Hulstkamp (*2*), 0.8585, and that by Tarova-Pollack, 0.8581 (*6*).

Glossary

d	density, g cm^{-3}
t	temperature, °C

Registry No. Cyclodecane, 293-96-9.

Literature Cited

(1) Barbarin-Castillo, J.-M. Ph.D. Thesis, University of Sheffield, U.K., 1984.
(2) Plattner, P. A., Hulstkamp, J. *Helv. Chim. Acta* **1944**, *27*, 220-230.
(3) Hales, J. L.; Gundry, H. A. *J. Phys. E* **1983**, *16*, 91-95.
(4) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 987-105.
(5) Meyer, E. F.; Hotz, C. A. *J. Chem. Eng. Data* **1976**, *21*, 274-278.
(6) Tarova-Pollack, M. B. *Zh. Obshch. Khim.* **1961**, *31*, 1976.

Received for review October 15, 1984. Accepted January 8, 1985. J.-M. B.-C. thanks the Consejo Nacional de Ciencia y Tecnologia de Mexico (CONACYT) for the bursary and the Universidad de Nuevo Leon for the leave of absence that enabled him to participate in this work. We gratefully acknowledge the receipt of a Grant-in-Aid from the Royal Society that permitted the purchase of the density balance from the National Physical Laboratory, London.

Excess Enthalpy and Liquid–Liquid Equilibrium Surfaces for the Cyclohexane–2-Propanol–Water System from 293.15 to 323.15 K

John R. Battler, William M. Clark, and Richard L. Rowley*[†]

Department of Chemical Engineering, Rice University, Houston, Texas 77251

Excess enthalpy data and liquid–liquid equilibrium (LLE) coexistence curves have been measured for ternary mixtures containing cyclohexane, 2-propanol, and water. Binary heats of mixing for cyclohexane–2-propanol and 2-propanol–water mixtures were measured at 293.15, 298.15, 303.15, and 323.15 K over the entire composition range with a Tronac flow calorimeter. Ternary, single-phase heats of mixing were measured at 293.15, 298.15, 303.15, and 308.15 K. Ternary liquid–liquid coexistence curves were measured at 298.15, 303.15, and 308.15 K by using the titration technique; tie lines were obtained from Karl Fischer water analyses of coexisting phases in conjunction with the measured coexistence curves. These results have been used to evaluate the explicit temperature dependence of liquid mixture models currently used to correlate LLE data against the Gibbs–Helmholtz identity which relates excess enthalpy and excess free energy. Existing models were found to be inadequate to predict phase behavior from excess enthalpy data using this identity. A recently proposed enthalpy-based method, previously used for binary systems, can be used to obtain reasonable binodal curves from heats of mixing although predicted tie lines are unreliable.

Introduction

Because of the importance of liquid–liquid equilibria (LLE) data to development of chemical and physical processes such as liquid–liquid extraction and tertiary oil recovery, efforts have been made to correlate LLE data using the same excess free energy (g^E) models that have proved effective in correlating vapor–liquid equilibrium (VLE) data (*1*, *2*). On the other hand, if the temperature dependence of existing g^E models is correct, then predictions of LLE data (as opposed to correlation of the experimental data) from excess enthalpy data, h^E, should be possible based on the Gibbs–Helmholtz equation

$$h^E = [\partial(g^E/T)/\partial(1/T)]_{P,x} \tag{1}$$

In theory, g^E models could be differentiated to obtain the corresponding h^E function in terms of the adjustable parameters of the models. These parameters could then be used in the original g^E function to predict LLE. The agreement of such predictions with experimental data constitutes a stringent test of the model's assumed temperature dependence. The use of such a technique for prediction of binary LLE can be found elsewhere (*3*) and is tested here for ternary LLE. Generally, h^E and LLE data have been correlated separately by using these models (*1*, *2*, *4*, *5*), but limited simultaneous fitting of LLE and h^E data has been done (*6*).

We report here experimental excess enthalpy data and LLE coexistence curves for the cyclohexane–2-propanol–water system over a small temperature range. These data have been used to test the explicit temperature dependence of liquid mixture models currently used for LLE correlation and that of an enthalpy-based local-composition model (EBLCM) recently proposed by Rowley and Battler (*3*) for prediction of binary LLE from h^E data. That method has been extended to ternary systems in this work.

Experimental Section

Heats of mixing were measured with a commercial, Tronac Model 450/550, isothermal calorimeter with a flow insert of design similar to that of Christensen et al. (*7*). As the calorimeter has been adequately described elsewhere, only modifications made in this laboratory will be detailed here. Two ISCO high-precision, positive-displacement, syringe-type pumps were used to establish constant flow rates through the flow mixing cell. The pumps' stepper motors were driven at constant but variable flow rates by a North Star Horizon microcomputer and a frequency-to-voltage converter built by Alan Pennock, a laboratory technician. The pumps (of variable flow rate from 0.008 to 200 mL/h) were calibrated over the range 0.10–1.30 mL/min by using replicate flow runs of distilled water. Pump calibrations were linear and indicated a reliability of better than 0.2% of the set flow rate over the entire calibrated range; the maximum observed deviation in replicate calibration runs was 0.4% at one of the slower flow rates. The pumps were thoroughly cleaned whenever a change in components was made and thoroughly rinsed and purged several times with the new fluid whenever a new component or mixture was introduced into the pump cylinders. Additionally, measured densities of the fluid before and after pumping were compared as a contamination check.

