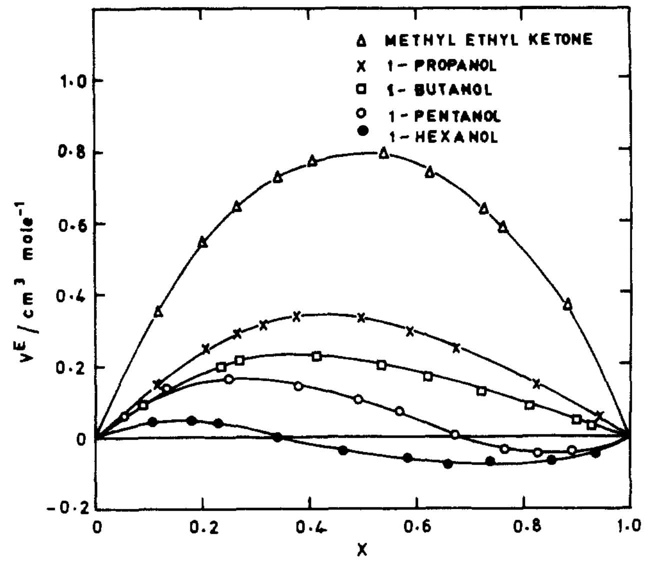

Figure 3. Plot of V^E as a function of composition for methyl ethyl ketone (1) + *n*-heptane (2) and 1-alkanol (1) + *n*-heptane (2) at 303.15 K: (Δ) methyl ethyl ketone; (X) 1-propanol; (□) 1-butanol; (O) 1-pentanol; (●) 1-hexanol.

The values of this ternary contribution are given in the fifth column of Table III.

The experimental results of V^E_{123} for the ternary systems were fitted by the method of the least squares to eq 3, where

$$V^E_{123} = V^E_{12}{}^* + V^E_{23}{}^* + V^E_{31}{}^* + X_1X_2X_3\,[A + BX_1(X_2 - X_3) + CX_1^2(X_2 - X_3)^2] \quad (3)$$

X_1, X_2, and X_3 are the mole fractions of methyl ethyl ketone, an alkanol, and *n*-heptane, respectively, and *A*, *B*, and *C* are constants. The starred quantities were evaluated by using the procedure described elsewhere (*2*) and the equations in Table II. The sum of $V^E_{12}{}^* + V^E_{23}{}^* + V^E_{31}{}^*$ for a ternary mixture is represented as V^E_{123} (b), and its values are included in the sixth column of Table III. The deviation $\Delta V^E_{123}{}^*$ was calculated by subtracting the sum $\sum V^E_{ij}{}^*$ from those of the experimental values given in the third column of Table III. Values of $\Delta V^E_{123}{}^*$ are presented in the seventh column of Table III. These were used to evaluate the constants *A*, *B*, and *C* in eq 3 by the least-squares method. The values of the constants and the standard deviations are presented in Table IV. The analysis shows that eq 3 satisfactorily represents the ternary data for the four systems.

Literature Cited

(1) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(2) Rastogi, R. P.; Nath, J.; Das, S. S. *J. Chem. Eng. Data*. **1977**, *22*, 249.
(3) Naidu, P. R.; Krishnan, V. R. *Trans. Faraday Soc.* **1965**, *61*, 1347.
(4) Reddy, K. S.; Naidu, P. R. *Can. J. Chem.* **1977**, *55*, 76.
(5) Timmermans, J. "*Physico-Chemical Constants of Pure Organic Compounds*"; Elsevier: New York, 1950; Tables.
(6) Rao, M. V. P. Ph.D. Thesis, Sri Venkateswara University, India, 1974; Chapter 2.
(7) Vogel, A. I. "Quantitative Inorganic Analysis"; Longmans, Green and Co.; London, 1975; Chapter 19.
(8) McLure, I. A.; Swinton, F. L. *Trans. Faraday Soc.* **1965**, *61*, 421.
(9) Stookey, D. J.; Sallak, H. M.; Smith, B. D. *J. Chem. Thermodyn.* **1973**, *5*, 751.

