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Quaternary Liquid−Liquid Equilibria for the Acetonitrile + 1-Propanol + Cyclohexane + Heptane System at 298.15 K

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Experimental quaternary liquid−liquid equilibrium results are reported for acetonitrile + 1-propanol + cyclohexane + heptane at 298.15 K. The results were well represented using a proposed local composition model with binary, ternary, and quaternary parameters. The model was further applied to reproduce five quaternary liquid−liquid equilibria and their component ternary liquid−liquid equilibria for mixtures containing alcohol, acetonitrile, or water.

Introduction

Ternary and quaternary (or multicomponent) liquid−liquid equilibria are of interest in extraction operation and useful for developing a thermodynamic predictive and correlative method. As part of a series of studies to measure quaternary liquid−liquid equilibrium data at 298.15 K for mixtures containing acetonitrile and alcohol, the present paper reports measurements for acetonitrile + 1-propanol + cyclohexane + heptane. A flexible correlating equation for the excess Gibbs free energy is presented to reduce the present and literature experimental data for quaternary systems, and their component ternary and binary phase equilibrium data are available from the literature.

Experimental Section

Materials. All chemicals were guaranteed reagent grade (Wako Pure Chemicals, purity > 99.0 mass %) and used without further purification. A gas chromatographic analysis showed no significant peaks of impurities for all the components. The densities of the chemicals used, measured with an Anton-Paar densimeter at 298.15 K, agreed satisfactorily with literature values (Riddick and Bunger, 1970), as shown in Table 1.

Table 1. Densities *d* of the Chemicals

	d(298.15 K)/g·cm^{-3}	
component	exptl	lit.[a]
acetonitrile	0.776 50	0.776 60
cyclohexane	0.773 91	0.773 89
heptane	0.679 55	0.679 51
1-propanol	0.799 78	0.799 75

[a] Riddick and Bunger, 1970.

Procedure. Liquid−liquid equilibrium measurements at 298.15 K were performed as described previously (Nagata and Nakamura, 1985). The compositions of quaternary equilibrated mixtures were analyzed with a Shimadzu glc (GC-8A) and a Shimadzu Chromatopac (C-R6A). The experimental errors of the observed variables were within ±0.002 in mole fraction and ±0.02 K in temperature.

Data Analysis

We have correlated phase equilibrium data using the following expression of excess Gibbs energy in a quaternary mixture

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i}^{4} x_i \ln\frac{\Phi'_i}{x_i} - 5\sum_{ii}^{4} x_i q_i \ln\left(\frac{\Phi_i}{\theta_i}\right) - \sum_{i}^{4} x_i \ln\left(\sum_{j}^{4}\Lambda_{ij}x_j + \frac{1}{2}\sum_{j}^{4}\sum_{k}^{4}\Lambda_{jki}x_jx_k + \frac{1}{6}\sum_{j}^{4}\sum_{k}^{4}\sum_{i}^{4}\Lambda_{jkli}x_jx_kx_l\right) + \sum_{i}^{4} x_i \ln(\sum_{j}^{4} x_j\rho_{ij}) \qquad (1)$$

where the segment fraction Φ_i, the modified segment fraction Φ'_i, the surface fraction θ_i, and the binary parameter Λ_{ij} given in terms of the energy parameter a_{ij} are defined as below

$$\Phi'_i = \frac{x_i r_i^{3/4}}{\sum_{j}^{4} x_j r_j^{3/4}} \qquad (2)$$

$$\Phi_i = \frac{x_i r_i}{\sum_{j}^{4} x_j r_j} \qquad (3)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j}^{4} x_j q_j} \qquad (4)$$

$$\Lambda_{ij} = \left(\frac{r_j}{r_i}\right)\exp\left(\frac{-a_{ij}}{T}\right) \qquad (5)$$

and r_i and q_i are the pure-component structural parameters, which are available from Prausnitz et al. (1980), $\rho_{ij} = r_j/r_i$, $\Lambda_{ii} = 1$, $\Lambda_{ij} \neq \Lambda_{ji}$, and the ternary parameters Λ_{jki}

