J. Chem. Eng. Data **1985**, *30*, 195-196

Liquid–Liquid Equilibria for Ternary Systems Containing Hydrocarbons and Propylene Carbonate

M. C. Annesini, F. Gironi, and L. Marrelli

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

I. Kikic*

Istituto di Chimica Applicata e Industriale Università di Trieste, 34127 Trieste, Italy

Experimental data of liquid–liquid equilibrium at 20 °C are reported for six ternary systems containing propylene carbonate with *n*-hexane–benzene, *n*-hexane–ethylbenzene, *n*-heptane–toluene, *n*-heptane–ethylbenzene, *n*-octane–*o*-xylene, and *n*-octane–ethylbenzene. The data are correlated by means of NRTL and UNIQUAC models and relative parameters are given.

Introduction

In the literature alkylene carbonates are indicated as good solvents for the separation of sour gases and for the recovery of some classes of hydrocarbon compounds (*1*, *2*). In spite of their physical properties and their potential application in industrial processes there are no extensive determinations of fluid-phase equilibrium data for systems containing propylene and ethylene carbonates. For these reasons we developed a research program dealing with measurements of vapor–liquid and liquid–liquid equilibria in systems containing propylene carbonate (PPC). Recently vapor–liquid equilibrium data for some binary systems of aromatic hydrocarbon–propylene carbonate were published (*3*). In this paper we report liquid–liquid equilibria for ternary systems paraffin–aromatic hydrocarbon–propylene carbonate at 20 °C.

Experimental Section

The glass equilibrium cells employed were the same as reported by Kikic et al. (*4*). The ternary mixtures were equilibrated at the specified temperatures ±0.1 °C (water bath) by agitation with a magnetic stirrer for at least 2 h, followed by a settling period of 20 h. For each phase three samples were withdrawn for GLC analysis by means of a syringe: selective holdup in the syringe was negligible. Particular attention was payed to the sampling operations: the syringe was heated to the same temperature of the equilibrium cells. The mixtures were analyzed by a thermal conductivity gas chromatograph (C. Erba Model ATc/t) equipped with a Shimadzu Cromatopac E-1A integrator and using a 2-m column packed with Chromosorb W DMCS 100/120 mesh coated with SE 30.

The chromatographic factors have been determined from mixtures of known composition analyzed by GLC. The expected error on the mole fraction is 0.002.

The chemicals were Fluka products and were used as purchased. The purity of the propylene carbonate was 99.5%; that of the hydrocarbons was 99.8%.

Results

The ternary systems studied were the following: *n*-hexane–benzene–propylene carbonate, *n*-hexane–ethylbenzene–propylene carbonate, *n*-heptane–toluene–propylene carbonate, *n*-heptane–ethylbenzene–propylene carbonate, *n*-octane–ethylbenzene–propylene carbonate, and *n*-octane–*o*-xylene–propylene carbonate. All the ternary equilibria were studied at 20 °C and for each system experimental measurements of conjugated phases were carried out. The results obtained are

Table I. Experimental Tie Lines (mol %) for the System Propylene Carbonate–Benzene–*n*-Hexane at 20 °C

propylene carbonate		benzene	
phase 1	phase 2	phase 1	phase 2
79.59	0.83	16.02	16.21
78.76	1.82	16.84	27.01
70.83	2.05	26.01	36.80
61.56	2.42	31.75	44.20
58.95	2.56	33.78	45.16

Table II. Experimental Tie Lines (mol %) for the System Propylene Carbonate–Ethylbenzene–*n*-Hexane

propylene carbonate		ethylbenzene	
phase 1	phase 2	phase 1	phase 2
87.01	1.00	7.30	24.64
85.11	1.37	8.26	30.12
78.85	2.45	14.55	40.88
76.62	3.66	17.10	47.68
73.18	5.88	20.67	55.03
51.30	17.43	39.64	59.65

