Liquid−Liquid Equilibria of Systems Containing Propylene Carbonate and Some Hydrocarbons

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Liquid−liquid equilibria for the ternary systems (octane + toluene + propylene carbonate), (2,2,4-trimethylpentane + ethylbenzene + propylene carbonate), (methylcyclohexane + benzene + propylene carbonate), and (1-decene + toluene + propylene carbonate) were studied over a temperature range of 293 K to 348 K. The results were used to estimate the interaction parameters between each of the three compounds present in each system for the NRTL and the UNIQUAC equations and between each of the main groups of hydrocarbons (CH_2, C═C, ACH, and $ACCH_2$) and propylene carbonate for the UNIFAC model as a function of temperature. The UNIQUAC and NRTL equations fit the experimental data with a root-mean-square deviation (rmsd) of 1.3%, while the UNIFAC model predicted the results with a rmsd of 8%. Among the three methods NRTL and UNIQUAC gave the best fit.

Introduction

A recent interest has focused on propylene carbonate as a low-cost solvent for aromatics extraction. Salem (1993) and Salem et al. (1994) have studied systems containing hydrocarbons with triethylene glycol and propylene carbonate at 25 °C. Kikic et al. (1985) studied some ternary systems containing propylene carbonate at 20 °C. Fried et al. (1986) studied the phase equilibria of propylene carbonate with methyl isobutyl ketone + water. Excess free energy equations, such as the nonrandom, two-liquid equation (NRTL) (Renon and Prausnitz, 1968) and the universal quasi-chemical equation (UNIQUAC) (Abrahams and Prausnitz, 1975) have been successfully applied for the correlation of several liquid−liquid systems. The experimental data were regressed to obtain numerical values for the interaction parameters of these equations at different temperatures. Experimental data have also been used to determine the interaction parameters of the universal function-group activity coefficients model (UNIFAC) (Fredenslund and Prausnitz, 1975). This model is particularly useful in predicting phase behavior for different conditions.

The objective of this work is to study the liquid−liquid phase equilibria of the ternary systems (octane + toluene + propylene carbonate), (2,2,4-trimethylpentane + ethylbenzene + propylene carbonate), (methylcyclohexane + benzene + propylene carbonate), and (1-decene + toluene + propylene carbonate) at several temperatures (293 K to 348 K). The experimental tie lines are correlated in terms of the NRTL and UNIQUAC equations. The UNIFAC predictive model was also tested.

Experimental Section

Chemicals. All the chemicals used in this study were supplied from Fluka and used without further purification. Their purities were determined by GC and are shown in Table 1.

Table 1. Purity of Chemicals Used in This Study (As Determined by GC)

chemical	purity (%)
octane	99.5
2,2,4-trimethylpentane	99.5
1-decene	98.5
methylcyclohexane	99.0
benzene	99.5
toluene	99.4
ethylbenzene	99.0
propylene carbonate	99.3

Table 2. The R_i/r_i and Q_i/q_i Values for the Groups/Components Present in the System

UNIFAC Model

group	R_i	Q_i
propylene carbonate	3.2815	2.736
CH_3	0.9011	0.848
CH_2	0.6744	0.540
CH	0.4469	0.228
C	0.2195	0.000
CH_2═CH	1.3454	1.176
ACH	0.5313	0.400
$ACCH_2$	1.0396	0.660
$ACCH_3$	1.2663	0.968

UNIQUAC Model

component	r_i	q_i
1-decene	6.9673	5.804
toluene	3.9228	2.968
octane	5.8486	4.936
methylcyclohexane	4.7200	3.776
benzene	3.1878	2.400
isooctane	5.8463	5.008
ethylbenzene	4.5972	3.508
propylene carbonate	3.2815	2.736

Apparatus and Procedure. The experimental apparatus used for extraction consists of a 85 cm^3 glass cell with a water jacket in order to maintain a constant temperature. The temperature was controlled within ±0.2 K. The cell was connected to a Haake K15 water bath fitted with a Haake DC1 thermostat. Mixtures, comprised of 7.5 g to 10 g of the paraffinic component, 13.5 g to 18 g of propylene carbonate, and up to 7 g of the aromatic component, were placed in the extraction vessel, stirred for 1 h, and then left to settle for 24 h. Samples were taken by a syringe from both the upper and lower layers. A series