[†] Present address: Department of Chemical Engineering, Brigham Young University, Provo, UT 84602.

0021-9568/85/1730-0254$01.50/0

The two liquids to be mixed were pumped through 1/16 in. o.d. stainless steel lines and through combination heat exchanger/pulse dampener coils made of the same 1/16 in. tubing submerged with the flow mixing cell in a constant-temperature bath. The heat exchanger coils consisted of approximately 50 coils, each, of the stainless steel tubing wound into a coil 0.115 m in diameter. Total flow rate of the fluid was maintained at 1.000 mL/min, which allowed adequate time for thermal equilibration within these heat exchangers. The bath temperature was maintained to ±0.001 K of the set point with a Tronac Model PTC-41 precision temperature controller. The set point and the above-mentioned bath fluctuations were monitored with a Hewlett-Packard Model 2804A quartz thermometer of 0.1 mK resolution and better than ±0.04 K calibrated accuracy, NBS traceable to IPTS-68. A back-pressure regulator in the combined calorimeter effluent stream maintained constant pressure, although all of the data reported in this work were measured at 1.0 atm.

The flow insert itself contains another short thermal equilibration section, essentially a parallel-flow, double-tube heat exchanger. While one of the feed lines forms the inner tube, the other, having been silver soldered into a 0.159 cm o.d., thin-walled, stainless steel tube, coaxial with the first tube, becomes the outer tube of the heat exchanger. Mixing occurs at a point where the inner tube abruptly ends dumping the two fluids together in the larger o.d. tube. The remainder of the tube, from the point of mixing to the flow insert's outlet, is filled with short segments of crimped stainless steel turnings to promote thorough mixing. The mixing tube is 1.83 m long and is coiled in a flat spiral which is mounted on the isothermal plate with a high thermal conductivity epoxy. Isothermicity of this plate is maintained with a Peltier cooler and wafer control heater as described elsewhere (*7*). The changes in pulse frequency of the control heater required to maintain isothermal conditions as fluid mixing occurs serve as the output data which are then transferred to the previously mentioned microcomputer for storage and analysis.

For binary runs, each pump was filled with a separate pure component; for ternary, a binary mixture of 2-propanol and water was used in one pump, pure cyclohexane in the other. The cyclohexane was Baker Analyzed reagent grade with a label-specified purity of better than 99.8%. The 2-propanol was Mallinckrodt lot KLLA with a water content of 0.004% by weight. Both were used without further purification. Water was distilled and deionized before use. Karl Fischer titration was used to verify the water content of 2-propanol–water mixtures before filling the pumps. Molar flow rates were determined from volumetric flow rates by using molecular weights and measured densities at 298.15 K, the ambient temperature of the pump cylinders. Densities were measured in this laboratory by using a $4^1/_2$ digit, Mettler Paar densitometer with a calibrated accuracy of ±0.0001 g/mL. Pure-component densities of cyclohexane, 2-propanol, and water were found to be 0.7736, 0.7808, and 0.9971 g/mL, respectively, at 298.15 K. Mixtures of water and 2-propanol, used in lieu of the pure component for the ternary runs, had densities of 0.8080 g/mL at 28.9 mol % water and 0.8090 g/mL at 29.7 mol %, both at 298.15 K.

Electrical and chemical calibrations were performed on the calorimeter. Electrical calibrations of the control heater's energy per pulse were made before and after each run; flow was entirely from one pump at the beginning and from the other at the end of the run. Heater calibrations generally agreed to better than 0.25%. Runs were made at roughly 10 different compositions, the computer decrementing the flow rate of one pump and incrementing the flow rate of the other to maintain a constant 1.000 mL/min overall flow rate for each new composition. Software control of the pumps required stable isothermal behavior before flow rates could be changed to the next mixing composition. Heats of mixing were determined from the change in control heater pulse rate, measured liquid densities, and calibrated flow rates. Three replicates were performed for each system at each temperature. Replicates agreed to within 2 J/mol over the entire composition range. Chemical calibration consisted of measuring heats of mixing for the cyclohexane–benzene system at 298.15 K and comparing with well-established literature data; the results are shown in Table I. The average absolute deviation (AAD) between the data from this calorimeter and that reported by Elliott and Wormald (*8*) was 0.41% with a maximum error of 0.75%. Based on this comparison, the heat of mixing data reported herein are expected to have an accuracy of ±0.5%.

