J. Chem. Eng. Data **2000,** *45,* 555−558

Ternary and Quaternary Liquid−Liquid Equilibria for the Water + Cyclohexane + Ethyl Acetate and Water + Cyclohexane + Ethyl Acetate + Acetic Acid Systems at the Temperature 298.15 K

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The experimental ternary and quaternary liquid−liquid equilibrium results are reported for the water + cyclohexane + ethyl acetate and water + cyclohexane + ethyl acetate + acetic acid systems at 298.15 K. The ternary results were correlated by using the extended UNIQUAC model with binary and ternary parameters obtained in fitting the model to binary phase equilibria and ternary liquid−liquid equilibrium tie-lines. The quaternary results were predicted using the binary and ternary parameters and further compared with those reproduced by using additional quaternary parameters.

Introduction

Liquid−liquid equilibria for multicomponent mixtures are not only useful for solvent extraction process design but also of interest in developing a thermodynamic predictive and correlative method (Prausnitz et al., 1980; Novák et al., 1987). In the recovery of acetic acid from aqueous and organic biphase mixtures, for example, the solubility and tie-line data of acetic acid in a wide variety of mixtures are important, where there is always a need for precise measurements and accurate and quantitative description of the ternary and quaternary liquid−liquid equilibria for the aqueous−organic mixtures. The Gibbs free energy models (Nagata, 1990; Tamura et al., 2000a,b) have been so far proposed to represent accurately multicomponent liquid−liquid equilibria by introducing ternary and quaternary parameters in addition to binary parameters.

In this paper we present the experimental ternary and quaternary liquid−liquid equilibria for the water + cyclohexane + ethyl acetate and water + cyclohexane + ethyl acetate + acetic acid systems measured at 298.15 K. Further, we represent accurately the experimental ternary and quaternary results by using the extended UNIQUAC model (Nagata, 1990), having the binary, ternary, and quaternary parameters without distorting a good description of the binary systems. The binary parameters were obtained fitting the model to the binary vapor−liquid equilibria and mutual solubilities relevant to the present ternary and quaternary liquid−liquid equilibria. The ternary and quaternary parameters were determined using the ternary and quaternary liquid−liquid equilibrium results.

Experimental Section

All chemicals were guaranteed reagent grade (Wako Pure Chemicals, nominal purity > 99.5 mass %) and used without further purification. The GLC analysis did not show any appreciable peaks of impurities for all the components and determined >99.8 mass % purities for acetic acid, cyclohexane, and ethyl acetate. The densities of the chemicals used, measured with an Anton-Paar densimeter (DMA-58) at 298.15 K, agreed satisfactorily with the literature values (Riddick et al., 1986) and are given in Table 1. All compounds were stored under dry nitrogen to avoid contamination by moisture.

Table 1. Densities, ρ, of the Chemicals

	ρ (298.15 K)/g·cm^{-3}	
component	exptl	lit.[a]
water	0.997 03	0.997 05
cyclohexane	0.773 86	0.773 89
ethyl acetate	0.894 52	0.894 55
acetic acid	1.043 90	1.043 92

[a] Riddick et al., 1986.

The liquid−liquid equilibrium apparatus and experimental procedure were previously described in detail (Tamura et al., 2000a). The measurements were performed at 298.15 K in a thermostated water bath. The equilibrium temperature was monitored with a calibrated quartz thermometer (Tokyo Denpa, DMT-610B) within an accuracy of ±0.01 K. The mixture placed in an equilibrium cell, whose volume is about 70 cm^3 in the absence of a vapor space, was stirred with a Teflon-coated magnetic stirrer for 3 h and then kept >3 h, enough for phase separation. The initial quaternary mixture in the cell was prepared by mixing binary mixtures of ethyl acetate and cyclohexane with pure water and then acetic acid stepwise to cover almost the full range of the two-phase region for the quaternary mixture. The compositions of the initial binary mixtures formed by ethyl acetate and cyclohexane were approximately 0.25, 0.5, and 0.75 in mole fraction of ethyl acetate. The detailed procedure of the quaternary liquid−liquid equilibrium measurement is described elsewhere (Arce et al., 1998; Tamura et al., 2000a).