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Table 3. Comparing Experimental and Predicted LLE Data for the Ternary System Methylcyclohexane (1) + Benzene (2) + Propylene Carbonate (3)

raffinate phase								extract phase							
$100x_1$				$100x_2$				$100x_1$				$100x_2$			
exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL
$T = 293.15$ K															
45.04	38.61	45.25	45.22	50.03	56.57	49.90	49.93	10.51	9.96	10.39	10.29	41.87	30.89	42.13	42.17
57.91	52.61	56.82	56.81	39.88	43.78	40.69	40.62	9.15	11.02	8.25	8.26	32.79	23.04	32.35	32.35
56.56	52.42	57.34	57.32	41.04	43.96	40.25	40.19	7.74	11.01	8.17	8.19	31.39	23.14	31.92	31.92
64.85	61.29	64.79	64.76	33.70	35.64	33.68	33.60	6.74	11.50	7.23	7.28	26.12	18.50	25.80	25.78
82.36	81.28	82.51	82.43	17.08	16.55	17.06	17.02	5.07	12.28	5.68	5.72	12.36	8.45	12.13	12.07
99.78	98.33	99.75	99.69	0.00	0.00	0.17	0.16	5.19	12.72	4.71	4.69	0.00	0.00	0.12	0.10
rms %	4.13	0.56	0.55		3.43	0.47	0.47		4.93	0.56	0.58		7.71	0.34	0.36
$T = 313.15$ K															
39.56	43.5	40.09	40.17	49.59	39.78	49.97	50.08	13.665	20.91	16.253	16.16	43.53	36.25	42.14	42.29
53.74	49.10	51.75	51.72	39.99	38.1	42.24	42.24	17.224	16.50	14.158	14.20	35.40	32.42	34.813	34.75
55.44	54.48	57.07	57	39.7	35.84	38.12	38.12	9.6139	13.02	13.407	13.50	31.85	28.09	31.519	31.42
63.6	57.97	63.43	63.36	33.43	34.08	32.87	32.84	15.052	11.180	12.595	12.72	25.82	25.17	27.51	27.39
82.23	76.31	81.74	81.77	16.51	21.60	16.53	16.39	12.464	5.5746	10.511	10.62	14.00	11.58	14.84	14.88
99.33	99.98	99.19	99.11	0	0	0	0.00	7.5579	3.0037	8.6895	8.55	0.00	0.00	0.00	0.00
rms %	4.19	1.09	1.10		4.85	1.16	1.17		4.96	2.63	2.59		3.70	0.99	0.95
$T = 333.15$ K															
12.13	29.00	16.07	23.50	44.75	44.28	46.17	43.28	13.17	25.32	15.18	22.04	46.83	43.28	51.26	41.00
54.22	45.34	50.00	52.67	38.45	36.80	39.29	37.24	26.64	17.90	18.66	19.94	32.17	32.25	30.19	32.57
53.78	48.75	52.08	53.94	39.63	34.44	37.92	36.44	20.18	16.94	18.47	19.84	30.07	29.85	29.38	32.32
60.41	54.81	59.02	62.01	32.88	29.99	32.96	30.81	15.93	15.45	17.75	18.71	28.74	25.64	26.11	29.13
80.71	74.91	80.19	82.22	16.19	13.89	15.45	14.26	16.17	11.60	15.60	15.45	12.19	11.86	12.52	14.35
97.91	91.15	97.24	97.90	0.00	0.00	0.00	0.09	14.04	9.17	14.38	13.81	0.00	0.00	0.00	0.09
rms %	9.12	2.55	4.77		2.69	1.02	1.91		6.82	3.52	4.69		1.93	2.27	2.71
$T = 348.15$ K															
33.25	43.00	46.50	44.50	33.61	31.06	35.91	35.99	50.09	41.00	43.96	43.50	37.17	31.57	36.78	36.15
57.53	58.57	61.44	60.57	36.38	24.19	27.16	28.80	23.11	27.98	31.00	31.61	35.51	31.18	32.28	31.48
71.03	65.53	67.78	68.50	15.51	19.96	22.59	23.39	24.48	23.30	27.95	28.46	32.63	28.55	26.65	25.95
62.65	65.34	67.92	67.91	31.74	20.08	22.48	23.82	21.20	23.42	27.89	28.66	26.65	28.64	26.52	26.39
79.60	74.06	77.44	78.80	14.26	14.10	15.01	15.41	31.93	18.30	25.13	25.87	14.30	23.02	17.34	17.34
95.69	92.16	93.30	94.98	0.00	0.00	1.51	1.57	28.74	9.80	22.64	23.76	0.00	0.00	1.69	1.80
rms %	5.43	6.32	5.34		7.20	6.18	5.65		10.47	6.33	6.44		4.95	3.12	3.52