Table I. Chemical Calibration Check of Flow Calorimeter Comparing Measured and Literature (*9*) Heats of Mixing for the Cyclohexane (1)–Benzene (2) System at 298.15 K

[comp 1], mol %	h^E, J/mol		
	exptl	lit.	AAD, %
88.09	327.77	327.7	0.02
76.68	560.87	561.0	0.02
65.73	709.60	710.2	0.08
55.22	782.43	785.4	0.38
45.12	789.83	794.4	0.58
35.40	738.20	743.1	0.66
26.05	632.83	636.4	0.56
17.05	472.23	475.8	0.75
8.37	261.57	263.2	0.62

The titration method was used to determine LLE coexistence curves. Each point on the binodal curve was located by titrating a solution in the homogeneous region with the appropriate pure component until the cloud point was reached as determined visually. The consolute component, 2-propanol, was added to return the mixture to the one-phase region for subsequent titration to the next cloud point. The somewhat subjective (visual) evaluation of the cloud point constitutes the largest experimental error. We estimate the accuracy of the cloud points to be ±0.25 wt %. A consistency check on identification of the end point was occasionally made by slightly overtitrating and then back-titrating from the two-phase region. Cloud points approached from either side agreed within experimental accuracy.

Coexistence curve measurements were made in 8-mL vials submerged to within $^1/_4$ in. of the septum seal in a Neslab, 45-L, TXV 45 HT, visibility bath maintained to ±0.02 K. Additions to the vial were made through a long chromatographic needle from a micrometer-headed, precision syringe of 0.0001-mL resolution. Volumetric additions were converted to mass additions by using the previously measured densities. A second chromatographic needle through the septum allowed displacement of air during sample addition; at no time was the septum seal below water level. An air-driven magnetic stirrer was used to provide constant stirring during the titrations.

The tie-line cell was a screw-cap vial with several small-diameter syringe needles epoxyed through the cap, each extending to a different depth in the fluid mixture. Mixtures were gravimetrically prepared in the tie-line cell itself and thermostated with constant stirring for 1 h. Subsequently, approximately 2 h was allowed for phase separation and equilibration. Top and bottom phase samples were withdrawn from needles located at the appropriate fluid depth. Purge samples were taken and discarded from each of the used sample needles prior to collection of the sample for analysis. Warmed syringes were used for sample manipulation to ensure phase homogeneity (as the resultant data show, the phase envelope shrinks with increasing temperature) and were then analyzed for water content via Karl Fischer titration to ±0.5 wt %. Water content and previously measured binodal curve data fixed the composition of the tie-line ends. The initial overall composition of the mixture provided a consistency check of the tie-line end points

Table II. Measured Excess Enthalpy for Cyclohexane (1)–2-Propanol (2) Mixtures

	h^E, J/mol			
[comp 1], mol %	293.15 K	298.15 K	303.15 K	323.15 K
93.08	401.99	423.83	488.38	694.92
86.43	549.83	578.13	654.04	915.41
80.04	655.55	687.23	766.86	1052.56
73.90	725.77	761.72	840.68	1143.69
67.98	757.10	799.08	879.27	1196.49
62.28	749.02	799.54	884.97	1216.80
56.79	742.74	797.30	883.02	1210.44
51.49	727.84	781.88	861.75	1185.29
46.38	702.15	754.08	830.49	1142.73
41.44	666.28	715.13	786.30	1081.96
36.67	624.39	669.01	733.46	1012.96
32.06	573.55	613.52	667.33	922.44
27.59	517.55	552.17	596.36	828.56
23.27	456.56	486.24	522.64	727.96
19.09	388.24	411.30	442.41	618.35
15.03	317.88	336.06	360.24	503.91
11.10	241.48	254.19	273.13	380.45
7.29	163.52	170.55	185.41	256.28

Table III. Measured Excess Enthalpy for 2-Propanol (1)–Water (2) Mixtures

	h^E, J/mol			
[comp 1], mol %	293.15 K	298.15 K	303.15 K	323.15 K
90.15	215.39	241.39	234.29	193.91
81.69	238.70	285.67	302.66	324.12
74.33	191.74	275.82	292.33	404.75
67.88	138.03	215.11	252.43	416.58
62.17	79.33	157.35	199.71	406.42
57.09	13.37	98.39	154.88	383.15
52.54	−30.72	57.42	91.03	345.60
48.43	−85.02	1.58	28.28	304.43
35.39	−300.28	−195.29	−164.14	130.99
26.05	−445.34	−371.38	−337.23	−43.52
19.01	−553.81	−502.39	−456.74	−168.85
13.53	−646.07	−582.50	−546.30	−264.64
9.14	−664.40	−622.48	−582.70	−325.24
5.54	−600.10	−581.01	−492.96	−311.13
2.54	−343.30	−329.23	−273.37	−181.96

since all three points must be collinear. Tie-line end points are expected to have the same accuracy as the coexistence curve data, ±0.25 wt %. As an additional check, the composition of two tie-line end points, one at 293.15 K and the other at 298.15 K, were analyzed for all three components by using a gas chromatograph for the cyclohexane and 2-propanol analyses in addition to Karl Fischer titrations for the water content. The results agreed within experimental uncertainty with the previously described method's results.

Results

Experimental heats of mixing for the two completely miscible binaries, cyclohexane–2-propanol and 2-propanol–water, are shown in Tables II and III, respectively, for 293.15, 298.15, 303.15, and 323.15 K. Ternary heats of mixing measured at 293.15, 298.15, 303.15, and 308.15 K, shown in Table IV, increased with increasing temperature. Experimental LLE binodal data measured, at 293.15, 303.15, and 323.15 K, and the measured tie lines are shown in Tables V and VI, respectively. The 298.15 K tie line agrees well with the solubility curve reported by Verhoeye (*9*).