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Table 2. Values of Binary Parameters in Eq 5 and Resulting Root-Mean Squared Deviations in Pressure, Temperature, and Liquid and Vapor Mole Fraction: δP, δT, δx, δy

system (1 + 2)	t/°C	no. of data points	a_{12}/K	a_{21}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$	ref
water + acetone	25.0	13	1313.51	−531.71	0.72	0.10	5.9	12.2	Beare et al. (1930)
water + acetic acid	100.3−115.2	11	1558.31	−851.17	0.82	0.43	4.1	21.0	Gmehling et al. (1981)
water + 1-propanol	89.3−94.8	19	519.29	−430.60	0.16	0.09	2.1	5.5	Kojima et al. (1968)
acetone + acetic acid	35.0	12	303.45	−186.00	0.14	0.01	0.5	4.1	waradzin and Surovy (1975)
acetone + 1-propanol	62.9−86.6	6	117.21	88.89	0.23	0.11	1.6	3.5	Gültekin (1989)
acetone + 1-butanol	58.1−115.0	15	171.19	78.28	0.31	0.16	1.7	19.7	Michalski et al. (1961)
acetone + chloroform	35.0	9	−0.05	−236.03	0.22	0.00	0.6	3.9	Kudryavtseva and Susarev (1963)
acetic acid + butyl acetate	117.9−125.2	15	601.16	−347.36	0.43	0.19	2.1	20.2	Hirata and Hirose (1966)
acetic acid + 1-butanol	115.7−120.3	18	−162.53	401.88	0.14	0.07	1.1	10.2	Rius et al. (1959)
acetic acid + chloroform	61.5−113.7	10	645.93	−76.04	0.52	0.23	6.0	22.9	Campbell and Gieskes (1964)
acetonitrile + methanol	25.0	10	78.50	282.54	0.17	0.02	0.5	5.1	Nagata (1987a)
acetonitrile + 1-propanol	45.0	9	462.62	77.48	0.20	0.00	0.5	4.7	Nagata (1987b)
acetonitrile + 2-propanol	50.0	15	389.51	65.84	0.12	0.00	0.5	3.2	Nagata and Katoh (1980)
cyclohexane + heptane	25.0	30	−85.00	123.65	0.009	0.00	0.1	0.7	Martin and Youings (1980)
cyclohexane + 1-propanol	25.0	27	102.09	787.28	0.20	0.00	0.3		Hwang and Robinson (1977)
cyclohexane + 2-propanol	50.0	9	30.58	804.17	0.22	0.06	0.9	7.4	Nagata et al. (1973)
methanol + 2-propanol	55.0	20	188.56	−219.36	0.23	0.07	0.9	4.0	Freshwater and Pike (1967)
1-propanol + 1-butanol	40.0	13	89.10	−81.33	0.009	0.00	0.0		Oracz (1986)
1-butanol + butyl acetate	116.8−121.2	9	67.11	132.26	0.10	0.05	0.9	8.5	Sheinker and Peresleni (1952)
1-propanol + heptane	25.0	14	960.46	123.61	0.02	0.00	0.0		Sipowska and Wieczorek (1980)
water + 1-butanol	25.0	M.S.[a]	132.36	173.67					Ruiz et al. (1984)
water + butyl acetate	25.0	M.S.	1026.5	−278.50					Ruiz et al. (1984)
water + chloroform	25.0	M.S.	1335.6	618.47					Sørensen and Arlt (1979)
acetonitrile + cyclohexane	25.0	M.S.	1183.2	442.73					Nagata and Ohta (1983)
acetonitrile + heptane	25.0	M.S.	1206.7	522.06					Nagata (1987a)
methanol + cyclohexane	25.0	M.S.	1083.3	−26.08					Nagata (1984)

[a] M.S., mutual solubility.