Table 4. Comparing Experimental and Predicted LLE Data for the Ternary System Octane (1) + Toluene (2) + Propylene Carbonate (3)

raffinate phase								extract phase							
$100x_1$				$100x_2$				$100x_1$				$100x_2$			
exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL
$T = 293.15$ K															
28.79	34.60	29.75	29.72	61.50	51.76	61.49	61.53	5.00	5.24	4.75	4.75	45.52	43.41	46.25	46.23
38.65	33.45	37.83	37.83	55.62	52.91	55.73	55.73	3.28	5.16	3.65	3.68	38.87	38.16	38.14	38.11
52.29	40.05	51.44	51.45	44.70	46.70	44.37	44.35	2.42	4.42	2.57	2.62	26.79	19.17	26.28	26.27
66.96	58.83	67.27	67.27	30.33	28.22	29.96	29.93	2.20	3.63	1.88	1.92	14.47	6.70	15.16	15.16
97.40	86.65	97.99	97.96	0.00	0.00	0.55	0.52	1.42	2.94	1.25	1.25	0.00	0.00	0.21	0.20
rms %	8.86	0.74	0.73		4.70	0.33	0.34		1.55	0.27	0.27		4.97	0.61	0.61
$T = 313.15$ K															
22.90	18.16	22.52	22.48	57.82	59.36	59.39	59.45	6.84	9.61	7.33	7.36	48.37	45.22	48.25	48.21
36.99	24.24	36.18	36.20	54.63	55.78	53.82	53.80	3.86	7.76	4.62	4.68	39.32	32.68	38.17	38.16
52.59	36.50	52.84	52.86	43.26	46.62	41.94	41.89	2.81	5.35	3.00	3.06	26.89	15.37	27.62	27.62
66.44	58.11	66.33	66.30	30.55	28.27	30.54	30.53	2.32	3.85	2.19	2.23	19.59	4.43	19.57	19.53
81.39	75.72	80.92	80.88	17.06	12.45	17.28	17.30	2.07	3.42	1.56	1.59	11.21	1.37	10.92	10.86
96.03	89.25	97.71	97.70	0.00	0.00	1.36	1.37	1.94	3.21	1.04	1.06	0.00	0.00	0.86	0.85
rms %	9.93	0.81	0.81		2.63	1.06	1.09		2.42	0.57	0.58		9.25	0.67	0.68
$T = 333.15$ K															
21.80	28.50	20.77	20.76	53.31	38.03	55.35	55.37	7.17	17.97	7.82	7.83	45.28	33.13	44.81	44.80
35.78	34.91	35.71	35.70	52.15	37.45	50.91	50.91	5.21	13.82	5.55	5.58	38.32	27.50	38.00	37.98
53.26	45.27	52.96	52.95	40.89	33.66	39.59	39.57	2.92	9.26	3.46	3.50	27.38	17.22	27.26	27.24
65.27	57.05	65.38	65.38	29.63	26.83	29.63	29.62	2.42	6.35	2.50	2.54	19.23	8.36	19.28	19.26
79.42	75.07	79.46	79.46	16.67	13.46	17.37	17.36	2.22	4.39	1.78	1.83	10.82	2.22	10.64	10.62
96.58	91.00	97.42	97.44	0.00	0.00	0.81	0.81	1.79	3.60	1.21	1.25	0.00	0.00	0.47	0.46
rms %	6.15	0.56	0.57		9.31	1.19	1.20		6.51	0.48	0.48		9.66	0.31	0.32
$T = 348.15$ K															
39.40	51.81	39.45	39.46	46.40	38.15	47.47	47.51	4.87	9.64	5.48	5.52	34.09	53.01	33.57	33.54
57.32	70.95	56.62	56.63	36.62	23.86	35.46	35.46	3.40	4.07	3.75	3.79	24.71	47.09	24.31	24.30
56.39	71.51	56.84	56.85	35.39	23.41	35.29	35.28	3.57	3.96	3.73	3.77	23.77	46.85	24.19	24.18
67.85	85.99	67.65	67.63	26.95	11.28	26.47	26.46	3.00	1.47	2.93	2.96	18.07	38.71	18.19	18.16
85.38	92.72	84.91	84.87	10.90	0.00	11.30	11.31	2.31	0.00	1.93	1.95	8.34	8.20	7.91	7.86
95.58	84.98	96.34	96.33	0.00	0.00	0.79	0.78	2.28	0.00	1.42	1.44	0.00	0.00	0.56	0.55
rms %	13.31	0.51	0.51		11.10	0.77	0.78		2.46	0.48	0.49		17.40	0.43	0.44