Table IV. Measured Excess Enthalpy for Cyclohexane (1)–2-Propanol (2)–Water (3) Mixtures

		h^E, J/mol			
[comp 1], mol %	[comp 2], mol %	293.15 K	298.15 K	303.15 K	308.15 K
2.68	69.19	234.38	334.17	367.75	408.13
5.70	67.05	316.19	422.40	463.07	505.19
8.76	64.87	384.58	499.55	542.82	590.24
11.98	62.58	443.26	549.54	607.06	659.08
15.36	60.18	492.67	606.04	665.35	723.11
18.91	57.66	533.63	649.22	711.76	774.55
22.66	54.99	567.15	682.77	749.31	815.37
26.62	52.17	594.01	710.18	779.86	851.37
30.81	49.19	615.02	735.17	808.83	886.14
35.24	46.04	630.78	751.92	825.56	906.57
39.95	42.70	641.68	762.43	836.04	921.27
44.95	39.14	647.44	766.90	840.67	925.90
50.27	35.35	647.06	762.24	834.51	922.88
55.95	31.32	638.32	743.47	820.23	905.58
62.02	27.00	617.45	715.24	789.81	874.57
68.52	22.38	578.63	676.83	745.23	829.71
75.52	17.41	513.41	605.23	669.66	751.98
83.05	12.05	411.19	496.67	561.36	642.15
91.18	6.27		283.41	387.94	

Table V. Binodal Curve for Cyclohexane (1)–2-Propanol (2)–Water (3) Mixtures

293.15 K		303.15 K		323.15 K	
[comp 1], mol %	[comp 2], mol %	[comp 1], mol %	[comp 2], mol %	[comp 1], mol %	[comp 2], mol %
62.40	27.75	63.46	26.65	65.27	24.78
47.57	34.64	48.12	34.06	48.66	33.48
37.85	37.62	38.34	37.10	38.74	36.66
30.38	39.28	31.19	38.39	31.56	37.98
24.39	40.18	25.52	38.90	26.06	38.29
19.56	40.48	20.92	38.92	21.79	37.92
15.90	40.02	17.05	38.67	18.45	37.04
12.95	39.21	13.98	38.00	15.67	36.00
10.64	38.07	11.50	37.03	13.26	34.93
8.72	36.78	9.50	35.85	11.21	33.77
7.20	35.33	7.80	34.60	9.43	32.60
5.93	33.83	6.46	33.17	7.88	31.42
4.92	32.23	5.34	31.70	6.54	30.22
4.03	30.69	4.43	30.18	5.41	28.95
3.31	29.11	3.63	28.72	4.49	27.62
2.76	27.49	3.02	27.15	3.74	26.24
2.20	26.02	2.46	25.69	3.08	24.89
1.82	24.46	2.00	24.23	2.56	23.49
1.46	22.98	1.63	22.76	2.11	22.13
1.15	21.55	1.25	21.42	1.69	20.85
0.90	20.15	1.03	19.98	1.38	19.51
		0.78	18.66	1.16	18.16
		0.61	17.32	0.97	16.84
		0.44	16.06	0.08	15.58

Table VI. Measured Tie Lines for the Cyclohexane (1)–2-Propanol (2)–Water (3) System

	water-rich phase		cyclohexane-rich phase	
T, K	[comp 1], mol %	[comp 2], mol %	[comp 1], mol %	[comp 2], mol %
293.15	16.37	40.13	44.82	35.54
298.15	17.49	39.68	37.23	37.61
303.15	7.01	33.77	46.73	34.59
303.15	9.02	35.54	42.85	35.83
303.15	10.58	36.46	40.42	36.37
303.15	12.82	37.58	36.70	37.42
303.15	13.95	37.97	34.40	37.89
303.15	17.16	38.64	30.34	38.47
303.15	19.37	38.86	28.45	38.65

The above data have been used to test the temperature dependence of the more commonly used local composition liquid mixture models. Recently, an attempt to predict binary LLE coexistence curves from heat of mixing data was reported (*3*). Prior work focused on possible simultaneous correlation of LLE, VLE, and excess enthalpy, often utilizing an empirical temperature dependence for the model parameters (*6*, *10*, *11*). Some success has been noted in VLE predictions from excess enthalpies by using local composition models (*12*–*15*), but generally simultaneous correlation of g^E and h^E has been un-