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Vapor-Liquid Phase Equilibrium in the Methane-Ethane-Propane-Toluene-1-Methylnaphthalene System at 220-400 °F and 200-2000 psia

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A static experimental cell was used for vapor-liquid phase equilibrium measurements on a methane-ethane-propane-toluene-1-methylnaphthalene system. Measurements were made at 220, 280, 340, and 400 °F and at pressures from 200 to 2000 psia. The data of this study were well represented by the Soave equation of state. Average errors in the predicted *K* values were ca. 5% for methane, ethane, propane, and toluene and 7% for 1-methylnaphthalene.

Introduction

The well-publicized energy situation in the United States has provided strong impetus toward the conversion of coal to liquid and gaseous products. However, coal-conversion processes often operate in regions of combined temperatures, pressures, and compositions not experienced in typical petroleum processing. Presently, much of the thermodynamic property information used in process calculations is based upon fragmentary data or, more often, upon considerable extrapolation (with respect to temperature and composition) of correlations designed for petroleum processing operations.

This study was designed to obtain experimental data on phase equilibrium in systems which simulate those found in various stages of coal-fluid processing. Based upon a literature survey (*1-4*), a system was chosen for study composed of 7% methane, 3.5% ethane, 3.5% propane, 43% toluene, and 43% 1-methylnaphthalene (weight basis). The results should be useful for testing models for prediction of phase behavior in some stages of coal-conversion processes.

Experimental Section

A static type of apparatus was adopted for vapor-liquid equilibrium measurements. It is similar to the apparatus described by Jacoby (*5*) and has been described in detail elsewhere (*6*).

Temperatures in the cell were measured by a calibrated platinum resistance thermometer to ±0.1 °F. The pressure in the system was monitored by a high temperature pressure

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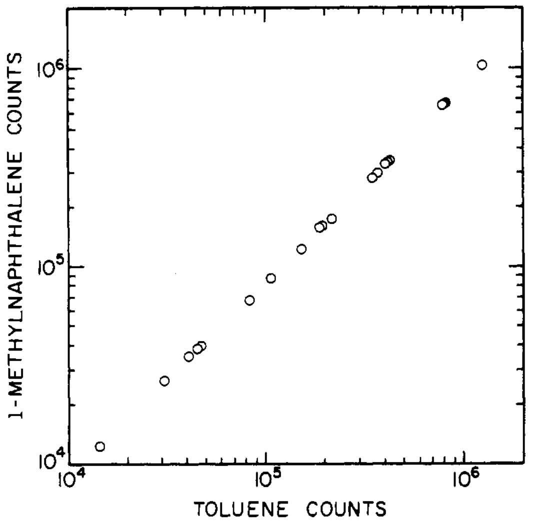

Figure 1. Typical chromatograph response.

transducer (Bell and Howell, Model 4-317-0001) which was mounted near the vapor sample outlet. Final pressure readings were taken on a calibrated Heise Bourdon tube gauge and are estimated to be accurate to ±3 psia.

Sample valves of the type described by Yarborough and Vogel (*7*) were modified for this work. The needle-type stem was modified to give a ball-type tip by press-fitting a ball bearing in the end of the stem, which resulted in a better seal on the samples. Samples were trapped beneath the stem in a conical-shaped cavity machined into a removable capsule. The size of the cavity was variable from 5 to 50 μL depending upon the amount of sample suitable for analysis.

Analysis

Equilibrium phase samples were analyzed by gas chromatography, using a Varian automatic gas chromatograph (Model 3700) equipped with a flame ionization detector, a CDS-111 data system, and a recorder. Columns of Porapak N (4 ft) and OV101 (5% OV101 on the Chromosorb G, 6 ft) were used in a column reversal mode to permit the heavy hydrocarbons (toluene and 1-methylnaphthalene) to be separated on the OV101 and the light hydrocarbons on the Porapak N. Figure 1 shows a typical detector response for a single mixture of toluene and 1-methylnaphthalene. The detector response was varied by 2 orders of magnitude by injecting various size samples. The slope of the line in Figure 1 is 0.994 (constant response corresponds to a slope of 1.00). Thus, sample analyses were performed by using constant relative response. Calibrations were done by analyses of a series of volumetrically prepared binary and multicomponent mixtures of known composition.

