J. Chem. Eng. Data **1984**, *29*, 429-431

C_{12}', C_{21}'	parameters in eq 1
C_{12}, C_{21}	parameters in eq 2
G^E	excess Gibbs energy
H^E	excess enthalpy
M_{ij}'	generic parameter, eq 1
M_{ij}	generic parameter, eq 2
M_{ij0}, M_{ij1}, M_{ij2}	constants, eq 3 and 4
P	total pressure
R	universal gas constant
S^E	excess entropy
T	absolute temperature, K
V_1^L, V_2^L	liquid molar volume of pure species, cm^3/mol
x_1, x_2	mole fractions

Registry No. Ethylene glycol, 107-21-1.

Literature Cited

(1) Touhara, H.; Nakanishi, K. "International Data Series B"; Engineering Sciences Data Unit Ltd: London, 1979; Vol. 1, Table 67.
(2) Gonzalez, C.; Van Ness, H. C. *J. Chem. Eng. Data* **1983**, *28*, 410.
(3) Gibbs, R. E.; Van Ness, H. C. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410.
(4) Winterhalter, D. R.; Van Ness, H. C. *J. Chem. Eng. Data* **1966**, *11*, 189.
(5) Van Ness, H. C.; Abbott, M. M. "Classical Thermodynamics of Nonelectrolyte Solutions: With Applications to Phase Equilibria"; McGraw-Hill: New York, 1982; pp 296–9, 348–55.
(6) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(7) Nath, A.; Bender, E. *J. Chem. Eng. Data* **1983**, *28*, 370.
(8) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(9) Hales, J. L.; Cogman, R. C.; Frith, W. J. *J. Chem. Thermodyn.* **1981**, *13*, 591.

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Excess Thermodynamic Properties for Water/Acetone

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Heat-of-mixing data at 50 °C are reported for the binary system water/acetone. These data, together with H^E data at 25 °C from the literature and a previously published correlation for G^E at 50 °C, are combined to provide correlations for H^E, G^E, and S^E that are functions of both composition and temperature.

The H^E data reported here for water/acetone at 50 °C along with the data set at 25 °C of Coomber and Wormald (*1*) are fitted simultaneously to determine temperature-dependent parameters in the Margules equation. These results combine with the correlation of Loehe et al. (*2*) for G^E at 50 °C to yield Margules equations with temperature-dependent parameters for both G^E and S^E.

Heat-of-mixing data were taken with an isothermal dilution calorimeter as described by Winterhalter and Van Ness (*3*). The acetone was OminSolv reagent from MCB Manufacturing Chemists, Inc., with an assay of 99.5 mol %; the water was doubly deionized. Boiling the reagents accomplished partial degassing, and they were loaded into the calorimeter while hot. This prevented the evolution of dissolved gases during mixing.

Results and Correlation

Correlation of all data is by the five-parameter Margules equation, written for H^E as

$$H^E/(x_1x_2RT) = A_{21}'x_1 + A_{12}'x_2 - (C_{21}'x_1 + C_{12}'x_2)x_1x_2 + D'(x_1x_2)^2 \quad (1)$$

and for G^E as

$$G^E/(x_1x_2RT) = A_{21}x_1 + A_{12}x_2 - (C_{21}x_1 + C_{12}x_2)x_1x_2 + D(x_1x_2)^2 \quad (2)$$

Table I. H^E-x Data for Water (1)/Acetone (2) at 50 °C

x_1	x_2	H^E, J/mol
0.0045	0.9955	19.3
0.0176	0.9824	70.4
0.0606	0.9394	210.9
0.1170	0.8830	328.8
0.1957	0.8043	404.2
0.2611	0.7389	400.8
0.3347	0.6653	344.8
0.4090	0.5910	248.6
0.4842	0.5158	127.7
0.5530	0.4470	4.1
0.6152	0.3848	-109.7
0.6687	0.3313	-205.2
0.7213	0.2787	-289.7
0.7664	0.2336	-350.7
0.7963	0.2037	-382.6
0.8213	0.1787	-387.5
0.8547	0.1453	-399.7
0.8929	0.1071	-384.5
0.9252	0.0748	-334.3
0.9486	0.0514	-265.1
0.9687	0.0313	-185.6
0.9828	0.0172	-110.8
0.9914	0.0086	-58.5
0.9973	0.0027	-18.5

where all parameters are functions of temperature. Since $S^E = (H^E - G^E)/T$, we also have

$$S^E/(x_1x_2R) = (A_{21}' - A_{21})x_1 + (A_{12}' - A_{12})x_2 - [(C_{21}' - C_{21})x_1 + (C_{12}' - C_{12})x_2]x_1x_2 + (D' - D)(x_1x_2)^2 \quad (3)$$