Table 5. Comparing Experimental and Predicted LLE Data for the Ternary System 1-Decene (1) + Toluene (2) + Propylene Carbonate (3)

raffinate phase								extract phase							
$100x_1$				$100x_2$				$100x_1$				$100x_2$			
exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL
T = 293.15 K															
23.67	22.94	23.71	23.74	65.37	65.19	65.93	65.98	4.30	0.00	3.57	3.08	34.24	0.76	34.64	34.90
36.10	33.43	35.67	35.61	58.49	55.80	57.83	57.76	3.70	0.00	3.48	3.01	33.75	0.66	33.80	34.01
46.51	43.50	46.24	46.48	49.63	46.52	48.96	48.64	3.00	0.00	2.90	2.64	24.77	0.56	24.95	25.41
61.29	58.24	60.87	60.80	35.76	32.64	35.66	35.62	2.30	0.00	2.46	2.41	15.92	0.39	15.52	15.54
76.65	74.17	77.07	76.88	19.95	17.39	20.30	20.36	1.79	0.00	2.17	2.35	7.70	0.21	7.63	7.26
96.61	92.12	97.41	97.35	0.00	0.00	0.57	0.46	1.53	0.00	1.96	2.41	0.00	0.00	0.19	0.13
rms %	2.95	0.46	0.43		2.35	0.53	0.62		2.94	0.40	0.73		22.73	0.26	0.46
T = 313.15 K															
32.79	88.59	33.39	33.30	54.36	9.98	53.05	53.92	9.74	0.04	9.65	10.66	40.50	42.63	40.92	40.21
44.88	88.38	44.21	44.22	46.32	10.21	47.20	47.37	8.83	0.05	7.22	8.22	30.98	35.42	31.38	30.70
61.54	89.08	61.97	61.87	33.64	9.48	33.85	33.59	6.25	0.06	5.24	5.56	16.98	23.94	17.82	17.70
78.97	91.41	78.99	78.67	19.28	7.08	18.97	18.79	3.37	0.07	4.35	3.95	8.22	13.93	7.94	7.95
99.03	98.35	99.22	98.78	0.00	0.00	0.00	0.00	2.94	0.08	3.87	2.90	0.00	0.00	0.00	0.00
rms %	34.41	0.45	0.44		28.31	0.73	0.55		6.76	1.04	0.64		4.59	0.47	0.39
T = 333.15 K															
31.76	84.05	33.85	33.40	50.44	14.01	48.69	49.86	11.21	0.10	13.57	13.53	39.66	40.62	39.03	39.17
42.74	83.14	41.14	41.33	43.65	14.93	45.23	44.81	14.66	0.06	10.87	11.54	31.15	33.36	32.61	32.11
62.32	79.82	61.36	61.25	30.63	18.19	30.28	29.63	9.20	0.01	7.02	7.61	16.64	17.16	17.38	17.25
76.45	77.78	76.90	76.79	17.38	20.15	16.60	16.62	4.31	0.00	5.62	5.53	8.10	10.45	8.35	8.12
93.66	98.66	94.59	94.81	0.00	0.00	0.15	0.77	3.13	0.00	4.68	4.06	0.00	0.00	0.07	0.30
rms %	30.66	1.34	1.21		21.51	1.12	0.88		9.48	2.40	2.00		1.52	0.79	0.57
T = 348.15 K															
63.25	59.50	67.02	66.97	27.46	18.53	24.82	24.02	6.68	2.02	11.38	11.95	14.36	35.36	15.10	13.72
31.69	28.28	38.28	38.26	47.58	42.25	44.78	47.71	15.61	7.61	21.29	21.18	40.76	45.20	40.09	40.67
48.11	38.50	42.98	43.60	43.49	35.78	42.59	42.70	25.58	4.49	18.73	20.44	33.51	41.71	35.92	34.97
63.75	58.07	58.78	58.25	27.28	19.90	31.67	30.88	21.69	2.06	13.11	15.19	20.03	35.54	21.47	21.04
78.21	62.90	78.75	77.75	15.58	14.91	14.43	15.34	7.29	2.09	9.71	9.08	7.95	35.66	7.64	6.37
92.26	85.43	93.58	93.65	0.00	0.00	0.66	1.86	7.47	0.00	8.37	7.52	0.00	0.00	0.31	0.37
rms %	8.48	4.30	4.28		6.09	2.47	2.20		12.90	5.50	4.67		16.00	1.23	1.02