Materials

Methane, ethane, and propane were purchased from Linde (Union Carbide) with reported purities of 99.97, 99.0, and 99.5%, respectively. Toluene obtained from Philips Chemical Co. was pure grade with a reported purity of 97.8%, and the 1-methylnaphthalene was from Aldrich Chemical Co. with a stated purity of 97%. Gas-chromatographic analyses indicated the actual purities to be higher than claimed. No thermal decomposition products were detected by gas chromatography at any of the conditions studied.

Results

Vapor-liquid equilibrium measurements were made at 220, 280, 340, and 400 °F from 200 to 2000 psia. Table I shows the nominal molar composition of the mixture used in the vapor-liquid equilibrium measurements at all isotherms. Table II and Figure 2 give the experimentally determined phase compositions and *K* values.

Table I. Nominal Overall Composition of the Multicomponent System

component	overall composition, mol %	component	overall composition, mol %
C_1	31	Tol	33
C_2	8	MN	22
C_3	6		

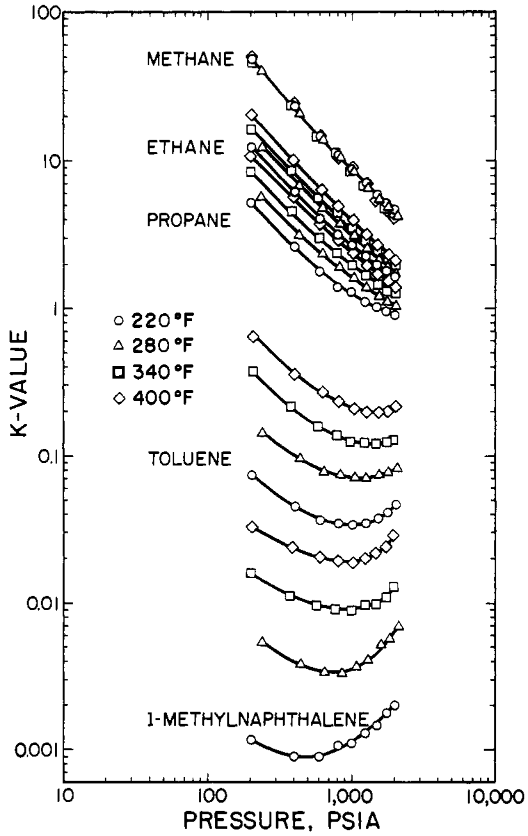

Figure 2. Vapor-liquid equilibrium data.

Each phase composition in the tables represents the mean of from 2 to 10 replicate sample analyses. Sufficient measurements were made to permit an estimate of the data uncertainties due to analytical errors. For each set of replicate samples, a mean value and an average absolute percent deviation from the mean were calculated. Then, mean values of these average absolute percent deviations, ϵ, for each sample type (methane vapor, methane liquid, etc.) at each isotherm were plotted as a function of their average mole fraction, z, in Figure 3.

Deviations of 0.1-12% were found from the above analysis and, as expected, Figure 3 shows considerable scatter. However, the general increase in percentage uncertainty as the mole fraction decreases is clearly evident. Also shown in Figure 3 is an estimate of experimental uncertainty given by Yarborough (*8*) in an independent study of multicomponent phase equilibrium. His estimate is in excellent agreement with our results. The uncertainties in this study can be described approximately by the relationship shown in the figure

$$\epsilon = 0.2/z^{0.55}$$

which leads to an uncertainty in the *K* value of component *i* (due to analytical uncertainties) described by

$$\%\ \text{error in}\ K_i = 0.2\ \{1/x_i^{1.1} + 1/y_i^{1.1}\}^{1/2}$$

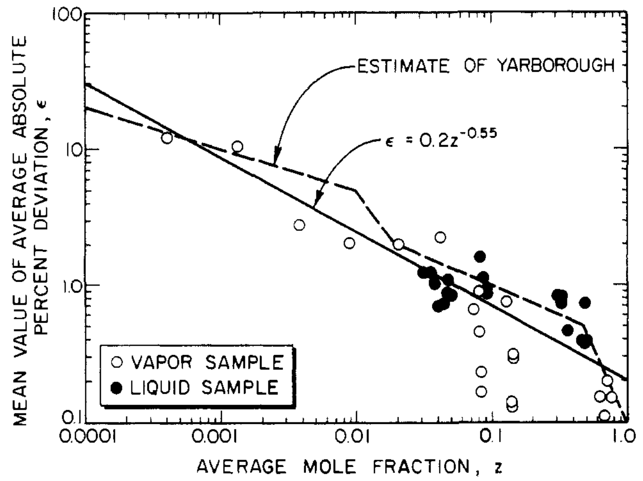

Figure 3. Uncertainties in sample compositions.