The assumption that H^E is linear in T and the imposition of the Gibbs/Helmholtz equation lead to the relations (*4*)

$$M_{ij}' = M_{ij0}/T + M_{ij2} \quad (4)$$

$$M_{ij} = M_{ij0}/T + M_{ij1} - M_{ij2} \ln T \quad (5)$$

where M_{ij}' and M_{ij} represent the parameters in eq 1–3, and M_{ij0}, M_{ij1}, and M_{ij2} are constants.

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Table II. Constants in Eq 4 and 5 for Calculation of Correlating Parameters for Water (1)/Acetone (2)

M_{ij0}	M_{ij1}	M_{ij2}
$A_{210} = -1984.71$	$A_{211} = 29.2125$	$A_{212} = 3.59876$
$A_{120} = -717.58$	$A_{121} = 25.3015$	$A_{122} = 3.69598$
$C_{210} = 3194.46$	$C_{211} = -111.3107$	$C_{212} = -17.78226$
$C_{120} = 442.74$	$C_{121} = -20.4657$	$C_{122} = -3.41164$
$D_0 = 8094.40$	$D_1 = -221.4391$	$D_2 = -34.08370$

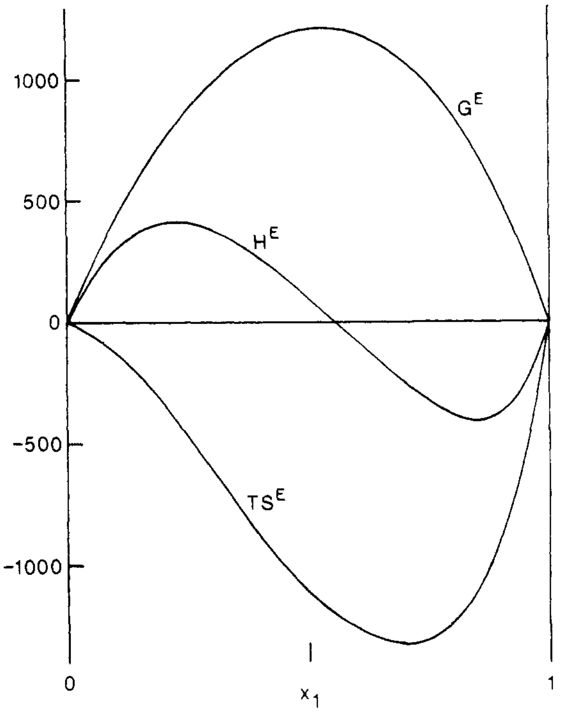

Figure 1. Excess properties for water (1)/acetone (2) at 50 °C in J/mol.

The H^E data at 50 °C reported here in Table I and the data at 25 °C of Coomber and Wormald (*1*) are fitted simultaneously by eq 1 with parameters given by eq 4. This establishes values for the constants M_{ij0} and M_{ij2}. The overall rms deviation of the fit is 5.7 J/mol; for the present data set the figure is 4.8 J/mol, and for the data of Coomber and Wormald 7.0 J/mol. The correlation for G^E at 50 °C presented by Loehe et al. (*2*) for water/acetone allows calculation of the constants M_{ij1} by eq 2 and 5. Values of all constants determined from the H^E and G^E correlations are listed in Table II.

At 50 °C, the base temperature of our correlations, eq 1–3 become

$$H^E/(x_1x_2RT) = -2.5430x_1 + 1.4754x_2 + (7.8969x_1 + 2.0416x_2)x_1x_2 - 9.0353(x_1x_2)^2$$

$$G^E/(x_1x_2RT) = 2.2767x_1 + 1.7251x_2 - (1.3226x_1 + 0.6172x_2)x_1x_2 + 0.5489(x_1x_2)^2$$

$$S^E/(x_1x_2R) = -4.8197x_1 - 0.2497x_2 + (9.2195x_1 + 2.6588x_2)x_1x_2 - 9.5842(x_1x_2)^2$$

Figure 1 shows plots of these relations.