The compositions of equilibrated mixtures for two layers were determined using a thermal conductivity GLC (Shimadzu, GC-8A) equipped with an electronic integrator (Shimadzu Chromatopac, C-R6A). A 3-m glass spiral column (i.d. 3 mm) packed with TSG-1 coated on Shincarbon-A was used to separate every component. The column oven temperatures of the injection port and detector were

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10.1021/je990327j CCC: $19.00

Table 2. Experimental Liquid−Liquid Equilibrium Mole Fractions for the Ternary System Water (1) + Ethyl Acetate (2) + Cyclohexane (3) at 298.15 K

phase I		phase II		phase I		phase II	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.0057	0.3100	0.9911	0.0088	0.0376	0.7239	0.9867	0.0132
0.0217	0.4894	0.9893	0.0106	0.0455	0.7599	0.9861	0.0138
0.0259	0.5670	0.9880	0.0119	0.1047	0.8003	0.9838	0.0161
0.0370	0.6457	0.9865	0.0134				

Table 3. Experimental Liquid−Liquid Equilibrium Mole Fractions for the Quaternary System Water (1) + Ethyl Acetate (2) + Acetic Acid (3) + Cyclohexane (4) at 298.15 K

phase I			phase II		
x_1	x_2	x_3	x_1	x_2	x_3
0.0108	0.1145	0.0630	0.5803	0.0753	0.3363
0.0129	0.0795	0.0960	0.4458	0.0808	0.4547
0.0232	0.0723	0.1341	0.3824	0.0873	0.5041
0.0284	0.1666	0.0644	0.6466	0.0800	0.2676
0.0043	0.0244	0.1181	0.3310	0.0352	0.6056
0.0069	0.0684	0.0536	0.5900	0.0496	0.3573
0.0077	0.0299	0.1556	0.2791	0.0459	0.6362
0.0090	0.0310	0.0981	0.4102	0.0363	0.5372
0.0104	0.0379	0.0818	0.4646	0.0403	0.4825
0.0157	0.3305	0.0572	0.8478	0.0321	0.1182
0.0180	0.1059	0.0496	0.6623	0.0500	0.2818
0.0019	0.0171	0.1630	0.2264	0.0268	0.6961
0.0054	0.0246	0.0627	0.5357	0.0207	0.4379
0.0067	0.0374	0.0429	0.6393	0.0238	0.3332
0.0070	0.0191	0.0722	0.5009	0.0188	0.4733
0.0076	0.0176	0.1440	0.2844	0.0217	0.6533
0.0089	0.0772	0.0315	0.7598	0.0240	0.2152
0.0112	0.0200	0.2413	0.1588	0.0317	0.7318
0.0129	0.1339	0.0256	0.8602	0.0167	0.1217
0.0133	0.0181	0.0892	0.4428	0.0217	0.5276
0.0220	0.0169	0.1142	0.4086	0.0162	0.5519

Table 4. Structural Parameters, *r*, *q*, and *q*′, for Pure Components

component	r_i	q_i	q_i'
water	0.92	1.40	0.96
cyclohexane	3.97	3.01	1.25[a]
ethyl acetate	3.48	3.12	1.26[a]
acetic acid	2.23	2.04	0.90

[a] $q_i' = q^{0.2}$.

set at 403 K. The detector current was 100 mA at a helium flow rate of 0.5 $cm^3 \cdot s^{-1}$. Calibration of the GLC was done using gravimetrically prepared mixtures. Consider that the ratio of the peak area, A_i, for a sample mixture was obtained by the GLC and the response factor, S_i, for each component was defined by $S_i = A_i/w_i$. Using the A_i and S_i for every component, predetermined as 1.82 for water, 1.27 for ethyl acetate, 1.35 for acetic acid, and 1.36 for cyclohexane, we can prepare a standard mixture whose mass composition, w_i, is known. The standard mixture was prepared by weighing on a Shimadzu AEX-180 balance precise to within 0.1 mg. We confirmed that the ratio of the peak area obtained for the standard mixture is equivalent to that of the sample mixture and then evaluated a true response factor, S_i, as follows:

$$S_i = (A_i/w_i)/\max(A_i/w_i) \tag{1}$$

where (A_i/w_i) means the response factor for the component having maximum concentration in the mixture. Finally, the mass composition of every component was calculated from eq 2 using the true response factor

$$w_i = (A_i/S_i)/\sum_i A_i/S_i \tag{2}$$

Three analyses at least were made to obtain a mean value for each mixture. The GLC analyses showed a good reproducibility. The experimental uncertainties of observed variables were estimated to be < ±0.001 in mole fraction.

The quaternary mixtures of the water + cyclohexane + ethyl acetate + acetic acid system, composed of two pairs of type I of the ternary systems water + ethyl acetate + acetic acid and water + cyclohexane + acetic acid and one pair of type II of the ternary system water + ethyl acetate + cyclohexane, show type C of the quaternary liquid−liquid equilibria according to the classification of Prausnitz et al. (1980). Tables 2 and 3 present the experimental tie-line data of the ternary water (1) + ethyl acetate (2) + cyclohexane (3) system and those of the quaternary water (1) + ethyl acetate (2) + acetic acid (3) + cyclohexane (4) system at 298.15 K.