Table 6. Comparing Experimental and Predicted LLE Data for the Ternary System Isooctane (1) + Ethylbenzene (2) + Propylene Carbonate (3)

raffinate phase								extract phase							
$100x_1$				$100x_2$				$100x_1$				$100x_2$			
exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL
T = 293.15 K															
99.90	99.90	99.84	99.79	0.00	0.00	0.08	0.05	1.31	0.86	1.01	1.00	0.00	0.00	0.04	0.02
96.16	97.82	96.14	96.07	3.65	2.05	3.73	3.71	0.92	0.96	1.11	1.10	2.18	2.54	1.99	1.94
93.67	97.82	93.60	93.53	6.10	2.05	6.24	6.21	1.21	0.96	1.17	1.17	3.42	2.54	3.24	3.18
90.74	91.39	90.87	90.80	8.99	8.34	8.92	8.89	0.90	1.07	1.23	1.24	4.46	5.39	4.49	4.44
84.67	85.78	84.73	84.67	14.99	13.78	14.92	14.86	1.12	1.22	1.37	1.40	7.06	8.80	7.07	7.04
73.81	76.09	73.63	73.59	25.71	22.99	25.60	25.49	1.17	1.55	1.60	1.65	11.45	14.88	11.08	11.13
48.12	56.26	48.12	48.12	48.58	40.62	48.55	48.57	2.82	2.69	2.07	2.14	18.83	28.53	19.27	19.22
rms %	3.65	0.09	0.11		3.62	0.09	0.12		0.26	0.39	0.38		3.98	0.24	0.23
T = 313.15 K															
99.80	99.65	99.74	99.69	0.00	0.00	0.24	0.21	2.35	0.00	1.64	1.66	0.00	0.00	0.14	0.12
91.87	92.00	91.75	91.68	7.80	7.41	8.09	8.03	2.47	0.00	1.99	2.01	4.80	14.81	4.72	4.70
89.81	90.11	90.06	89.98	9.77	9.26	9.73	9.67	1.74	0.00	2.07	2.09	5.57	14.90	5.64	5.61
88.97	90.00	89.09	89.01	10.60	9.36	10.67	10.60	1.80	0.00	2.12	2.13	6.27	14.90	6.15	6.12
77.84	79.73	77.63	77.56	21.59	19.33	21.44	21.35	2.41	0.01	2.65	2.67	11.83	17.98	11.57	11.56
72.34	74.49	72.04	71.99	26.99	24.35	26.44	26.36	2.23	0.01	2.89	2.90	13.96	20.22	13.68	13.69
52.22	58.85	52.29	52.32	41.86	39.01	42.11	42.17	3.77	0.05	3.46	3.45	18.08	28.29	18.26	18.26
rms %	2.76	0.18	0.20		1.78	0.28	0.31		2.46	0.47	0.47		7.96	0.18	0.18
T = 318.15 K															
98.21	99.63	96.11	96.17	0.00	0.00	0.00	0.00	3.12	0.00	3.14	3.00	0.00	0.00	0.00	0.00
88.19	90.94	88.55	88.56	6.89	8.47	7.50	7.54	2.98	0.00	3.14	3.07	3.03	7.78	2.61	2.62
83.93	86.69	84.15	84.15	10.80	12.61	11.86	11.90	4.25	0.00	3.14	3.10	4.76	8.90	4.20	4.22
76.82	78.94	76.52	76.54	19.24	20.07	19.41	19.41	2.92	0.00	3.13	3.16	7.81	11.40	7.11	7.12
71.43	75.06	72.83	72.84	21.52	23.76	23.05	23.04	2.89	0.00	3.13	3.18	8.80	12.76	8.59	8.61
64.74	66.76	64.72	64.74	32.41	31.56	31.03	30.97	1.17	0.01	3.11	3.23	11.53	15.86	12.05	12.04
46.69	52.46	46.23	46.12	49.13	44.43	49.04	49.02	3.73	0.02	3.02	3.24	21.32	23.00	21.31	21.09
rms %	3.21	0.99	0.98		2.21	0.91	0.93		3.13	0.90	0.92		3.58	0.43	0.43
T = 323.15 K															
98.18	99.61	97.03	96.83	0.00	0.00	0.00	0.00	3.17	0.00	2.35	2.28	0.00	0.00	0.00	0.00
88.37	90.67	88.35	88.28	7.72	8.71	7.72	7.71	3.00	0.00	2.84	2.80	3.45	7.78	3.52	3.45
85.35	88.19	85.71	85.67	9.58	11.12	10.06	10.05	3.01	0.00	2.97	2.95	4.43	8.46	4.49	4.42
74.18	77.50	74.69	74.78	19.41	21.41	19.86	19.90	3.29	0.00	3.52	3.56	8.21	12.09	8.35	8.37
70.98	73.68	70.83	70.95	23.28	25.03	23.35	23.42	3.48	0.00	3.71	3.77	10.14	13.54	9.71	9.78
46.33	53.47	46.06	46.02	47.85	43.54	47.78	47.76	3.76	0.02	4.71	4.81	20.81	22.65	20.16	20.06
rms %	3.76	0.55	0.63		2.20	0.27	0.29		3.29	0.53	0.59		3.29	0.33	0.35
T = 338.15 K															
98.01	99.53	97.73	97.36	0.00	0.00	0.10	0.00	3.38	0.00	2.75	3.49	0.00	0.00	0.06	0.00
89.32	90.00	89.54	89.33	7.52	9.22	7.45	7.54	3.68	0.00	3.43	3.81	3.71	12.42	4.18	3.63
86.05	87.07	84.95	84.81	11.44	12.06	11.53	11.73	5.68	0.00	3.75	3.99	6.42	12.44	6.01	5.56
72.31	75.06	72.91	73.20	22.65	23.55	22.12	22.35	3.55	0.01	4.47	4.41	9.23	14.83	10.18	10.25
65.39	68.17	65.69	66.07	27.59	30.01	28.44	28.73	4.42	0.01	4.85	4.64	13.28	16.90	12.61	13.01
45.13	46.81	44.88	44.81	46.96	48.83	47.05	46.73	4.22	0.05	5.82	5.21	22.24	25.20	21.02	21.43
rms %	1.91	0.56	0.74		1.50	0.42	0.50		4.22	1.14	0.88		5.25	0.73	0.65

