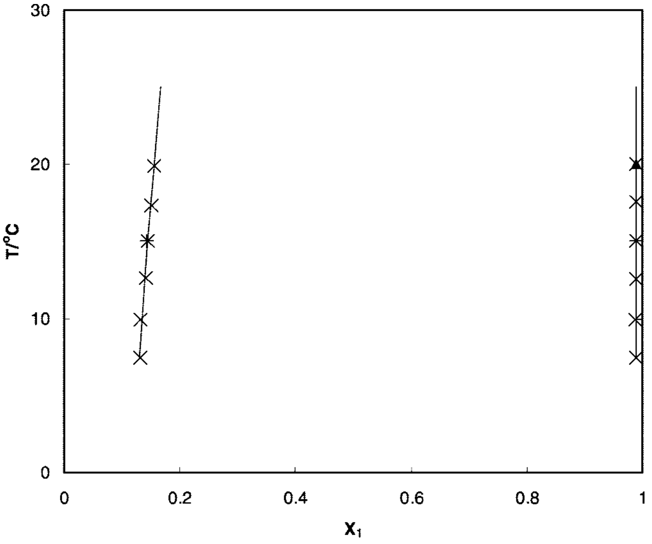

Figure 4. Water/butylene carbonate LLE data: +, ×, this work; ▲, Macdonald et al.;[9] —, calculated from the NRTL model.

Table 6. Results of Liquid–Liquid Equilibrium Measurements for the Water (1)/Butylene Carbonate (2) System

	carbonate phase			aqueous phase		
T/K	x_1^α	$x_{1,\mathrm{calcd}}^\alpha$	$x_1^\alpha - x_{1,\mathrm{calcd}}^\alpha$	x_1^β	$x_{1,\mathrm{calcd}}^\beta$	$x_1^\beta - x_{1,\mathrm{calcd}}^\beta$
Composition Analysis Technique: Density measurements						
280.60	0.1328	0.1300	0.0028	0.9896	0.9890	0.0006
283.05	0.1328	0.1348	−0.0020	-	0.9890	-
283.10	-	0.1350	-	0.9873	0.9890	−0.0017
285.70	-	0.1402	-	0.9887	0.9890	−0.0003
285.75	0.1418	0.1403	0.0015	-	0.9890	-
288.15	0.1448	0.1451	−0.0003	-	0.9890	-
288.20	-	0.1453	-	0.9893	0.9890	0.0003
290.45	0.1502	0.1499	0.0003	-	0.9890	-
290.70	-	0.1504	-	0.9892	0.9890	0.0002
293.05	0.1561	0.1553	0.0008	-	0.9890	-
293.20	-	0.1556	-	0.9891	0.9890	0.0001
Composition Analysis Technique: Karl Fischer Titration						
288.15	0.1433	0.1451	−0.0018	0.9885	0.9890	−0.0005

reported by Catherall and Williamson[4] at $T = 293.25$ K is significantly lower than our and literature[5–7] results. More experimental LLE data at temperatures over 303 K are needed as well to resolve a disagreement between literature data (Figure 1). The water/PC NRTL model also possesses good predictive capabilities of single-liquid phase regions. An excellent agreement between the NRTL predicted and experimental *P*,*T*,*x* data of Lam and Benoit[5] is demonstrated in Figure 2. The model provides correct enthalpy of mixing values as confirmed by comparison with experimental data of Courtot-Coupez and L'Her[8] (Figure 3).

Water/Butylene Carbonate. Experimental and calculated liquid–liquid equilibrium data for water/BC are presented in Table 6. Measurements were conducted from (280.65 to 293.15) K and at ambient pressure. Only one externally measured data point[9] on water solubility in BC was available for comparison with our experimental data. Figure 4 demonstrates good agreement between all experimental results and calculated LLE from the NRTL model. The deviations between experimental data and the model, $(x_1 - x_{1,\mathrm{calcd}})$, were less than 0.0015.

Literature Cited

(1) Chernyak, Y.; Clements, J. H. Vapor Pressure and Heat Capacity of Alkylene Carbonates. *J. Chem. Eng. Data* **2004**, *49*, 1180–1184.

(2) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

(3) Mettelin, A. C.; Verhoeye, L. A. J. The Correlation of Binary Miscibility Data by Means of the NRTL Equation. *Chem. Eng. Sci.* **1975**, *30*, 193–200.

(4) Catherall, N. F.; Williamson, A. G. Mutual Solubilities of Propylene Carbonate and Water. *J. Chem. Eng. Data* **1971**, *16*, 335–336.

(5) Lam, S. Y.; Benoit, R. L. Some thermodynamic properties of the dimethylsulfoxide-water and propylene carbonate -water systems at 25 °C. *Can. J. Chem.* **1974**, *52*, 718–722.

(6) Hong, C. S.; Waksiak, R.; Finston, H.; Fried, V. Some Thermodynamic Properties of Systems Containing Propylene Carbonate and Ethylene Carbonate. *J. Chem. Eng. Data* **1982**, *27*, 146–148.

(7) Rajapakse, N.; Finston, H. L.; Fried, V. Liquid-Liquid Phase Equilibria in the Propylene Carbonate + Methyl Isobutyl Ketone + Water System. *J. Chem. Eng. Data* **1986**, *31*, 408–410.

(8) Courtot-Coupez, J.; L'Her, M. Propertietes physiques des melanges eau-carbonate de propylene a 25 °C. Milieux riches en eau. *C. R. Acad. Sci. Paris* **1972**, *275*, 103–106.

(9) Macdonald, I. A.; Howes, D. A.; Betteley, J. The Determination of the Water Solubility of Butylene Carbonate. Huntington Research Centre Ltd., UK: Unpublished data, 1989.

Received for review November 21, 2007. Accepted December 24, 2007.

JE700689W