Table VII. Model Parameters Fitted from Experimental h^E Data

parameter	cyclohexane–2-propanol	2-propanol–water	cyclohexane–water
	NRTL Model		
a_{21}, J/mol	350.19	−2481.25	−2463.99
a_{12}, J/mol	6375.06	10606.61	10453.55
AAD, %	14.08	221.20	9.55
	Modified NRTL Model		
a_{21}, J/mol	4320.22	−19339.88	−86792.84
a_{12}, J/mol	−18737.81	1083.72	770.94
b_{21}, J/(mol K)	−60.97	109.60	352.19
b_{12}, J/(mol K)	95.83	−54.87	−136.85
AAD, %	3.24	55.45	5.70
	UNIQUAC Model		
a_{21}, K	792.37	−120.49	370.85
a_{12}, K	119.91	658.09	445.09
AAD, %	15.61	130.30	19.37
	Modified UNIQUAC Model		
a_{21}, K	600.57	−1055.10	79.89
a_{12}, K	559.08	−314.43	1390.53
b_{21}, K^2	−75290.03	362906.47	26410.63
b_{12}, K^2	90623.20	−41445.41	8599.36
AAD, %	8.21	54.06	6.13
	Wang–Chao Model		
a_{21} J/mol	69.70	9069.96	−1072.99
a_{12}, J/mol	1741.35	1318.46	1286.77
AAD, %	13.99	190.58	14.09
	EBLCM Model		
a_{21}, J/mol	−889.61	−2012.06	−2276.71
a_{12}, J/mol	11831.73	−7373.82	−11040.92
h_{21}, J/mol	2187.92	1677.85	−318.34
h_{12}, J/mol	40239.66	−1161.48	557.04
b, J/(mol K)	50.77	52.38	77.13
AAD, %	2.43	43.89	2.37

reliable (*11*, *16*) and applicable to only a few systems (*17*).

The models tested here were the NRTL (*18*), modified NRTL (*2*), UNIQUAC (*19*), modified UNIQUAC (*2*), Wang–Chao (*20*), and a recently proposed enthalpy-based local composition model (EBLCM) (*3*). The excess free energy, excess enthalpy, and activity coefficient equations for all of the models except EBLCM are available in the literature and are, therefore, not reproduced here for the sake of brevity. The modified UNIQUAC equation uses the two-parameter expression $a_{ij} + b_{ij}/T$ to replace the temperature-independent parameter in the original UNIQUAC equation while the modified NRTL model uses $a_{ij} + b_{ij}T$. The applicable EBLCM equations for multicomponent mixtures can be written as

$$h^E = \sum_i x_i \sum_j x_j h_{ji} G_{ji} / (\sum_k x_k G_{ki}) + \sum_i \sum_j x_i x_j b_{ij} (T - 300)/2 \qquad (2)$$

$$g^E = T(g^E/T)|_{T_{ref}} - RT \sum_i \sum_j \{(h_{ji}/a_{ji}) x_i \times \ln [(\sum_k x_k G_{ki})/(\sum_k x_k G_{ki,ref})]\} - \sum_i x_i \sum_j x_j [b_{ij} \ln (T/T_{ref}) + 300 b_{ij}(1 - T/T_{ref})]/2 \qquad (3)$$

$$\ln \gamma_i = \ln \gamma_{i,ref} - (\beta_i - \beta_{i,ref}) + (\alpha_i - \alpha_{i,ref}) - \delta_i \qquad (4)$$

where

$$G_{ji} = \exp(-a_{ji}/RT) \qquad (5)$$

$$\alpha_i = \sum_j \sum_k h_{kj} x_j [1 - G_{ij}/(\sum_l x_l G_{lj})]/a_{kj} \qquad (6)$$

$$\beta_i = \sum_j (h_{ji}/a_{ji}) \ln (\sum_k x_k G_{ki}) \qquad (7)$$

$$\delta_i = [T \ln (T/T_{ref}) + 300(1 - T/T_{ref})]\lambda_i/2RT \qquad (8)$$

$$\lambda_i = \sum_j x_j b_{ij} + \sum_l x_l \sum_j x_j (b_{lj} - b_{ij}) \qquad (9)$$

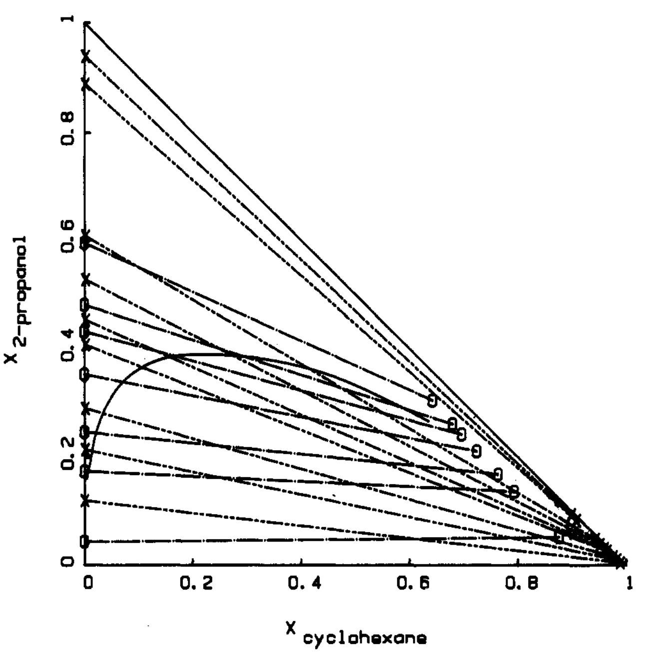

Figure 1. Phase behavior of the cyclohexane–2-propanol–water system at 303.15 K: (—) experimental binodal curve; (O—·—O) UNIQUAC predicted tie lines; (X—--—X) modified UNIQUAC predicted tie lines.

and a_{ji}, h_{ji}, and b_{ji} ($=b_{ij}$;b_{ii} = 0) are adjustable parameters. Adjustable parameters in each of the h^E equations were fitted to the experimental data of Tables II–IV by using a maximum likelihood technique (*1*). The parameters obtained from the fit and the percent AAD for each model are shown in Table VII. It is apparent that the models have trouble correlating the 2-propanol–water system's change from endothermic to exothermic mixing; it is therefore to be expected that the resultant LLE predictions will be quite poor. While the EBLCM with its larger number of parameters does a much better job of fitting the h^E data for all of the tested systems, it still has some trouble fitting this "S"-type behavior although the qualitative shape was at least correct for this model. It seems that a model with only a few parameters with the flexibility necessary to accurately fit the complexities of very nonideal systems is yet to be developed.