Table 3. Values of Ternary Parameters in Eq 6 and Resulting Root-Mean Squared Deviation

system (1 + 2 + 3)	no. of tie lines	Λ_{231}	Λ_{132}	Λ_{123}	F/mol % pred[a]	F/mol % corr[b]	ref
methanol + 2-propanol + cyclohexane	7	−0.0090	0.7986	−0.1009	3.85	0.51	Nagata (1984)
water + acetic acid + chloroform	8	0.1444	−1.8492	−0.9469	4.65	0.30	Ruiz and Prats (1983a)
water + acetone + chloroform	8	0.3378	−0.7686	−0.7200	1.50	0.29	Ruiz and Prats (1983a)
1-butanol + acetone + water	5	2.1675	−3.0030	−3.8212	3.33	0.46	Ruiz and Prats (1983b)
water + acetic acid + 1-butanol	5	−0.1445	−6.4760	0.8265	1.44	0.36	Ruiz et al. (1984)
water + 1-propanol + 1-butanol	9	−1.4653	−0.5285	1.1220	1.69	0.41	Ruiz and Prats (1983b)
water + acetic acid + butyl acetate	15	1.1282	0.0259	1.1166	7.76	1.20	Ruiz et al. (1984)
water + 1-butanol + butyl acetate	4	−1.0914	0.8874	−0.4099	0.67	0.42	Ruiz et al. (1984)
acetonitrile + methanol + cyclohexane	7	−0.4616	0.0573	−0.0165	2.58	0.60	Nagata (1987a)
acetonitrile + 1-propanol + cyclohexane	8	0.1617	0.0723	−0.0285	2.81	0.55	Nagata (1987b)
acetonitrile + 2-propanol + cyclohexane	6	0.1667	−0.1247	−0.0679	0.60	0.42	Nagata (1994)
acetonitrile + 1-propanol + heptane	8	0.3085	−0.2037	−0.1279	5.18	0.39	Nagata (1987b)
acetonitrile + cyclohexane + heptane	8	0.1070	−0.4055	−0.0130	0.54	0.41	Nagata et al. (1995)

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

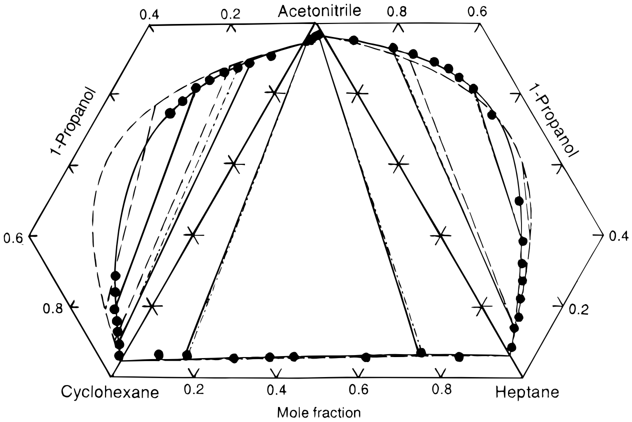

Figure 1. Experimental and calculated liquid−liquid equilibria for ternary systems constituting quaternary acetonitrile + 1-propanol + cyclohexane + heptane at 298.15 K: (- - -) predicted with only binary parameters; (—) correlated with binary and ternary parameters; (●− • − • −●) experimental tie line.

($=\Lambda_{kji}$) and quaternary parameters Λ_{jkli} ($=\Lambda_{jlki} = \Lambda_{kjli} = \Lambda_{klji} = \Lambda_{ljki} = \Lambda_{lkji}$) are incorporated to improve the flexibility of the model. These parameters are obtained by fitting this model to ternary and quaternary liquid−liquid equilibria. The first two terms of eq 1, proposed by Gmehling *et al.* (1990), accounting for combinatorial contribution, are included in a previous local composition model (Nagata *et al.*, 1996). The activity coefficient of component 1, derived by partial differentiation with respect to the mole number, is given by The expression of ln γ_2 is obtained by interchanging the subscripts 1 to 2, 2 to 3, 3 to 4, and 4 to 1. In a similar way, the expressions ln γ_3 and ln γ_4 can be given by cyclic advancement of the subscripts.