Table III. Experimental Tie Lines (mol %) for the System Propylene Carbonate–Toluene–*n*-Heptane at 20 °C

propylene carbonate		toluene	
phase 1	phase 2	phase 1	phase 2
89.01	0.34	9.22	24.18
86.84	0.59	10.86	26.38
79.90	3.26	18.30	43.36
74.85	4.03	22.21	46.50
70.00	4.55	26.44	51.62

Table IV. Experimental Tie Lines (mol %) for the System Propylene Carbonate–Ethylbenzene–*n*-Heptane

propylene carbonate		ethylbenzene	
phase I	phase II	phase I	phase II
90.29	1.40	6.65	26.04
91.76	1.65	7.72	29.75
86.48	2.43	11.09	35.98
84.80	3.01	12.67	39.90
83.09	4.76	14.28	45.34
78.47	8.27	19.45	54.99

Table V. Experimental Tie Lines (mol %) for the System Propylene Carbonate–*o*-Xylene–*n*-Octane

propylene carbonate		*o*-xylene	
phase I	phase II	phase I	phase II
90.73	0.85	7.88	28.87
86.89	1.58	11.27	32.61
80.53	2.77	17.78	53.64
79.90	3.50	18.10	54.12
75.51	5.14	22.28	60.37
52.04	18.16	43.04	66.46

0021-9568/85/1730-0195$01.50/0

Table VI. Experimental Tie Lines (mol %) for the System Propylene Carbonate–Ethylbenzene–*n*-Octane at 20 °C

propylene carbonate		ethylbenzene	
phase I	phase II	phase I	phase II
87.03	3.01	9.54	25.30
85.56	3.28	10.84	28.44
79.77	4.15	16.78	43.90
71.60	5.11	23.62	54.74
48.76	13.47	42.81	66.67

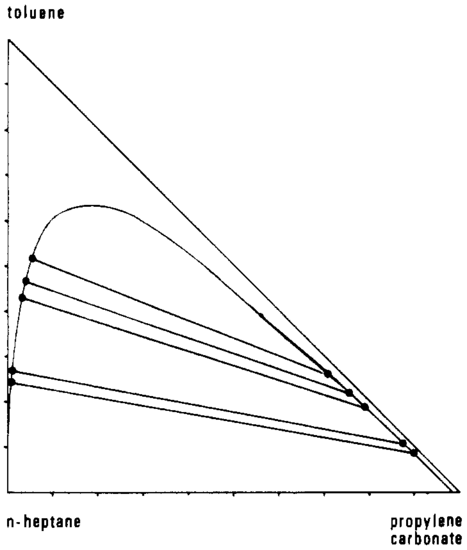

Figure 1. Experimental tie lines at 20 °C for the system *n*-heptane–toluene–propylene carbonate.

Table VII. NRTL Parameters (K) for the Binaries Investigated

binary	A_{ij}	A_{ji}
PPC–*n*-hexane	492.90	2039.8
PPC–*n*-heptane	823.39	1342.1
PPC–*n*-octane	604.34	957.04
PPC–benzene	−1748.8	418.46
PPC–toluene	−37.478	530.03
PPC–ethylbenzene	81.244	548.94
PPC–*o*-xylene	38.836	725.61
n-hexane–benzene	−2054.1	495.26
n-hexane–ethylbenzene	872.45	−529.00
n-heptane–toluene	217.93	−200.36
n-heptane–ethylbenzene	778.30	−470.30
n-octane–ethylbenzene	−261.81	551.35
n-octane–*o*-xylene	−463.32	848.27

Table VIII. UNIQUAC Parameters (K) for the Binaries Investigated

binary	A_{ij}	A_{ji}
PPC–*n*-hexane	−26.165	910.35
PPC–*n*-heptane	38.453	454.01
PPC–*n*-octane	−1.5720	477.60
PPC–benzene	−147.35	80.623
PPC–toluene	−37.368	152.61
PPC–ethylbenzene	−19.261	184.92
PPC–*o*-xylene	270.09	−61.889
n-hexane–benzene	−140.13	−47.362
n-hexane–ethylbenzene	394.84	−222.69
n-heptane–toluene	−108.57	95.497
n-heptane–ethylbenzene	−219.17	337.54
n-octane–ethylbenzene	−42.191	82.063
n-octane–*o*-xylene	−56.452	65.530