In order to fit model parameters with excess enthalpy data, some of the constants in existing equations were fixed at values suggested by their authors rather than treated as adjustable parameters. This was done to help preserve physical meanings for parameters which are lost when too many of them must be simultaneously fit. This is evidenced by the often poorer predicted phase behavior obtained without significantly improved h^E fits when these constants were treated as additional adjustable parameters. Therefore, the nonrandomness factor was taken as 0.2 in both versions of the NRTL model while the coordination number, z, was considered temperature independent and equal to 6 in the Wang–Chao equation and 10 in UNIQUAC.

Using the parameters obtained from the excess enthalpy data, we made predictions of the ternary phase diagram at 303.15 K for each of the six models and they are plotted in Figures 1–3. These calculations were done by using isoactivity conditions in coexisting phases

$$\ln (\gamma_i' x_i') = \ln (\gamma_i'' x_i''); \qquad i = 1, 2, 3 \qquad (10)$$

where the prime and double prime represent values in the two separate phases.

Predicted tie lines for both UNIQUAC versions indicate phase separation over nearly the entire composition range of the

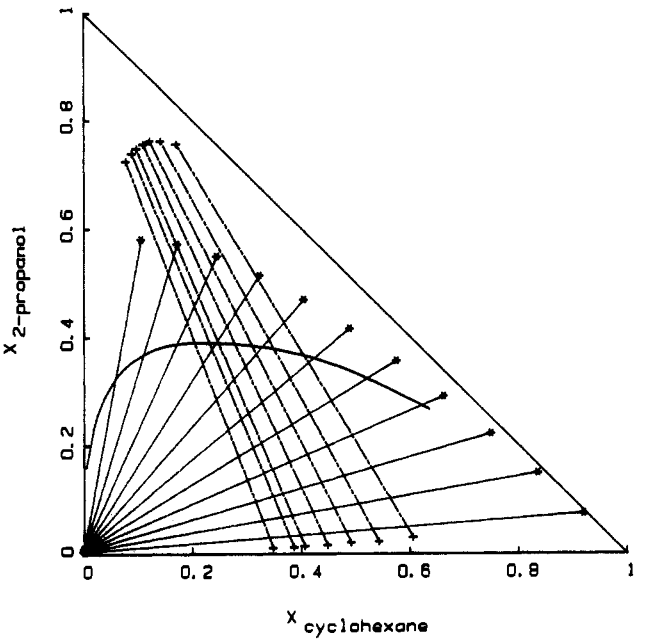

Figure 2. Phase behavior of the cyclohexane-2-propanol-water system at 303.15 K: (—) experimental binodal curve; (+— - —+) Wang-Chao predicted tie lines; (*—*) EBLCM predicted tie lines based on UNIFAC reference excess free energy.

ternary mixture as shown in Figure 1. This corresponds to a type II behavior (a band of phase separation across the entire phase diagram) while the actual behavior is of type I (exhibiting a plait point). Not shown in Figure 1, but quite disturbing, is the fact that the binary parameters for the cyclohexane-2-propanol system predict binary phase separation whereas the two components are actually soluble in all proportions. Also to be noted from Figure 1 is the slightly improved LLE surface of the original UNIQUAC over the temperature-modified version although the latter correlates the h^E data better. It appears unwise to introduce empirical temperature dependences into these models except for correlational work.

NRTL predictions of the LLE behavior were even less acceptable. Both the original version and the temperature-modified version predicted complete solubility of all three components over the entire composition range. This tendency has been noted in attempts at LLE prediction from VLE-fit parameters (*2*). The Wang-Chao equation's predictions are shown in Figure 2. They are erroneous, exhibiting tie lines approximately perpendicular to the actual ones with the wrong pair of components undergoing phase separation.

The EBLCM predictions require excess free energy data at some reference temperature. The method therefore requires more data than the other models; it utilizes heat of mixing data to extrapolate (with respect to temperature) from reference VLE data. It is well-known that the other models cannot predict LLE using VLE parameters (*1*). The VLE data of Verhoeye (*9*) at 330.15 K were used for the reference data, the experimental data first fitted to a Redlich-Kister expansion. Binary parameters for the two miscible pairs were fitted entirely from the binary VLE data while binary parameters for the immiscible pair and the ternary parameters were all fitted from the ternary data. The values of the parameters obtained for the reference g^E data are shown in Table VIII.