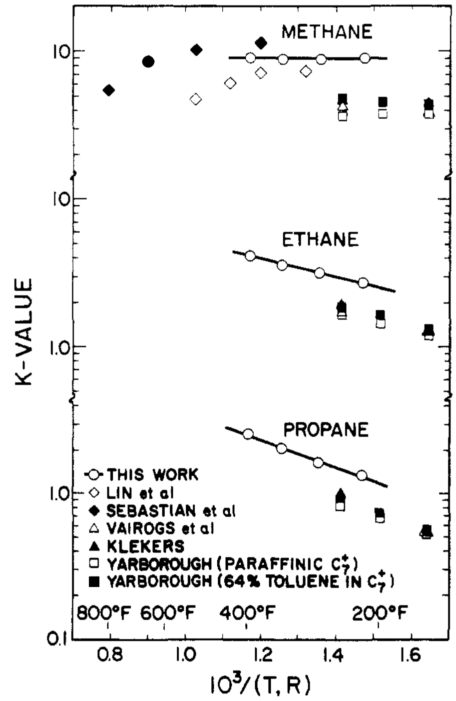

Figure 4. Comparison of methane, ethane, and propane K values at 1000 psia.

This equation suggests that analytical uncertainties lead to maximum uncertainties in the K values which range from 3% for methane to 17% for 1-methylnaphthalene.

There have been relatively few vapor-liquid equilibrium studies on multicomponent systems closely related to the present work. Vairogs et al. (*9*) reported K values for multicomponent hydrocarbon mixtures which included methane, ethane, propane, *n*-pentane, *n*-hexane, and *n*-decane, at pressures of 100-7000 psia at temperatures of 150 and 250 °F. Klekers (*10*) measured data on the same system with 1-methylnaphthalene substituted for *n*-decane. Yarborough (*8*) made measurements in systems containing nitrogen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, *n*-pentane, *n*-decane and also with toluene added to yield a C_7^+ fraction containing 64 mol % toluene. K values in binary systems of methane + toluene (*11*, *12*) and methane + 1-methylnaphthalene (*13*) have been also measured. Figures 4 and 5 present comparisons of K values from these investigators at a pressure of 1000 psia.

Figure 4 shows K values of methane, ethane, and propane in various solvents. The data of Yarborough (*8*), Vairogs et al. (*9*), and Klekers (*10*) show that the addition of aromatic components to the mixtures containing *n*-paraffin hydrocarbons causes the light-hydrocarbon K values to increase. In the present study, the K values of methane, ethane, and propane in the purely aromatic solvent are much higher than (almost twice) those in the intermediate and heavy *n*-paraffin hydrocarbons measured by Yarborough (*8*) and Vairogs et al. (*9*). In our mixed aromatic solvent composed of toluene and 1-methylnaphthalene, the methane K values are intermediate between those in methane + toluene reported by Lin et al. (*11*) and in methane + 1-methylnaphthalene reported by Sebastian et al. (*13*). Figure 5 shows that the toluene and 1-methylnaphthalene K-value data agree fairly well among the several investigations.