Table 7. Rmsd Values for the Different Models for the Ternary System Methylcyclohexane (1) + Benzene (2) + Propylene Carbonate (3)

T, K	UNIFAC	UNIQUAC	NRTL
293.15	5.31	0.49	0.50
313.15	4.45	1.62	1.59
333.15	5.93	2.5	3.73
348.15	7.34	5.65	5.35

Table 8. Rmsd Values for the Different Models for the Ternary System Octane (1) + Toluene (2) + Propylene Carbonate (3)

T, K	UNIFAC	UNIQUAC	NRTL	UNIFAC[a]	UNIFAC[b]
293.15	5.65	0.53	0.52	13.66	11.76
313.15	7.02	0.8	0.81	14.13	10.41
333.15	8.07	0.72	0.72	11.03	10.26
348.15	12.34	0.56	0.57	12.7	16.57

[a] Kikic et al. (1985). *b*Salem (1993).

Table 9. Rmsd Values for the Different Models for the Ternary System 1-Decene (1) + Toluene (2) + Propylene Carbonate (3)

T, K	UNIFAC	UNIQUAC	NRTL
293.15	11.61	0.42	0.57
313.15	22.65	0.72	0.51
333.15	19.33	1.54	1.28
348.15	11.53	3.75	3.39

Table 10. Rmsd Values for the Different Models for the Ternary System Isooctane (1) + Ethylbenzene (2) + Propylene Carbonate (3)

T, K	UNIFAC	UNIQUAC	NRTL
293.15	3.25	0.24	0.24
313.15	4.48	0.3	0.31
318.15	3.08	0.84	0.85
323.15	3.19	0.44	0.49
338.15	3.58	0.76	0.71

of liquid liquid equilibrium (LLE) measurements over a temperature range of 293 K to 348 K were performed.

The equilibrium concentrations of the three components in each of the ternary systems in each phase were measured using gas chromatography. A Chrompack CP9001 gas chromatograph equipped with a TCD (thermal conductivity detector) was used. A 2 m × $^1/_4$ in. × 4 mm i.d. SS column coated with 100−120 mesh of Poropak Q was used. The carrier gas (helium, grade 6) flow rate was maintained at 30 mL/min. The injection port and column were maintained at (513 K), and the detector port was at (543 K). The constituents were separated and analyzed under isothermal oven conditions of 513 K.