Calculated Results

Liquid−liquid equilibrium calculations were performed by solving the isoactivity relation of each component in two liquid phases. The binary energy parameters were obtained from vapor−liquid equilibrium data and mutual solubilities. Binary phase equilibrium data reduction was

Table 4. Experimental and Calculated Liquid−Liquid Equilibrium Mole Fractions for the Quaternary System Acetonitrile (1) + 1-Propanol (2) + Cyclohexane (3) + Heptane (4) at 298.15 K

x_1^{I}		x_2^{I}		x_3^{I}		x_1^{II}		x_2^{II}		x_3^{II}	
exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
0.8716	0.8906	0.0488	0.0452	0.0646	0.0514	0.0563	0.0608	0.0085	0.0130	0.6918	0.2434
0.7805	0.7951	0.1178	0.1132	0.0810	0.0729	0.0750	0.0732	0.0321	0.0380	0.6601	0.6578
0.7214	0.7402	0.1453	0.1491	0.1052	0.0875	0.0948	0.0832	0.0585	0.0557	0.6251	0.6367
0.6611	0.6810	0.1848	0.1845	0.1196	0.1055	0.1120	0.0974	0.0770	0.0782	0.5990	0.6086
0.5163	0.5242	0.2719	0.2559	0.1641	0.1691	0.1765	0.1715	0.1504	0.1671	0.4973	0.4897
0.8965	0.9025	0.0453	0.0428	0.0349	0.0312	0.0517	0.0646	0.0081	0.0113	0.4595	0.4537
0.8099	0.8151	0.1113	0.1083	0.0458	0.0433	0.0563	0.0723	0.0282	0.0333	0.4469	0.4381
0.7335	0.7363	0.1643	0.1621	0.0583	0.0570	0.0860	0.0843	0.0565	0.0588	0.4216	0.4223
0.6728	0.6521	0.2003	0.2126	0.0708	0.0739	0.1038	0.1063	0.1119	0.0957	0.3828	0.3902
0.6164	0.6246	0.2244	0.2272	0.0863	0.0799	0.1259	0.1162	0.1134	0.1103	0.3687	0.3760
0.5608	0.5709	0.2489	0.2522	0.1004	0.0936	0.1503	0.1492	0.1516	0.1505	0.3379	0.3395
0.8162	0.8125	0.1260	0.1171	0.0183	0.0209	0.0650	0.0754	0.0255	0.0351	0.2172	0.2129
0.7039	0.7043	0.2007	0.1916	0.0294	0.0306	0.0923	0.0952	0.0642	0.0739	0.2045	0.2024
0.6538	0.6338	0.2409	0.2328	0.0296	0.0373	0.1106	0.1174	0.1043	0.1092	0.1874	0.1835
0.6213	0.6186	0.2393	0.2409	0.0412	0.0395	0.1272	0.1269	0.1236	0.1213	0.1782	0.1807

Table 5. Values of Quaternary Parameters in Eq 6 and Resulting Root-Mean Squared Deviation at 298.15 K

system (1 + 2 + 3 + 4)	no. of tie lines	Λ_{2341}	Λ_{1342}	Λ_{1243}	Λ_{1234}	*F*/mol %	ref
acetonitrile + 1-propanol + cyclohexane + heptane	15	1.4771	−1.5318	5.5178	−2.2529	0.80	this work
water + acetone + acetic acid + chloroform	32	0.4264	13.7029	−3.6720	−5.0041	0.50	Ruiz and Prats (1983a)
water + acetone + 1-propanol + 1-butanol	26	−93.563	11.0101	44.5431	18.0928	0.41	Ruiz and Prats (1983b)
water + acetic acid + 1-butanol + butyl acetate	40	−6.5460	31.8099	−9.4089	−2.7944	0.91	Ruiz et al. (1984)
acetonitrile + 2-propanol + methanol + cyclohexane	14	0.5408	−2.5640	0.9001	0.4162	0.69	Nagata (1994)