As shown in Figure 3, the binodal curve itself is traced out quite well by EBLCM. Similar agreement was also found at 293.15 and 323.15 K. Surprisingly, the tie lines change slope somewhat dramatically at higher cyclohexane compositions yielding poor tie-line predictions closer to the plait point without significantly worsening the binodal agreement. As it has been noted that EBLCM is quite sensitive to the quality of the reference data (*3*), it is assumed that a better fit of the reference data would provide better tie-line agreement but it appears that numerous parameters would be required to fit the ternary data adequately. Even with the Redlich-Kister expansion of Table VIII, the errors in activity coefficients were on the order of 7% for ternary points. Nevertheless, qualitative information on the binodal curve is possible (although the tie-line predictions will be unreliable) even with somewhat rough reference data as is shown in Figure 2, where UNIFAC has been used for the EBLCM reference at 298.15 K.

Table VIII. Fitted Parameters, c_{ij}, for the Reference Temperature Data (*4*) Using the Equation $g^E/RT_{ref} = \sum_{i=1}^{3} x_i(1 - x_i)\sum_{j=0}^{3} c_{ij}[x_i - (1 - x_i)]^j + x_1x_2x_3\sum_{i=1}^{3} c_{i+3,0}(1 - 2x_i)$ for the Cyclohexane (1)-2-Propanol (2)-Water (3) System

i/j	0	1	2	3
1	1.7386	0.2595	0.3966	0.2009
2	1.8251	−0.4237	0.1524	−0.6856
3	4.5091	1.5476	−0.2784	0.1737
4	−0.2252			
5	5.4268			
6	−2.2138			

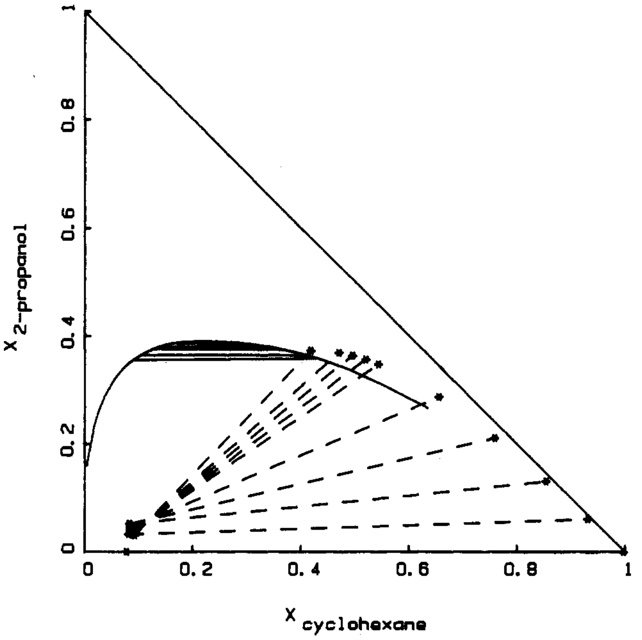

Figure 3. Phase behavior of the cyclohexane-2-propanol-water system at 303.15 K: (—) experimental binodal curve and tie lines; (*— — —*) EBLCM predicted tie lines.

Conclusions

The excess enthalpy and LLE behaviors of the cyclohexane-2-propanol-water system have been experimentally investigated at 293, 303, and 323 K. These data have been used to test the efficacy of currently popular liquid mixture models in predicting LLE from h^E data in accordance with the Gibbs-Helmholtz equation. It was found that existing models are inadequate to fit heats of mixing, especially for systems exhibiting S-shaped excess enthalpy vs. composition plots, that phase behavior predictions based on enthalpy-fit parameters were erroneous for the system modeled here, that modification of these equations with temperature-dependent parameters generally produced better h^E fits but poorer LLE predictions, and that the EBLCM model was able to produce reasonably good binodal curve results although the tie lines were erroneous at higher cyclohexane concentrations.

Glossary

h^E	excess enthalpy
g^E	excess Gibbs free energy
R	gas constant
T	temperature
x_i	mole fraction of component i
P	pressure
a_{ji}	adjustable parameter for i–j interactions
h_{ji}	adjustable parameter for i–j interactions
G_{ji}	nonrandomness weighting factor defined by eq 5
b_{ji}	adjustable parameter for i–j interactions
T_{ref}	reference temperature for EBLCM model
z	coordination number

Greek Letters

α	defined in eq 6
β	defined in eq 7
γ_i	activity coefficient of component i
δ	defined in eq 8
λ	defined in eq 9

Registry No. Cyclohexane, 110-82-7; 2-propanol, 67-63-0.

Literature Cited

(1) Prausnitz, J. M.; Anderson, J. F.; Grens, E.; Eckert, C. A.; Hsieh, R.; O'Connell, J. "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1980.

(2) Sorensen, J. M.; Arlt, W. "Liquid-Liquid Equilibrium Data Collection"; Dechema: Frankfurt, 1979; Vol. 5, Part 1.

(3) Rowley, R. L.; Battler, J. R. *Fluid Phase Equilib.* **1984**, *18*, 111-30.

(4) Magnussen, T.; Sorensen, J. M.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1980**, *4*, 151-62.

(5) Simonetty, J.; Yee, D.; Tassios, D. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 174-80.

