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Quaternary Liquid−Liquid Equilibria of Acetonitrile + 2-Propanol + Cyclohexane + Heptane at 298.15 K

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Liquid−liquid equilibria for acetonitrile + 2-propanol + cyclohexane + heptane at 298.15 K were measured. The results were well correlated with the extended UNIQUAC and modified Wilson models with binary, ternary, and quaternary parameters.

Introduction

As part of continuous studies of liquid−liquid equilibria (LLE) on solutions involving an alcohol and acetonitrile, this work reports quaternary LLE for the acetonitrile + 2-propanol + cyclohexane + heptane system at 298.15 K. The measured results are correlated with the extended UNIQUAC and modified Wilson models with binary, ternary, and quaternary parameters (Nagata, 1990; Nagata and Watanabe, 1992). Binary and ternary phase equilibrium data constituting acetonitrile + 2-propanol + cyclohexane + heptane data are available in the literature: vapor−liquid equilibria (VLE); acetonitrile + 2-propanol at 323.15 K (Nagata and Katoh, 1980); 2-propanol + cyclohexane at 323.15 K (Nagata et al., 1973); 2-propanol heptane at 303.15 K (Barraza and Edwards, 1981); cyclohexane + heptane at 298.15 K (Martin and Youlings, 1980); mutual solubilities at 298.15 K; acetonitrile + cyclohexane (Nagata and Ohta, 1983), acetonitrile + heptane (Nagata, 1987): ternary LLE at 298.15 K, acetonitrile 2-propanol + cyclohexane (Nagata, 1994); acetonitrile 2-propanol + heptane (Nagata, 1988); acetonitrile + cyclohexane + heptane (Nagata et al., 1995).

Experimental Section

All guaranteed reagent grade chemicals (Wako Pure Chemical Industries Ltd.) were used without further purification. Glc analysis did not detect any appreciable peaks. The purities of chemicals used were better than 99.8 mol %. The densities of chemicals were measured with an Anton Paar densimeter and agreed well with literature values (Riddick et al., 1970) as shown in Table 1. LLE measurements were performed as described previously (Nagata and Nakamura, 1985). Mutual solubilities for acetonitrile + cyclohexane or heptane at 298.15 ± 0.02 K agreed well with previous results (Nagata and Ohta, 1983; Nagata, 1987). The liquid-phase compositions of quaternary equilibrated samples were analyzed with a Shimadzu glc (GC-8A) and Shimadzu Chromatopac (C-R6A). Table 2 shows the experimental tie-line results for acetonitrile + 2-propanol + cyclohexane + heptane at 298.15 K ± 0.02 K. The experimental error of the measured mole fractions was at most ± 0.002.

Table 1. Densities *d* of the Chemicals

component	d (298.15 K)/g·cm^{-3} exptl	lit.[a]
acetonitrile	0.776 65	0.776 60
cyclohexane	0.773 91	0.773 89
heptane	0.679 55	0.679 51
2-propanol	0.781 29	0.781 26

[a] Riddick and Bunger, 1970.

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

phase I				phase II			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.8223	0.0846	0.0756	0.0175	0.0698	0.0327	0.6662	0.2313
0.7270	0.1531	0.0953	0.0246	0.1112	0.0562	0.6225	0.2101
0.6421	0.2008	0.1240	0.0331	0.1265	0.1226	0.5591	0.1918
0.5543	0.2389	0.1583	0.0485	0.1616	0.1649	0.5006	0.1729
0.8521	0.0707	0.0464	0.0308	0.0654	0.0180	0.4459	0.4707
0.8114	0.1073	0.0477	0.0336	0.0919	0.0336	0.4302	0.4443
0.7223	0.1608	0.0657	0.0512	0.1037	0.1053	0.3857	0.4053
0.6331	0.2147	0.0820	0.0702	0.1304	0.1496	0.3452	0.3748
0.5339	0.2494	0.1132	0.1035	0.1734	0.1861	0.3095	0.3310
0.7494	0.1742	0.0239	0.0525	0.0863	0.0490	0.2136	0.6511
0.6877	0.2110	0.0300	0.0713	0.1032	0.0864	0.1905	0.6199
0.6467	0.2234	0.0382	0.0917	0.1239	0.1162	0.1806	0.5793
0.5936	0.2621	0.0405	0.1038	0.1415	0.1471	0.1678	0.5436
0.5376	0.2719	0.0520	0.1385	0.1828	0.1872	0.1491	0.4809
0.9162	0.0253	0.0196	0.0389	0.0599	0.0137	0.2233	0.7031

Table 3. Antoine Coefficients *A*, *B*, and *C*[a]

component	A	B	C
acetonitrile	6.40524	1420.20	−31.909[b]
cyclohexane	5.96988	1203.53	−50.29
heptane	6.02730	1268.115	−56.25
2-propanol	7.24270	1580.92	−53.54

$$\log(P_i/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) + C]$$

[a] Riddick and Bunger, 1970. [b] Brown and Smith, 1954.