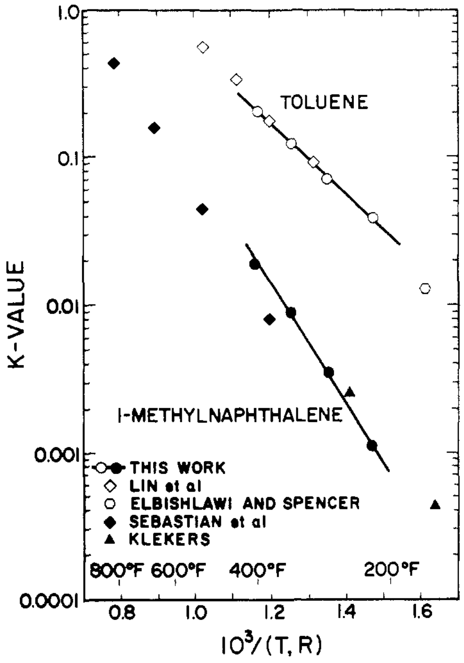

Figure 5. Comparison of toluene and 1-methylnaphthalene K values at 1000 psia.

Correlation

The data from this work have been represented adequately by the Soave (*14*) version of the Redlich-Kwong equation using six empirical interaction parameters, one for each paraffin-aromatic pair in the system. Specifically, the mixing rules employed are

$$b_m = \sum_{i=1}^{n} y_i b_i$$

$$a_m = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij}$$

$$a_{ij} = (1 - C_{ij})(a_i a_j)^{1/2}$$

where C_{ij} is the empirical unlike-pair interaction parameter. The same rules apply to the liquid phase, with x replacing y. Values of the pure-substance parameters, a_k and b_k, were evaluated from relationships suggested by Soave (*14*).

The above model requires values of the empirical parameters, C_{ij}, for each binary pair appearing in the system. Yarborough (*15*) has demonstrated that there is no significant advantage for using hydrocarbon-hydrocarbon interaction parameters in predictions for ternary systems. Therefore, the interaction parameters among methane, ethane, and propane and between toluene and 1-methylnaphthalene were set to zero in