The gas chromatograph was calibrated by the external standard calibration method. Calibration mixtures were prepared by weighing in different ratios the pure components. The accuracy of weighing was ±0.0001 g. The standard accuracy and reproducibility for all the components were found to be ±0.5% and ±0.3%, respectively. It was also possible to measure mole fractions at the same levels.

Models and Predictions

If a liquid mixture of a given composition and at a known temperature is separated into two phases (i.e., at equilibrium), the composition of the two phases can be calculated from the following equations

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \tag{1}$$

$$z_i = z_i^{\mathrm{I}} + z_i^{\mathrm{II}} \tag{2}$$

where z_i, z_i^{I}, and z_i^{II} are the numbers of moles of component *i* in the system and in phases I and II, respectively, and γ_i^{I} and γ_i^{II} are the corresponding activity coefficients of component *i* in phases I and II, as calculated from the equilibrium equations, NRTL and UNIQUAC. The generated binary- and ternary-component equilibria data are used to determine interaction parameters between paraffinic/aromatic hydrocarbons and propylene carbonate; these

Table 11. Optimum Interaction Parameters According to the Equation $a_{ij} = a^0_{ij} + b_{ij}\,(T/\mathrm{K} - 273)$

i	*j*	a^0_{ij}/K	b_{ij}	a^0_{ij}/K	b_{ij}	system
		UNIFAC				
$ACCH_2$	propylene carbonate	1983.407	−13.213 9	−26.4183	−7.427 32	1
CH_2	propylene carbonate	903.8089	−9.853 07	−41.854	8.030 682	2
ACH	propylene carbonate	1649.162	−11.430 6	−58.9282	−4.127 01	3
C=C	propylene carbonate	1680.802	5.993 193	1783.331	5.406 953	4
		UNIQUAC				
octane	toluene	−8.88807	2.945 396	−69.3212	0.169 752	1
octane	propylene carbonate	477.7634	−0.340 53	41.68019	0.488 119	1
toluene	propylene carbonate	313.6611	−2.641 79	−172.186	3.358 883	1
isooctane	ethylbenzene	108.2593	2.112 29	−31.1341	−1.518 91	2
isooctane	propylene carbonate	975.8325	−8.068 1	5.377527	0.090 741	2
ethylbenzene	propylene carbonate	−78.6774	13.676 2	95.19605	−4.087 41	2
methylcyclohexane	benzene	141.15	0.486 102	−205.134	4.341 687	3
methylcyclohexane	propylene carbonate	848.0834	−4.906 53	6.779589	−1.004 55	3
benzene	propylene carbonate	166.6301	1.236 204	−138.655	3.030 308	3
decene	toluene	141.15	0.486 102	−205.134	4.341 687	4
decene	propylene carbonate	848.0834	−4.906 53	6.779589	−1.004 55	4
		NRTL				
octane	toluene	−484.4778	8.340 679	201.7234	2.763 571	1
octane	propylene carbonate	921.2547	−1.444 76	801.1418	3.353 091	1
toluene	propylene carbonate	729.7363	−6.174 39	−426.109	10.175 97	1
isooctane	ethylbenzene	318.6299	−2.546 59	16.64056	0.501 133	2
isooctane	propylene carbonate	1808.685	−17.084	888.0624	−2.425 69	2
ethylbenzene	propylene carbonate	293.3056	12.126 33	267.5872	−4.986 24	2
methylcyclohexane	benzene	−54.4137	4.682 625	−303.401	10.793 03	3
methylcyclohexane	propylene carbonate	1641.223	−6.896 87	560.3804	−6.223 22	3
benzene	propylene carbonate	661.0645	−0.205 27	−498.041	9.137 608	3
decene	toluene	−54.4137	4.682 625	−303.401	10.793 03	4
decene	propylene carbonate	1641.223	−6.896 87	560.3804	−6.223 22	4

in turn are used to estimate the activity coefficients from the NRTL and the UNIQUAC equations. In a similar fashion the interaction parameters between CH_2, C═C, ACH, and $ACCH_2$ and propylene carbonate groups were used to predict the activity coefficients from the UNIFAC model. Interaction parameters between certain group pairs have already been reported in the literature (Hansen et al., 1980), and these values have been used where required. The values of these interaction parameters are given in Table 12.