(6) Malanowski, S.; Skjold-Jorgensen, S.; Rasmussen, P.; Fredenslund, Aa. *Chem. Eng. Sci.* **1981**, *36*, 1727-9.

(7) Christensen, J. J.; Hansen, L. D.; Eatough, D. J.; Izatt, R. M. *Rev. Sci. Instrum.* **1976**, *47*, 730-4.

(8) Elliott, K.; Wormald, C. J. *J. Chem. Thermodyn.* **1976**, *8*, 881-3.

(9) Verhoeye, L. A. J. *J. Chem. Eng. Data* **1968**, *13*, 462-7.

(10) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086-109.

(11) Skjold-Jorgensen, S.; Rasmussen, P.; Fredenslund, Aa. *Chem. Eng. Sci.* **1980**, *35*, 2389-403.

(12) Hanks, R. W.; Gupta, A. C.; Christensen, J. J. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 504-9.

(13) Hanks, R. W.; Tan, R. L.; Christensen, J. J. *Thermochim. Acta* **1978**, *27*, 9-18.

(14) Tan, R. L.; Hanks, R. W.; Christensen, J. J. *Thermochim. Acta* **1978**, *23*, 29-40.

(15) Pando, C.; Renuncio, J. A. R.; Hanks, R. W.; Christensen, J. J. *Thermochim. Acta* **1983**, *62*, 113-24.

(16) Hanks, R. W.; Tan, R. L.; Christensen, J. J. *Thermochim. Acta* **1978**, *23*, 41-55.

(17) Nicholaides, G. L.; Eckert, C. A. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 331-40.

(18) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135-44.

(19) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116-28.

(20) Wang, W.; Chao, K. C. *Chem. Eng. Sci.* **1983**, *38*, 1483-92.

Received for review May 29, 1984. Accepted October 29, 1984. Support of the heat of mixing work under NSF Grant No. CPE-8022908 and of the LLE studies under The Robert A. Welch Foundation Grant No. C-801 is gratefully acknowledged as are the fellowship supports for W.M.C. by the AMOCO Foundation and for J.R.B. by Phillips Petroleum.

Vapor–Liquid Equilibria in Mixtures Containing Carbon Dioxide, Toluene, and 1-Methylnaphthalene

William O. Morris and Marc D. Donohue*

Department of Chemical Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

Vapor–liquid equilibrium compositions were determined at pressures ranging from 259 to 14 450 kPa for three systems: the binaries carbon dioxide–toluene and carbon dioxide–1-methylnaphthalene; and the ternary carbon dioxide–toluene–1-methylnaphthalene. Binary equilibrium compositions are reported at 353.15, 383.15, and 413.15 K for the carbon dioxide–toluene system, and 353.15 and 413.15 K for the carbon dioxide–1-methylnaphthalene system. The liquid-phase solubility of carbon dioxide is found to be greater in toluene than in 1-methylnaphthalene. The ternary system was investigated at 353.15 and 413.15 K and with two initial liquid molar ratios of 1-methylnaphthalene to toluene: 9 to 1, and 4 to 1. The presence of toluene in the ternary system is found to increase the liquid-phase solubility of carbon dioxide. The vapor-phase solubility of 1-methylnaphthalene at 353.15 K is determined to be greater because of the presence of toluene, while the solubility at 413.15 K is found to be inhibited by the presence of toluene.

Introduction

Carbon dioxide is found in abundance in the natural gas and petroleum industries. Heavy aromatic compounds are also frequently encountered in these industries. The efficient design of separation and other processing equipment often requires accurate high-pressure vapor–liquid equilibrium data. High-pressure binary vapor–liquid equilibrium data on carbon dioxide–aromatic systems are scarce, and ternary equilibrium data on carbon dioxide–aromatic–aromatic systems are virtually nonexistent.

In this paper, we report vapor–liquid equilibrium data on three systems: the binary carbon dioxide–toluene; the binary carbon dioxide–1-methylnaphthalene; and the ternary carbon dioxide–toluene–1-methylnaphthalene. Equilibrium data are reported at temperatures of 353.15 (80.0 °C), 383.15 (110.0 °C), and 413.15 (140.0 °C) K, and pressures ranging from about 207 (30 psia) to 14 480 (2100 psia) kPa. The ternary system is investigated to determine how small amounts of toluene, when added to the carbon dioxide–1-methylnaphthalene system, affect the equilibrium compositions.

Ng and Robinson (*1*) report similar data on the carbon dioxide–toluene system at temperatures of 311.26 (38.11 °C), 352.56 (79.44 °C), 393.71 (120.56 °C), and 477.04 (203.89 °C) K. Tremper and Prausnitz (*2*) report the solubility of carbon dioxide in 1-methylnaphthalene at low pressures and temperatures up to 473.15 K (200 °C). Sebastian and co-workers (*3*) report the vapor–liquid equilibrium of the carbon dioxide–1-methylnaphthalene system at temperatures of 463.05 (189.9 °C), 543.45 (270.3 °C), 623.55 (350.4 °C), and 703.55 (430.4 °C) K, but pressures ranging from 2070 (300 psia) to only 5170 (750 psia) kPa. The only data found in the literature for a