Table II. Experimental Phase Equilibrium Data

press., psia		methane	ethane	propane	toluene	1-methyl-naphthalene
220 °F						
200	*y*	0.6625	0.1805	0.115 0	0.04155	0.000 462 0
	x	0.01380	0.01455	0.021 95	0.5575	0.392 0
	K	48.1	12.4	5.24	0.0746	0.001 18
400	*y*	0.7100	0.1670	0.095 05	0.02470	0.000 335 0
	x	0.03055	0.02765	0.035 95	0.5365	0.369 5
	K	23.2	6.14	2.64	0.0460	0.000 906
600	*y*	0.7415	0.1590	0.080 45	0.01905	0.000 317 0
	x	0.05030	0.03945	0.044 60	0.5155	0.350 0
	K	14.7	4.03	1.80	0.0370	0.000 906
800	*y*	0.7575	0.1520	0.073 25	0.01695	0.000 364 5
	x	0.06940	0.04810	0.050 90	0.4910	0.340 5
	K	10.9	3.16	1.44	0.0345	0.001 07
1000	*y*	0.7695	0.1450	0.068 75	0.01650	0.000 355 5
	x	0.08745	0.05390	0.052 70	0.4820	0.324 0
	K	8.80	2.69	1.31	0.0342	0.001 10
1250	*y*	0.7845	0.1360	0.062 60	0.01615	0.000 399 0
	x	0.1115	0.06030	0.055 65	0.4635	0.309 0
	K	7.04	2.26	1.12	0.0349	0.001 29
1500	*y*	0.7940	0.1295	0.058 85	0.01680	0.000 429 0
	x	0.1355	0.06535	0.057 35	0.4460	0.296 0
	K	5.86	1.98	1.03	0.0377	0.001 45
1750	*y*	0.8030	0.1230	0.055 35	0.01780	0.000 514 0
	x	0.1560	0.06855	0.057 70	0.4275	0.290 0
	K	5.15	1.80	0.959	0.0416	0.001 77
2000	*y*	0.8085	0.1190	0.052 85	0.01910	0.000 561 0
	x	0.1755	0.07190	0.058 55	0.4120	0.282 0
	K	4.61	1.65	0.903	0.0464	0.001 99
280 °F						
239	*y*	0.6350	0.1670	0.111 0	0.08185	0.001 885
	x	0.01615	0.01410	0.019 85	0.5730	0.377 0
	K	39.3	12.1	5.60	0.143	0.005 00
439	*y*	0.6795	0.1665	0.099 30	0.05335	0.001 360
	x	0.03330	0.02510	0.031 05	0.5580	0.352 5
	K	20.4	6.63	3.20	0.0956	0.003 86
640	*y*	0.7050	0.1610	0.090 15	0.04265	0.001 025
	x	0.05150	0.03420	0.038 35	0.5425	0.333 5
	K	13.7	4.71	2.35	0.0786	0.003 08
839	*y*	0.7240	0.1545	0.082 55	0.03810	0.001 030
	x	0.06905	0.04150	0.043 30	0.5240	0.322 5
	K	10.5	3.72	1.91	0.0728	0.003 20
1035	*y*	0.7380	0.1480	0.076 55	0.03640	0.001 170
	x	0.08810	0.04770	0.046 80	0.5050	0.312 5
	K	8.37	3.10	1.64	0.0720	0.003 74
1292	*y*	0.7510	0.1415	0.071 55	0.03470	0.001 200
	x	0.1165	0.05655	0.051 00	0.4285	0.297 5
	K	6.43	2.51	1.40	0.0725	0.004 03
1542	*y*	0.7650	0.1340	0.066 20	0.03335	0.001 310
	x	0.1415	0.06360	0.054 70	0.4560	0.284 5
	K	5.41	2.11	1.21	0.0732	0.004 61
1792	*y*	0.7745	0.1280	0.061 85	0.03410	0.001 515
	x	0.1610	0.06665	0.055 30	0.4405	0.276 5
	K	4.81	1.92	1.12	0.0774	0.005 48
2043	*y*	0.7810	0.1235	0.059 80	0.03455	0.001 565
	x	0.1855	0.07040	0.056 20	0.4250	0.263 0
	K	4.21	1.75	1.06	0.0813	0.005 94
340 °F						
204	*y*	0.5565	0.1480	0.103 5	0.1855	0.006 925
	x	0.01230	0.008945	0.012 00	0.5235	0.443 5
	K	45.2	16.5	8.60	0.354	0.015 6
381	*y*	0.6280	0.1550	0.099 95	0.1125	0.004 590
	x	0.02675	0.01770	0.021 60	0.5355	0.398 5
	K	23.5	8.74	4.63	0.210	0.011 5
591	*y*	0.6640	0.1545	0.094 60	0.08280	0.003 730
	x	0.04575	0.02720	0.030 95	0.5235	0.372 5
	K	14.5	5.69	3.06	0.158	0.010 0
793	*y*	0.6870	0.1510	0.088 40	0.07035	0.003 280
	x	0.06125	0.03375	0.036 60	0.5140	0.354 5
	K	11.2	4.47	2.41	0.137	0.009 26
996	*y*	0.7080	0.1455	0.082 15	0.06145	0.003 050
	x	0.08120	0.04075	0.040 70	0.4980	0.339 5
	K	8.72	3.57	2.02	0.123	0.008 99
1244	*y*	0.7210	0.1405	0.077 15	0.05830	0.003 205
	x	0.1050	0.04775	0.044 95	0.4775	0.325 0
	K	6.87	2.94	1.72	0.122	0.009 88
1501	*y*	0.7355	0.1350	0.072 20	0.05455	0.003 025
	x	0.1335	0.05475	0.048 90	0.4595	0.303 5
	K	5.51	2.46	1.48	0.119	0.009 98
1742	*y*	0.7445	0.1300	0.068 40	0.05380	0.003 190
	x	0.1535	0.05960	0.050 75	0.4440	0.291 5
	K	4.84	2.18	1.35	0.121	0.010 9
1978	*y*	0.7495	0.1260	0.065 50	0.05535	0.003 725
	x	0.1695	0.06220	0.051 55	0.4335	0.283 0
	K	4.42	2.03	1.27	0.128	0.013 2
400 °F						
207	*y*	0.4925	0.1305	0.088 90	0.2700	0.018 10
	x	0.009990	0.006505	0.008 065	0.4305	0.545 0
	K	49.3	20.1	11.0	0.627	0.033 2
399	*y*	0.5715	0.1455	0.094 50	0.1780	0.010 45
	x	0.02390	0.01445	0.016 25	0.5070	0.4385
	K	23.9	10.1	5.81	0.351	0.0239
611	*y*	0.6150	0.1490	0.092 55	0.1350	0.008 365
	x	0.04250	0.02350	0.024 95	0.5105	0.398 5
	K	14.5	6.33	3.71	0.265	0.021 0
806	*y*	0.6390	0.1480	0.089 00	0.1165	0.007 335
	x	0.05910	0.03030	0.030 50	0.5080	0.372 0
	K	10.8	4.89	2.92	0.229	0.019 7
1019	*y*	0.6605	0.1455	0.084 40	0.1030	0.006 690
	x	0.07470	0.03685	0.035 05	0.5015	0.352 0
	K	8.84	3.94	2.41	0.205	0.019 0
1261	*y*	0.6785	0.1405	0.079 00	0.09510	0.006 885
	x	0.09955	0.04400	0.039 55	0.4820	0.334 5
	K	6.82	3.19	2.00	0.197	0.020 6
1493	*y*	0.6890	0.1370	0.075 35	0.09155	0.006 990
	x	0.1245	0.05060	0.043 25	0.4670	0.315 0
	K	5.54	2.71	1.74	0.196	0.022 2
1766	*y*	0.6700	0.1325	0.071 30	0.08915	0.007 310
	x	0.1480	0.05585	0.045 35	0.4515	0.299 5
	K	4.73	2.37	1.57	0.197	0.024 4
1980	*y*	0.7030	0.1290	0.068 65	0.09115	0.008 305
	x	0.1720	0.06100	0.048 25	0.4330	0.286 0
	K	4.09	2.11	1.42	0.211	0.029 1