$$
\begin{aligned}
\ln \gamma_1 = {} & \ln\left(\frac{\Phi'_1}{x_1}\right) + 1 - \frac{\Phi'_1}{x_1} - 5q_1\left(\ln\frac{\Phi_1}{\theta_1} + 1 - \frac{\Phi_1}{\theta_1}\right) - \\
& \ln\Big(\sum_i^4 \Lambda_{1i}x_i + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4\Big) + \\
& \ln\Big(\sum_j^4 x_j\rho_{1j}\Big) + \sum_k^4\left(\frac{x_j\rho_{k1}}{\sum_j x_j\rho_{kj}}\right) - \\
& x_1\left(\frac{1 - \Lambda_{231}x_2x_3 - \Lambda_{241}x_2x_4 - \Lambda_{341}x_3x_4 - 2\Lambda_{2341}x_2x_3x_4}{\sum_i^4 \Lambda_{1i}x_i + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4}\right) - \\
& x_2\left(\frac{\Lambda_{21} + \Lambda_{132}x_3(1-x_1) + \Lambda_{142}x_4(1-x_1) - \Lambda_{342}x_3x_4 + \Lambda_{1342}x_3x_4(1-2x_1)}{\sum_i^4 \Lambda_{2i}x_i + \Lambda_{132}x_1x_3 + \Lambda_{142}x_1x_4 + \Lambda_{342}x_3x_4}\right) - \\
& x_3\left(\frac{\Lambda_{31} + \Lambda_{123}x_2(1-x_1) + \Lambda_{143}x_4(1-x_1) - \Lambda_{243}x_2x_4 + \Lambda_{1243}x_2x_4(1-2x_1)}{\sum_i^4 \Lambda_{3i}x_i + \Lambda_{123}x_1x_2 + \Lambda_{143}x_1x_4 + \Lambda_{243}x_2x_4}\right) - \\
& x_4\left(\frac{\Lambda_{41} + \Lambda_{124}x_2(1-x_1) + \Lambda_{134}x_3(1-x_1) - \Lambda_{234}x_2x_3 + \Lambda_{1234}x_2x_3(1-2x_1)}{\sum_i^4 \Lambda_{4i}x_i + \Lambda_{124}x_1x_2 + \Lambda_{134}x_1x_3 + \Lambda_{234}x_2x_3}\right)
\end{aligned} \tag{6}
$$

carried out according to a computation method described by Prausnitz *et al.* (1980) using pertinent properties necessary in the calculations and the following thermodynamic equations.

$$Py_i\phi_i = x_i\gamma_i P_i^\circ\phi_i^\circ \exp\{V_i^\circ(P - P_i^\circ)/RT\} \tag{7}$$

$$\ln \phi_i = \Big(2\sum_j y_jB_{ij} - \sum_i\sum_j y_iy_jB_{ij}\Big)P/RT \tag{8}$$

where P is the total pressure, ϕ is the fugacity coefficient, y is the vapor mole fraction, γ is the activity coefficient, and P° and V° are the pure-component vapor pressure and liquid molar volume. P° values were calculated using the Antoine equation with coefficients taken from the literature (Brown and Smith, 1954; Riddick and Bunger, 1970), and a modified Rackett equation was used to estimate V° (Spencer and Danner, 1972). The pure and cross second virial coefficients B were obtained by the method of Hayden and O'Connell (1975). Table 2 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.

The ternary parameters were evaluated by minimizing the following objective function using a simplex method of Nelder and Mead (1965)

$$F = 100\Big[\sum_k^M \min \sum_i^3\sum_j^2 (x_{ijk,\mathrm{exptl}} - x_{ijk,\mathrm{calcd}})^2/6M\Big]^{0.5} \tag{9}$$

where min denotes minimum values, i = 1, 2, 3 (components), j = I, II (phase), and k = 1, 2, ..., M (tie lines). Table 3 shows the values of ternary parameters and F of eq 9, along with the results predicted by using the binary parameters alone. Figure 1 shows the calculated and experimental results for ternary systems constituting the quaternary system acetonitrile + 1-propanol + cyclohexane + heptane.

The quaternary parameters were similarly obtained by fitting the model with the binary and ternary parameters to quaternary liquid−liquid equilibria. The quaternary liquid−liquid equilibrium results obtained with the binary, ternary, and quaternary parameters are compared with the experimental results in Table 4. Table 5 gives the values of the quaternary parameters and the root-mean squared deviations (RMS) for five systems.

Conclusions

Quaternary liquid−liquid equilibria have been measured for acetonitrile + 1-propanol + cyclohexane + heptane at 298.15 K, and the results were correlated with the proposed model. Agreement between the experimental results and calculated values was good. The workability of the model was confirmed by comparing the calculated phase equilibrium compositions with the experimental results for 13 ternary and 5 quaternary systems.

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