

## Glossary

$A, B, C$	constants of the Antoine equation
$A_k$	constants of the Redlich-Kister equation
$d$	density
$n_D$	refractive index
$P$	pressure
$x, y$	mole fraction in liquid and vapor, respectively
$w$	weight fraction
$\gamma$	activity coefficient

Registry No. TAME, 994-05-8; methanol, 67-56-1.

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Received for review October 25, 1983. Accepted April 25, 1984.

## Excess Thermodynamic Properties for Water/Ethylene Glycol

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Isothermal  $P$ - $x$  data at 60 °C and heat-of-mixing data at 50 °C are reported for the binary system water/ethylene glycol. These data, together with  $P$ - $x$  data at 50 °C and  $H^E$  data at 25 °C from the literature, are reduced to provide correlations for  $H^E$ ,  $G^E$ , and  $S^E$  as functions of both composition and temperature.

The heat-of-mixing measurements reported here for water/ethylene glycol at 50 °C combine with the comprehensive data set at 25 °C of Touhara and Nakanishi (1) to establish the temperature dependence of  $H^E$ . The vapor/liquid equilibrium measurements reported for 60 °C augment a comparable set of  $P$ - $x$  data at 50 °C published earlier (2), and together they form the basis for correlation of  $G^E$ .

The ethylene glycol was 99<sup>+</sup> mol % reagent from MCB Manufacturing Chemists, Inc. The water was doubly deionized. For  $P$ - $x$  measurements in the static VLE apparatus of Gibbs and Van Ness (3) both reagents were thoroughly degassed. The isothermal dilution calorimeter used for the  $H^E$  measurements was essentially that of Winterhalter and Van Ness (4). We have found that for aqueous systems the usual procedure of loading the calorimeter at room temperature with undegassed reagents is unsatisfactory, because subsequent heating to 50 °C and mixing lead to the evolution of dissolved gases. Loading the calorimeter with reagents at temperatures greater than 50 °C and then sealing it solves the problem.

### Results and Correlation

Table I presents the experimental values of total vapor pressure at 60 °C as a function of composition; Table II gives values of  $H^E$  at 50 °C.

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Table I.  $P$ - $x$  Data for Water (1)/Ethylene Glycol (2) at 60 °C<sup>a</sup>

$x_1$	$x_2$	$P$ /kPa
0.0	1.0000	0.214
0.0188	0.9812	0.543
0.0487	0.9513	1.058
0.1008	0.8992	1.997
0.1497	0.8503	2.892
0.1989	0.8011	3.813
0.2479	0.7521	4.760
0.2973	0.7027	5.790
0.3477	0.6523	6.678
0.3975	0.6025	7.724
0.4478	0.5522	8.718
0.4982	0.5018	9.721
0.4987	0.5013	9.717
0.5487	0.4513	10.713
0.5989	0.4011	11.751
0.6489	0.3511	12.746
0.6988	0.3012	13.757
0.7489	0.2511	14.836
0.8003	0.1997	15.880
0.8504	0.1496	16.879
0.9001	0.0999	17.906
0.9495	0.0505	18.923
0.9797	0.0203	19.428
1.0000	0.0	19.931

<sup>a</sup>  $B_{11} = -930$ ,  $B_{22} = -1697$ ,  $B_{12} = -1050$ ,  $V_1^L = 18$ ,  $V_2^L = 58$ .

Correlation of all data is through the four-parameter Margules equation, written for  $H^E$  as

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

and for  $G^E$  as

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

**Table II.**  $H^E$ - $x$  Data for Water (1)/Ethylene Glycol (2) at 50 °C

$x_1$	$x_2$	$H^E$ /(J/mol)
0.0234	0.9766	-42.3
0.0523	0.9477	-95.3
0.1094	0.8906	-188.5
0.1699	0.8301	-282.1
0.2343	0.7657	-370.7
0.2880	0.7120	-436.8
0.3382	0.6618	-495.0
0.3973	0.6027	-555.1
0.4483	0.5517	-605.4
0.5468	0.4532	-676.5
0.5965	0.4035	-697.3
0.6470	0.3530	-705.1
0.6908	0.3092	-699.8
0.7297	0.2703	-684.7
0.7575	0.2425	-665.6
0.7582	0.2418	-660.4
0.8199	0.1801	-593.1
0.8808	0.1192	-469.7
0.9344	0.0656	-300.6
0.9786	0.0214	-113.5

where all parameters are functions of temperature. As a result of the Gibbs/Helmholtz equation

$$\frac{H^E}{x_1 x_2 RT} = -T \frac{d(G^E/(x_1 x_2 RT))}{dT} \quad (\text{constant } x)$$

the parameters  $M_{ij}'$  in eq 1 are related to the parameters  $M_{ij}$  of eq 2 by

$$M_{ij}' = -T(dM_{ij}/dT)$$

If we assume that  $H^E$  is linear in  $T$ , then the parameters  $M_{ij}$  and  $M_{ij}'$  are given by (5)

$$M_{ij} = M_{ij0}/T + M_{ij1} - M_{ij2} \ln T \quad (3)$$

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

The  $H^E$  data at 50 °C reported here were fitted by eq 1 with a rms deviation of 2.5 J/mol. Similarly, the  $H^E$  data at 25 °C of Touhara and Nakanishi (1) were fitted with a rms deviation of 2.3 J/mol. These results provide two sets of parameter values  $M_{ij}'$  in eq 1 from which sets of values for  $M_{ij0}$  and  $M_{ij2}$  are found by eq 4. Substitution in eq 3, which provides parameter values for eq 2, leaves only the  $M_{ij1}$  values to be found from VLE data. We have available the  $P$ - $x$  data at 60 °C reported here and the  $P$ - $x$  data at 50 °C of Gonzalez and Van Ness (2). These two sets of data were reduced simultaneously by Barker's method (6) to find the values of the  $M_{ij1}$  in eq 3 (and hence the  $M_{ij}$  values in eq 2) which minimize the sum of squares of the deviations between observed and calculated pressures. The resulting rms value of the pressure deviations is 0.024 kPa. The constants in eq 3 and 4 determined by reduction of all data are listed in Table III.