Analysis of Results

The experimental results were reproduced using the extended UNIQUAC model (Nagata, 1990). The model includes the binary parameters τ_{ij} ($\tau_{ii} = 1$, $\tau_{ij} \neq \tau_{ji}$) and additional ternary τ_{jki} ($\tau_{iii} = 1$, $\tau_{jki} = \tau_{kji}$) and quaternary τ_{jkli} ($\tau_{iiii} = 1$, $\tau_{jkli} = \tau_{jlki} = \tau_{kjli} = \tau_{klji} = \tau_{ljki} = \tau_{lkji}$) parameters to represent precisely both of the ternary and quaternary liquid−liquid equilibria as well as constituent binary vapor−liquid equilibria and mutual solubilities. The activity coefficient of every component in the quaternary mixture is expressed elsewhere (Nagata, 1990). The pure-component size and area parameters, *r* and *q*, listed in Table 4, were taken from the tabulation (Prausnitz et al., 1980), and the interaction correction factors, *q*′, for water, cyclohexane, and ethyl acetate were available from Nagata (1990). The *q*′ for acetic acid was adjusted to reproduce the binary vapor−liquid equilibria as well as ternary liquid−liquid equilibria of the mixtures including acetic acid, and consequently was set to 0.90 in the present work. The coordination number was set equal to 10. The binary parameter, τ_{ij}, is expressed by the binary energy parameters, a_{ij}, as

$$\tau_{ji} = \exp(-a_{ji}/T) \tag{3}$$

The binary energy parameters of miscible constituent mixtures were obtained from the binary vapor−liquid equilibria by the following thermodynamic equations.

$$Py_i\Phi_i = x_i\gamma_i P_i^\circ \Phi_i^\circ \exp\{V_i^\circ(P - P_i^\circ)/RT\} \tag{4}$$

$$\ln \Phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})P/RT \tag{5}$$

where *P* is the total pressure, Φ is the fugacity coefficient, *y* is the vapor mole fraction, γ is the activity coefficient, and *P*° is the pure-component vapor pressure, calculated using the Antoine equation with coefficients taken from the literature (Riddick et al., 1986). *V*° is the liquid molar volume, obtained by a modified Rackett equation (Spencer and Danner, 1972). The pure and cross second virial coefficients, *B*, for the vapor mixtures of ethyl acetate and cyclohexane were estimated by the method of Hayden and O'Connell (1975). The fugacity coefficient of the vapor mixtures containing acetic acid was calculated by the chemical theory of vapor-imperfections (Nothnagel et al., 1973)

Table 5. Values of Binary Parameters in Eq 3 and Resulting Root-Mean-Squared Deviations in Pressure, Temperature, and Liquid and Vapor Mole Fraction: δP, δT, δx, and δy

system (1 + 2)	T/K	no. of data points	a_{12}/K	a_{21}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$	ref
water + cyclohexane	298.15	M.S.[a]	1545.4	2063.1					Sorensen and Arlt (1979)
water + ethyl acetate	298.15	M.S.	313.10	670.65					Merriman (1913)
water + acetic acid	293.15	10	-384.67	774.79	0.025	0.00	0.5	4.8	Lazeeva and Markuzin (1973)
cyclohexane + ethyl acetate	293.15	14	180.11	122.31	0.101	0.00	0.4	2.6	Slavin and Abramzon (1977)
cyclohexane + acetic acid	298.15	17	690.23	397.20	0.147	0.00	1.0	9.3	Lark et al. (1984)
ethyl acetate + acetic acid	315.15	6	496.94	-185.43	0.260	0.02	1.3	8.2	Gmheling et al. (1982)

[a] M.S., mutual solubility.

Table 6. Values of Ternary Parameters and Resulting Root-Mean-Squared Deviations at 298.15 K

system (1 + 2 + 3)	no. of tie-lines	τ_{231}	τ_{132}	τ_{123}	F/mol %		ref
					pred[a]	corr[b]	
water + cyclohexane + ethyl acetate	7	−0.1056	−0.1024	−1.2296	1.57	0.51	this work
water + cyclohexane + acetic acid	10	−0.0289	−0.3322	0.0397	1.68	0.84	Iguchi and Fuse (1970)
water + ethyl acetate + acetic acid	3	0.4425	0.2357	−0.0030	0.92	0.60	Blanco et al. (1980)

[a] Only binary parameters. [b] Used binary and ternary parameters.