Discussion

Equations 1–5 should provide reasonable values of the excess properties H^E, G^E, and S^E over a temperature range at least from 0 to 100 °C. If this is indeed true, then we should be able to predict accurately the vapor/liquid equilibrium relations for the water/acetone system at atmospheric pressure, 101.33 kPa. This is a BUBL *T* calculation as described by Van Ness and Abbott (*4*): given *x* and *P*, calculate *y* and *T*. One requires activity coefficients for the species in the liquid phase, here calculated from eq 2 and 5, and fugacity coefficients for the species in the vapor phase, here calculated from the two-term virial equation with second virial coefficients from the Hayden/O'Connell correlation (*5*). Vapor pressures of the pure species are given by Antoine equations with coefficients for water from Reid, Prausnitz, and Sherwood (*6*) and for acetone from Ambrose et al. (*7*).

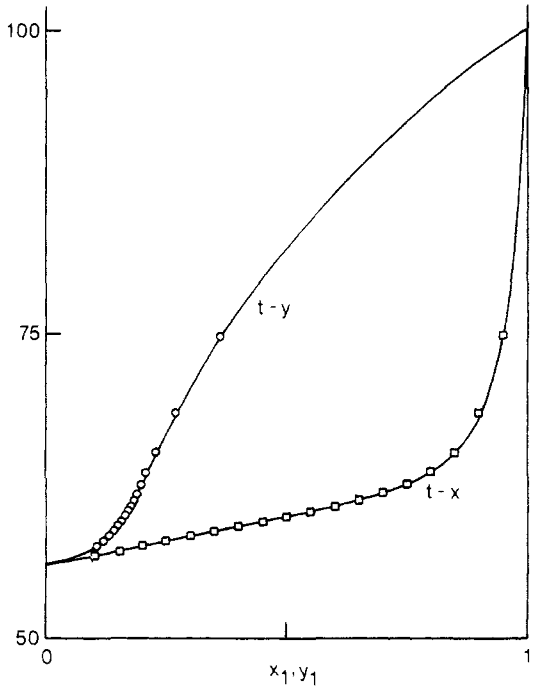

Figure 2. Temperature (*t*, °C)–composition diagram for water (1)/acetone (2) at 101.33 kPa. Lines represent calculated values; points are from Kojima et al. (*8*).

The results of such calculations are described by the *t*–*x* and *t*–*y* curves of Figure 2. These lines clearly provide an excellent correlation of the VLE data of Kojima et al. (*8*) for water/acetone at 101.33 kPa. In fact, the rms difference between calculated and measured temperatures is only 0.13 °C and the rms difference between calculated and reported values of y_1 is less than 0.003. Also well described are the VLE data of Verhoeye and de Schepper (*9*), the only other modern set of measurements at atmospheric pressure. These calculations most likely provide results that are at least as reliable as any determined by direct experiment. Moreover, they yield values in the water-rich region, where reliable experimental data are lacking.

Glossary

A_{12}', A_{21}'	parameters in eq 1 and 3
A_{12}, A_{21}	parameters in eq 2 and 3
C_{12}', C_{21}'	parameters in eq 1 and 3
C_{12}, C_{21}	parameters in eq 2 and 3
D'	parameter in eq 1 and 3
D	parameter in eq 2 and 3
G^E	excess Gibbs energy
H^E	excess enthalpy
M_{ij}'	generic parameter, eq 1
M_{ij}	generic parameter, eq 2
M_{ij0}, M_{ij1}, M_{ij2}	constants, eq 4 and 5
R	universal gas constant
S^E	excess entropy

T absolute temperature, K
x_1, x_2 mole fractions, liquid phase
y_1, y_2 mole fractions, vapor phase

Registry No. Acetone, 67-64-1.

Literature Cited

(1) Coomber, B. A.; Wormald, C. J. *J. Chem. Thermodyn.* **1976**, *8*, 793.
(2) Loehe, J. R.; Van Ness, H. C.; Abbott, M. M. *J. Chem. Eng. Data* **1981**, *26*, 178.
(3) Winterhalter, D. R.; Van Ness, H. C. *J. Chem. Eng. Data* **1966**, *11*, 189.
(4) Van Ness, H. C.; Abbott, M. M. "Classical Thermodynamics of Nonelectrolyte Solutions: With Applications to Phase Equilibria"; McGraw-Hill: New York, 1982; pp 296-9, 348-55.
(5) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(6) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3d ed.; McGraw-Hill: New York, 1977; p 632.
(7) Ambrose, D.; Sprake, C. H. S.; Townsend, R. *J. Chem. Thermodyn.* **1974**, *6*, 693.
(8) Kojima, K.; Tochigi, K.; Seki, H.; Watase, K. *Kagaku Kogaku* **1968**, *32*, 149.
(9) Verhoeye, L.; de Schepper, H. *J. Appl. Chem. Biotechnol.* **1973**, *23*, 607.