Data Analysis

Binary VLE data were regressed to obtain energy parameters in the extended UNIQUAC model (Nagata, 1982) using a computer program similar to that described by Prausnitz et al. (1980) and the following thermodynamic equations:

$$Py_i\phi_i = x_i\gamma_i P_i^\circ \phi_i^\circ \exp\{V_i^\circ(P - P_i^\circ)/RT\} \tag{1}$$

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

where P is the total pressure, y_i is the vapor-phase mole

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Table 4. Results of Fitting the Extended UNIQUAC Model to Vapor−Liquid and Liquid−Liquid Equilibria and Root-Mean Square Deviations δP, δT, δx, and δy for Binary Systems

system (1 + 2)	T/K	a_{12}/K	a_{21}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$
acetonitrile + 2-propanol	323.15	70.27	356.68	0.1077	0.02	0.50	3.30
acetonitrile + cyclohexane	298.15	432.82	948.55				
acetonitrile + heptane	298.15	439.86	990.57				
2-propanol + cyclohexane	323.15	123.13	869.11	0.1693	0.04	0.60	5.60
2-propanol + heptane	303.15	139.42	820.38	0.5666	0.06	3.40	15.60
cyclohexane + heptane	298.15	94.67	−62.42	0.0093	0.00	0.10	0.70

Table 5. Binary Wilson-like Parameters

system (1 + 2)	T/K	a_{12}/K	a_{21}/K	α_{12}	α_{21}
acetonitrile + 2-propanol	323.15	945.69	−26.29	1.0	1.0
acetonitrile + cyclohexane	298.15	1217.82	679.03	1.1	1.1
acetonitrile + heptane	298.15	1195.2	734.38	1.1	1.1
2-propanol + cyclohexane	323.15	829.21	148.18	1.0	1.0
2-propanol + heptane	303.15	633.97	236.16	1.0	1.0
cyclohexane + heptane	298.15	−18.94	77.56	1.0	1.0

Table 6. Results of Fitting the Models to Ternary Liquid−Liquid Equilibria at 298.15 K

system	ternary parameters		F/mol %	
(1 + 2 + 3)	I[a]	II[b]	I[a]	II[b]
acetonitrile +	$\tau_{231} = 0.1502$	$\Lambda_{231} = 0.1973$	0.397	0.413
2-propanol +	$\tau_{132} = -0.1743$	$\Lambda_{132} = -0.1147$		
cyclohexane	$\tau_{123} = -0.0364$	$\Lambda_{123} = -0.1761$		
acetonitrile +	$\tau_{231} = -0.0298$	$\Lambda_{231} = -0.0390$	0.631	1.033
2-propanol +	$\tau_{132} = -0.0228$	$\Lambda_{132} = 0.2408$		
heptane	$\tau_{123} = -0.1674$	$\Lambda_{123} = -0.1961$		
acetonitrile +	$\tau_{231} = 0.0399$	$\Lambda_{231} = 0.0683$	0.370	0.402
cyclohexane +	$\tau_{132} = -0.4633$	$\Lambda_{132} = -0.1782$		
heptane	$\tau_{123} = 0.1260$	$\Lambda_{123} = 0.0351$		

Extended UNIQUAC model. [b]Modified Wilson model.

Table 7. Results of Fitting the Models to Quaternary Liquid−Liquid Equilibria for the Acetonitrile (1) + 2-Propanol (2) + Cyclohexane (3) + Heptane (4) at 298.15 K

quaternary parameters		F/mol %	
I[a]	II[b]	I[a]	II[b]
$\tau_{2341} = 0.2418$	$\Lambda_{2341} = -1.0024$	0.970	1.009
$\tau_{1342} = -0.6403$	$\Lambda_{1342} = 1.4270$		
$\tau_{1243} = -1.1583$	$\Lambda_{1243} = -0.8900$		
$\tau_{1234} = 2.4858$	$\Lambda_{1234} = 0.4099$		

[a] Extended UNIQUAC model. [b] Modified Wilson model.

fraction, ϕ_i is the vapor-phase fugacity coefficient, γ_i is the activity coefficient, P_i°, ϕ_i°, and V_i° are the pure-component vapor pressure, obtained using the Antoine equation with coefficients in Table 3, vapor-phase fugacity coefficient, and liquid molar volume estimated from a modified Rackett equation (Spencer and Danner, 1972), R is the gas constant

B are the pure and cross second virial coefficients calculated using the method of Hayden−O'Connell (1975). In binary VLE data analysis the standard deviations for the experimental values were taken as 0.13 kPa for pressure, 0.05 K for temperature, 0.001 for liquid-phase mole fraction, and 0.003 for vapor-phase mole fraction. Mutual solubilities were used to estimate binary energy parameters by solving the isoactivity relation of each component in two liquid phases. Table 4 gives the binary parameters of the extended UNIQUAC model and the root-mean square deviations between the experimental and most probable calculated values of the measured variables: δP for pressure, δT for temperature, and δx for liquid-phase mole fraction, and δy for vapor-phase mole fraction. Table 5 shows the Wilson-like parameters; those for the completely miscible mixtures were mainly taken from Gmehling et al. (1978, 1982, 1983) and α_{12} and α_{21} are empirically assigned for the partially miscible mixtures. Table 6 gives the ternary parameters of the extended UNIQUAC and modified Wilson models and the root-mean square deviations for the ternary systems defined by the objective function

$$F = 100[\sum_k \min \sum_i \sum_j (x_{ijk,\mathrm{exptl}} - x_{ijk,\mathrm{calcd}})^2/M]^{1/2} \qquad (3)$$

where min means minimum values, $i = 1-3$ for ternary systems or $1-4$ for quaternary systems, j = phases I or II, $k = 1, 2, ..., n$ (tie lines), $M = 2ni$, and x = liquid-phase mole fraction. Table 7 shows the calculated quaternary results. Both models give nearly the same results.

Conclusion

Liquid−liquid equilibria have been measured for acetonitrile + 2-propanol + cyclohexane + heptane at 298.15 K, and the results were satisfactorily correlated with the extended UNIQUAC and modified Wilson models having binary, ternary, and quaternary parameters.

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