Table III. Empirical Interaction Parameters for Soave Equation

components *i*/*j*	interaction parameter, C_{ij}	source ref
C_1/Tol	0.091	*11*
C_2/Tol	0.034	this work
C_3/Tol	0.024	this work
C_1/MN	0.116	*13*
C_2/MN	0.062	this work
C_3/MN	0.042	this work

Table IV. Accuracy of Predictions by Soave Equation

component	av abs dev in predicted *K* value, %	component	av abs dev in predicted *K* value, %
C_1	5.6	Tol	4.9
C_2	4.7	MN	7.0
C_3	4.5		

this study. Four of the six interaction parameters among the other pairs were evaluated by fitting the experimental *K*-value data of the present work directly. The pair-interaction parameters for methane with toluene and 1-methylnaphthalene were evaluated from the binary phase equilibrium data reported by Lin et al. (*11*) and Sebastian et al (*13*). (*K* values at 207 and 399 psia at 400 °F from the present study were deleted in the correlation work. Under these two conditions, the liquid volume fraction in the system was very small, and these data gave unusually large errors in the prediction.) In all cases, the parameters were determined by minimizing the sum-of-squares of percent errors in predicted K values, the sum being taken over all components.

Tables III and IV present the results of the final correlation. Average errors in predicted K values of methane, ethane, propane, toluene, and 1-methylnaphthalene range from 4.5 to 7.0%. The predicted K values of methane, ethane, and propane are generally low at low pressure and high at high pressure for each isotherm using the interaction parameters obtained in this work. The predicted K values of toluene are low at high pressures and high at low pressures. The predicted K values of 1-methylnaphthalene show somewhat larger errors, as expected, and no consistent error trends.

Conclusion

Equilibrium liquid and vapor compositions and K values have been obtained in a five-component light hydrocarbon–aromatic solvent system. The data of this work have been represented by the Soave equation of state. The correlating parameters should be of use in the prediction of phase behavior in systems containing light hydrocarbons in aromatic solvents.

Glossary

a, b	parameters in Soave equation of state
C	interaction parameter
K_i	phase equilibrium ratio for component i, y_i/x_i
x	liquid mole fraction
y	vapor mole fraction
z	mole fraction
ϵ	mean value of average absolute percent deviation