Table 7. Values of Quaternary Parameters and Resulting Root-Mean-Squared Deviations at 298.15 K

system (1 + 2 + 3 + 4)	no. of tie-lines	τ_{2341}	τ_{1342}	τ_{1243}	τ_{1234}	F/mol %		ref
						pred[a]	corr[b]	
water + cyclohexane + ethyl acetate + acetic acid	21	0.9910	−0.0389	−11.0121	0.4023	1.54	1.26	this work

[a] Only binary and ternary parameters. [b] Used binary, ternary, and quaternary parameters.

$$\Phi_i = \frac{y_i}{y_{i_1}} \exp(-PB_{ii}^{\mathrm{F}}/RT) \tag{6}$$

where y_{i_1} is the monomer mole fraction of component i in the vapor phase and B_{ii}^{F} is the free contribution to the second virial coefficients of component i, calculated from the Hayden and O'Connell method. The binary energy parameters for the immiscible mixtures water + cyclohexane and water + ethyl acetate were calculated from mutual solubility data by solving the isoactivity relation of each component in two liquid phases I and II

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{7}$$

and the material balance

$$\sum_i x_i^{\mathrm{I}} = \sum_i x_i^{\mathrm{II}} = 1 \tag{8}$$

Table 5 gives the values of the binary energy parameters and the root-mean-squared deviations between the experimental and calculated values for the binary vapor−liquid equilibria. In the parameter estimation the maximum likelihood principle (Prausnitz et al., 1980) was used, where the standard deviations for the experimental values were taken as 0.13 kPa for pressure, 0.05 K for temperature, 0.001 for the liquid mole fraction, and 0.003 for the vapor mole faction.

Multicomponent liquid−liquid equilibrium calculations were performed by the thermodynamic criteria and material balance equation expressed by eqs 7 and 8. The ternary parameters were evaluated by minimizing the following objective function using a simplex method of Nelder and Mead (1965)

$$F = 10^2[\sum_k \min \sum_i \sum_j (x_{ijk,\mathrm{exptl}} - x_{ijk,\mathrm{calcd}})^2/M]^{0.5} \tag{9}$$

where min denotes minimum values, i = 1−3 for ternary mixtures or 1−4 for quaternary mixtures, j = phases I or II, k = 1, 2, ..., n (tie-lines), $M = 2ni$, x = liquid-phase mole fraction, and the subscripts exptl and calcd stand for experimental and calculated values. Table 6 shows the values of the ternary parameters and F of eq 9 in the ternary correlation, along with the results predicted by using the binary parameters alone. Figure 1 compares the calculated and experimental results for the ternary mixtures constituting the quaternary mixtures water + cyclohexane + ethyl acetate + acetic acid. The prediction by using the binary parameters alone cannot always give the accurate description for the ternary liquid−liquid equilibria, but the correlation obtained by including the ternary parameters describes the systems much better.

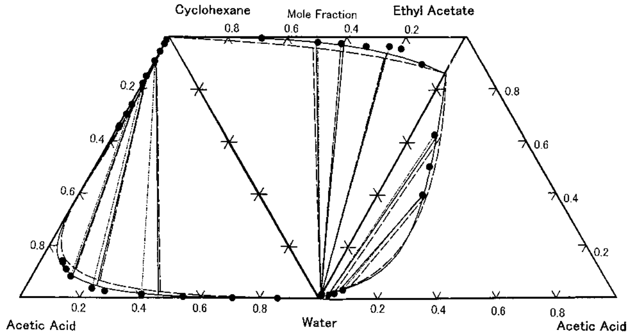

Figure 1. Experimental and calculated liquid−liquid equilibria at 298.15 K for ternary mixtures constituting quaternary water + cyclohexane + ethyl acetate + acetic acid: (−•−) experimental tie-line; (− − −) predicted by an extended UNIQUAC model with only binary parameters, taken from Table 5; (—) correlated by an extended UNIQUAC model with binary and ternary parameters, taken from Tables 5 and 6.

The quaternary parameters were obtained similarly by fitting the model with the binary and ternary parameters to the quaternary liquid−liquid equilibria. The quaternary liquid−liquid equilibrium results obtained with the binary, ternary, and quaternary parameters are compared with the experimental results. Table 7 gives the values of the quaternary parameters and the root-mean-squared deviations between the experimental and calculated values. The quaternary correlation obtained by using the binary, ternary, and quaternary parameters shows slightly better agreement with the experimental values than the prediction done by the binary and ternary parameters.

Conclusion

Ternary and quaternary liquid−liquid equilibria have been measured for the water + cyclohexane + ethyl acetate system and the water + cyclohexane + ethyl acetate + acetic acid system at 298.15 K, and the results were compared with the values calculated by the extended UNIQUAC model. Quantitatively good agreement between the experimental results and calculated values was obtained by the model including ternary and quaternary parameters in addition to binary parameters.

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Received for review December 22, 1999. Accepted March 8, 2000.

JE990327J