The R_i and Q_i values for the UNIFAC groups and the r_i and q_i values for the UNIQUAC compounds are shown in Table 2. Equations 1 and 2 were solved for the mole fraction (x_i) of component i in each liquid phase. This method of calculation gives a single tie line.

Results and Discussion

The measured equilibrium mole percentages are shown in Tables 3−6. These data were used to calculate the optimum UNIFAC interaction parameters between the main groups of hydrocarbons (CH_2, C═C, ACH, and $ACCH_2$) and propylene carbonate. They were also used to determine the optimum UNIQUAC and NRTL interaction parameters between octane, 2,2,4-trimethylpentane, methylcyclohexane, 1-decene, toluene, ethylbenzene, benzene, and propylene carbonate.

Optimal interaction parameters between compounds for NRTL and UNIQUAC and between functional groups for the UNIFAC were found by using an iterative computer program developed by Sorensen (1980). The objective function in this case was minimized by minimizing the square of the difference between the mole fractions predicted by the respective method and these experimentally measured.

The resulting values of the interaction parameters between each pair of the UNIFAC groups and UNIQUAC and NRTL compounds were fitted linearly with the temperature according to the following equation

$$a_{ij} = a^0{}_{ij} + b_{ij}(T/\mathrm{K} - 273.15) \tag{3}$$

where T is the temperature in kelvin and $a^0{}_{ij}$ and b_{ij} are the optimum interaction parameters between each two groups or components in the system. The values of these parameters for the three methods are shown in Table 11. The corresponding calculated tie lines are shown in Tables 3−6.

The percentage root-mean-square deviations (rmsd %) are calculated from the results of each method at a given temperature according to the following equation

$$\text{rmsd } \% = (100\%)\{\sum_k[\sum_i\sum_j (x_{i,\text{exp}} - x_{i,\text{calcd}})_j^{\,2}]/4n\}^{1/2} \tag{4}$$

where i is the aromatic or paraffinic hydrocarbon component, j is the extract or raffinate phase, and k = 1, 2, ..., n (tie lines).

The average rmsd percent values for the three methods for all systems studied are reported in Tables 7−10. The predictions from the UNIQUAC model have the least rmsd value, the average rmsd value being 1.29%. The average rmsd value for the NRTL predictions corresponding to the interaction parameters optimized in this work (1.30%) are comparable to those of the UNIQUAC equation. The UNIFAC equation has also predicted the overall composition with a reasonable error, though its average rmsd value (8.16%) is higher than those of the NRTL and UNIQUAC equations, as would be expected. It is therefore considered to be less accurate than the NRTL and the UNIQUAC equations in correlating the phase equilibria of the studied systems.

Table 12. Reported[a] Optimum Interaction Parameters According to the Equation $a_{ij} = a^0{}_{ij}/K + b_{ij}(T/\mathrm{K} - 273)$

i	j	$a^0{}_{ij}$/K	b_{ij}	$a^0{}_{ij}$/K	b_{ij}
		UNIFAC			
ACH	CH_2	−6.727	−0.5662	64.45	0.3745
ACH	$ACCH_2$	−155.4	−1.489	366.6	13.22
$ACCH_2$	CH_2	252.5	2.65	−93.37	−1.103
ACH	C═C	25.94	−1.578	−16.53	1.759
$ACCH_2$	C═C	−18.43	1.812	−149.2	8.782
C═C	CH_2	144.8	−2.689	−102.3	0.6741

[a] Hansen et al. (1980).

Equilibria data for the toluene−heptane−propylene carbonate system was studied by Kikic et al. (1985) at 20 °C and at 25 °C by Salem (1993). These data were used to generate UNIFAC interaction parameters between the main groups of hydrocarbons (CH_2, ACH, and $ACCH_2$) and propylene carbonate. These values were then used to predict equilibrium data for the toluene−octane−propylene carbonate system at the temperatures studied in this work. The degree of fit between actual (experimental) and predicted values, as given by the rmsd values, are reported in Table 8. Predicted data generated by this work gave the lowest rmsd values.

Conclusions

Four ternary systems have been studied for phase equilibria between propylene carbonate and some hydrocarbons. The experimental equilibrium data were successfully correlated using the NRTL and UNIQUAC equations with linear temperature-dependent parameters. The UNIFAC predictive model was also tested. It was found from this work that NRTL and UNIQUAC gave almost equal rmsd % of 1.3% versus 8.16% given by UNIFAC. However, UNIFAC remains the only predictive method among the three.

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