Subscripts

i, j	components in a mixture
m	mixture property

Literature Cited

(1) Wiser, W. H.; Anderson, L. L.; Qader, S. A.; Hill, G. R. *J. Appl. Chem. Biotechnol.* **1971**, *21*, 82.
(2) Karr, C., Jr.; Abel, W. T.; Comberiati, J. R. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1976**, *21*, 207.
(3) Campbell, J. H.; Stephens, D. R. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1976**, *20*, 94.
(4) Dooley, J. E.; Thompson, C. J. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1976**, *21*, 243.
(5) Jacoby, R. H.; Rzasa, M. J. *Trans. Soc. Pet. Eng. AIME* **1952**, *195*, 99.
(6) Li, Y. H.; Dillard, K. H.; Robinson, R. L. *J. Chem. Eng. Data* **1981**, *26*, 53.
(7) Yarborough, L.; Vogel, J. L. *Chem. Eng. Prog., Symp. Ser.* **1967**, *63*, 1.
(8) Yarborough, L. *J. Chem. Eng. Data* **1972**, *17*, 129.
(9) Vairogs, J.; Klekers, A. J.; Edmister, W. C. *AIChE J.* **1971**, *17*, 308.
(10) Klekers, A. J. Ph.D. Thesis, Oklahoma State University, Stillwater, OK, 1976.
(11) Lin, H.-M.; Sebastian, H. M.; Simnick, J. J.; Chao, K.-C. *J. Chem. Eng. Data* **1979**, *24*, 146.
(12) Elbishlawi, M.; Spencer, J. R. *Ind. Eng. Chem.* **1951**, *43*, 1611.
(13) Sebastian, H. M.; Simnick, J. J.; Lin, H.-M.; Chao, K.-C. *J. Chem. Eng. Data* **1979**, *24*, 149.
(14) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(15) Yarborough, L. *Adv. Chem. Ser.* **1979**, *No. 102*, 385.

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Activity Measurements in Aqueous Mixed Electrolyte Solutions. 2. Hydrochloric Acid–Choline Chloride and Hydrochloric Acid–Acetylcholine Chloride Mixtures of Constant Total Ionic Strength

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Emf measurements have been made in cells without liquid junction of the type Pt,H_2(1 atm)|$HX(m_1)$,$MX(m_2)$|AgCl,Ag, containing mixtures of (I) HCl and $CH_2(OH)CH_2N(CH_3)_3Cl$ and (II) HCl and $CH_2(OOCCH_3)CH_2N(CH_3)_3Cl$ in different proportions, but at constant total ionic strength (μ = 3, 2, 1, 0.5, 0.25, 0.1). Measurement have been carried out at 10 °C intervals, over the temperature range 5–35 °C. The Ag–AgCl electrodes, prepared by the thermoelectrolytic method, used in pairs for each measurement, gave results which closely agreed. The values for the standard electrode potential, $E°$, and the interaction coefficient, α_{12}, for each constant total ionic strength mixture at all of the four temperatures have been evaluated by the computerized least-squares method. Interpretation of the results has been made in terms of the multicomponent ionic equilibrium theory of Scatchard ("neutral electrolyte as components" treatment) and of Pitzer.

Introduction

The determination of the activity coefficient of one electrolyte in the presence of another has evoked interest for a fairly long time. The specific ionic interaction principle postulating the existence of short-range interactions among ions of unlike sign of charge was enunciated by Brönsted (*1*, *2*) and was applied to dilute solutions by Guggenheim (*3*–*5*). Modifications were suggested for concentrated solutions by Scatchard (*6*, *7*). Pitzer and Brewer (*8*) used the Guggenheim equations with Scatchard modifications (*6*) (BSG theory) to give a simple and compact summary of experimental data.

From emf measurements at constant total ionic strength, some simple empirical relationships have been discovered to hold in both dilute and concentrated solutions (*9*). It has been found, for the HCl–MCl mixture, for example, that the activity coefficient of the first component ($\log \gamma_1$) can, in general, be expressed as

$$\log \gamma_1 = \log \gamma_1{}^0 - \alpha_{12}m_2 - \beta_{12}m_2{}^2 \qquad (1)$$

where $\gamma_1{}^0$ is the activity coefficient of hydrochloric acid in its own solution (without MCl) at a molality equal to the total molality of the solution to which γ_1 refers. The quantities α_{12}, β_{12}, ... are functions of the total ionic strength but not of the ionic strength fraction of the second component y_2 ($=m_2/m$). In many cases the simple linear equation, the so-called Harned rule (*9*)

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