### Discussion

The excess entropy is given by

$$TS^E = H^E - G^E$$

Thus, by eq 1 and 2 we get

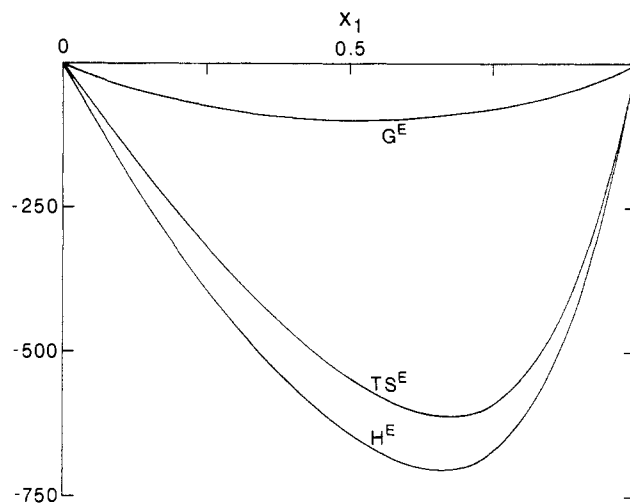
$$S^E/(x_1 x_2 R) = (A_{21}' - A_{21})x_1 + (A_{12}' - A_{12})x_2 - [(C_{21}' - C_{21})x_1 + (C_{12}' - C_{12})x_2]x_1 x_2 \quad (5)$$

and by eq 3 and 4

$$M_{ij}' - M_{ij} = M_{ij2}(1 + \ln T) - M_{ij1} \quad (6)$$

**Table III.** Constants in Eq 3 and 4 for Calculation of Correlating Parameters for Water (1)/Ethylene Glycol (2)

$M_{ij0}$	$M_{ij1}$	$M_{ij2}$
$A_{210} = -2059.209$	$A_{211} = 31.24356$	$A_{212} = 4.33806$
$A_{120} = 258.827$	$A_{121} = -9.50026$	$A_{122} = -1.47594$
$C_{210} = -4535.562$	$C_{211} = 82.06843$	$C_{212} = 11.80013$
$C_{120} = -1994.695$	$C_{121} = 36.25889$	$C_{122} = 5.23041$



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

Equations 1-6 should provide reliable values of the excess properties  $H^E$ ,  $G^E$ , and  $S^E$  for the water/glycol binary system over a temperature range of at least 25-75 °C, and reasonable values from 0 to 100 °C.

At 50 °C ( $T = 323.15$  K), eq 1, 2, and 5 become

$$H^E/(x_1 x_2 RT) = -2.03424x_1 - 0.67499x_2 + (2.23534x_1 + 0.94225x_2)x_1 x_2$$

$$G^E/(x_1 x_2 RT) = -0.19456x_1 - 0.17116x_2 + (0.14957x_1 + 0.13569x_2)x_1 x_2$$

$$S^E/(x_1 x_2 R) = -1.83968x_1 - 0.50383x_2 + (2.08577x_1 + 0.80656x_2)x_1 x_2$$

Figure 1 shows these results in graphical form. Although the system is strongly exothermic at this temperature, it shows relatively small deviations from Raoult's law.

Recently, Nath and Bender (7) have published  $P$ - $x$  data for water/ethylene glycol at 65.1, 77.7, and 90.3 °C. We have calculated values of  $P$  from our correlation at the temperatures and  $x_1$  values of these data and find that calculated and experimental values are in quite satisfactory agreement, with rms differences of from 0.40 to 0.53 kPa. These BUBL  $P$  calculations are described by Van Ness and Abbott (5). In addition to liquid-phase activity coefficients, they require vapor-phase fugacity coefficients, calculated here from the two-term virial equation with second virial coefficients from the correlation of Hayden and O'Connell (8). For pure-component vapor pressures, we used the values reported by Nath and Bender for water, but since they did not report values for ethylene glycol, we calculated values from the equation given by Hales et al. (9).

### Glossary

- $A_{12}'$ ,  $A_{21}'$  parameters in eq 1
- $A_{12}$ ,  $A_{21}$  parameters in eq 2
- $B_{11}$ ,  $B_{22}$ ,  $B_{12}$  second virial coefficients,  $\text{cm}^3/\text{mol}$

$C_{12}'$ , $C_{21}'$	parameters in eq 1
$C_{12}$ , $C_{21}$	parameters in eq 2
$G^E$	excess Gibbs energy
$H^E$	excess enthalpy
$M_y'$	generic parameter, eq 1
$M_y$	generic parameter, eq 2
$M_{y0}$ , $M_{y1}$ , $M_{y2}$	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 <sup>3</sup> /mol
$x_1$ , $x_2$	mole fractions

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

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Received for review November 9, 1983. Accepted April 23, 1984. M.A.V. is grateful to the U.S.-Spanish Joint Committee for Scientific and Technological Cooperation for the award of a postdoctoral research grant.

## 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 Loëhe 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

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

and for  $G^E$  as

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

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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

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

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

$$M_{y1}' = M_{y0}/T + M_{y2} \quad (4)$$

$$M_y = M_{y0}/T + M_{y1} - M_{y2} \ln T \quad (5)$$

where  $M_{y1}'$  and  $M_y$  represent the parameters in eq 1-3, and  $M_{y0}$ ,  $M_{y1}$ , and  $M_{y2}$  are constants.