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Vapor/Liquid/Liquid Equilibrium and Heats of Mixing for Diethyl Ether/Water at 35 °C

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Isothermal $P-x$ data and H^E data at 35 °C are reported for the system diethyl ether/water. These data are reduced to provide correlating expressions for G^E and H^E.

Liquid mixtures of diethyl ether and water exhibit partial miscibility. Available solubility data (none modern) are summarized by Sørensen and Arlt (*1*); they show that at room temperature the solubility of ether in water is less than 2 mol % and decreases with increasing temperature, whereas the solubility of water in ether is about 5 mol %, increasing with increasing temperature. Useful data therefore require measurements in the dilute region of each species. Both the total-pressure vapor/liquid equilibrium (VLE) apparatus designed by Gibbs and Van Ness (*2*) and modified by DiElsi et al. (*3*) and the dilution calorimeter described by Winterhalter and Van Ness (*4*) are suitable for such measurements. However, one must be meticulous in making runs, and exercise patience, as equilibrium conditions are only slowly attained after mixing.

The anhydrous ethyl ether was HPLC grade supplied by Fisher Scientific Co. with minimum assay of 99.9 mol %. The water was doubly deionized with conductivity less than 1 × 10^{-6} Ω^{-1}. For VLE measurements, both reagents were thoroughly degassed. The measured vapor pressure of diethyl ether at 35 °C is 103.264 kPa compared with the value of 103.387 kPa reported by Ambrose et al. (*5*). For water, our value of 5.633 kPa compares with the value of 5.628 kPa reported by Ambrose and Lawrenson (*6*).

Results and Data Reduction

Vapor/Liquid/Liquid/Equilibria. Table I contains experimental total-pressure data for the two regions of VLE. In the region of vapor/liquid/liquid equilibrium (VLLE), the observed three-phase equilibrium pressure is essentially constant, and measurements in this region establish this pressure as $P^* = 104.70 \pm 0.03$ kPa.

For initial reduction of the two-phase equilibrium $P-x$ data, we make direct use of Barker's method (*7*), which is based on the following equilibrium equation:

$$P = x_1\gamma_1P_1^{\text{sat}}/\Phi_1 + x_2\gamma_2P_2^{\text{sat}}/\Phi_2 \qquad (1)$$

Here, the Φ_i are factors of order unity which take into account vapor-phase nonideality and the effect of pressure on liquid-phase fugacity. The γ_i reflect liquid-phase nonideality and are calculated from an assumed expression for G^E/RT. One determines by regression values of the parameters in this expression that minimize the sum of squares of the differences between the experimental values of P and those given by eq 1.

Table I. $P-x$ Data for Diethyl Ether (1)/Water (2) at 35 °C

x_1	x_2	P, kPa
0.0000	1.0000	5.633
0.0014	0.9986	18.759
0.0028	0.9972	33.033
0.0042	0.9958	45.083
0.0055	0.9945	57.298
0.0069	0.9931	68.679
0.0083	0.9917	79.064
0.0096	0.9904	89.632
0.0111	0.9889	100.205
	miscibility gap	
0.9536	0.0464	104.656
0.9617	0.0383	104.588
0.9715	0.0285	104.445
0.9818	0.0182	104.172
0.9901	0.0099	103.802
1.0000	0.0000	103.264

The $P-x$ data of Table I for both regions of VLE are well correlated by the modified Margules equation with a single set of parameters:

$$G^E/RT = \{A_{21}x_1 + A_{12}x_2 - \alpha_{12}\alpha_{21}x_1x_2/(\alpha_{12}x_1 + \alpha_{21}x_2)\}x_1x_2 \qquad (2)$$

From the resulting activity coefficients one then calculates the equilibrium y_i values for the regions of VLE:

$$y_i = x_i\gamma_iP_i^{\text{sat}}/(\Phi_iP) \qquad (3)$$

The results of this initial fit are represented by Figure 1. The intersections of both the $P-x$ curve and the $P-y$ curve for the VLE region dilute in ether with the three-phase-pressure line at $P^* = 104.70$ kPa are very sharp and allow us to establish unequivocal values of x_1^α, the lower miscibility limit, and y_1^*, the three-phase vapor composition. Thus, we find that $x_1^\alpha = 0.01172$ and $y_1^* = 0.9463$. The value of x_1^α may be compared with 0.0125 interpolated from the smoothed values given

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