Table IX. Rms Values Obtained with the NRTL and UNIQUAC Models

	rms	
system	NRTL	UNIQUAC
PPC–benzene–*n*-hexane	0.6594	0.7409
PPC–ethylbenzene–*n*-hexane	0.5147	0.6681
PPC–toluene–*n*-heptane	0.5838	0.6423
PPC–ethylbenzene–*n*-heptane	0.6520	0.7253
PPC–ethylbenzene–*n*-octane	0.6322	0.7315
PPC–*o*-xylene–*n*-octane	0.6825	0.6112

reported in Tables I–VI whereas Figure 1 shows, as an example, the data for the system *n*-heptane–toluene–propylene carbonate. For all the ternary systems a type 1 isotherm is observed since propylene carbonate is completely miscible with aromatic hydrocarbons.

The experimental data were correlated by means of NRTL (*5*) and UNIQUAC (*6*) models. When the NRTL model was used, the parameter α was fixed at the value 0.2. For the UNIQUAC model the r and q values for propylene carbonate were calculated starting from Bondi values (*7*) taking into account the molecular structure of the compound; in particular the numerical values used are the following: $r = 3.5843$, $q = 3.178$. A computer program developed by Sorensen et al. (*8*) was used in the data reduction with the objective function defined in terms of concentrations.

In order to obtain the same numerical values for the parameters of the binary systems which are present in the different ternary systems the experimental data are fitted all together. The values of the parameters obtained from the fitting with the NRTL and UNIQUAC models are reported in Tables VII and VIII, respectively. The results of the fitting are compared on the basis of the root mean square (rms) defined as

$$\mathrm{rms} = 100\Big[\sum_k \min_{\overrightarrow{i\ j}} (x_{ijk}(\mathrm{exptl}) - x_{ijk}(\mathrm{calcd}))^2/6M\Big]^{1/2}$$

$i = 1, 2, 3$; $j = \mathrm{I}, \mathrm{II}$; $k = 1, ..., M$ (n tie lines); which takes into account both the shape of the binodal curve and the slope of the tie lines. In Table IX rms values are reported. Generally the NRTL equation gives rms values slightly lower than those of the UNIQUAC equation but the difference is not significant. The correlation of the experimental data by means of the NRTL equation with $\alpha = 0.3$ gave results very much like the ones obtained with $\alpha = 0.2$ and previously reported. An analysis on artificial systems (*9*) leads to the conclusion that an rms = 0.8 corresponds to an uncertainty in the mole fraction of 0.016 that is the expected error of the experimental determinations.

Registry No. PC, 108-32-7; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; *o*-xylene, 95-47-6.

Literature Cited

(1) Kohl, A. L.; Buckingham, P. A. *Pet. Refiner* **1960**, *39*, 193.
(2) Koppers, G. British Patent 1 138 004, 1968.
(3) Annesini, M. C.; De Santis, R.; Kikic, I.; Marrelli, L. *J. Chem. Eng. Data* **1984**, *29*, 39.
(4) Kikic, I.; Alessi, P.; Lapasin, R. *Chem. Eng. J.* **1979**, *18*, 39.
(5) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(6) Abrams, D.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(7) Bondi, A. "Physical Properties of Molecular Crystals, Liquids, and Glasses"; Wiley: New York, 1968.
(8) Sorensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *3*, 47.
(9) Kikic, I.; Alessi, P.; Lapasin, R.; Fermeglia, M. "Proceedings of the ISEC Conference, Denver, Sept 1983"; AIChE: Denver, CO, 1983; p 544.

Received for review April 4, 1984. Accepted August 13, 1984. We thank Ministero della Pubblica Istruzione (Italy) for financial support.