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# Excess Thermodynamic Properties for Acetonitrile/Water

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**Heat-of-mixing data for the binary liquid system acetonitrile/water at 50 °C are reported. These data, together with $H^E$ data at 5 and 25 °C from the literature and a previously published set of VLE data at 50 °C, are combined to provide correlations for $H^E$, $G^E$, and $S^E$ that are functions of both composition and temperature.**

Experimental heat-of-mixing data at 50 °C for the acetonitrile/water system, taken with the apparatus of Winterhalter and Van Ness (*1*), are listed in Table I. The acetonitrile was OmniSolv reagent from MCB Manufacturing Chemists, Inc., with an assay of 99.8 mol %; the water was doubly deionized. Boiling the reagents accomplishes partial degassing, and they are loaded into the calorimeter while hot. With this procedure, no evolution of dissolved gases occurs during a run.

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

| $x_1$ | $x_2$ | $H^E$/J mol$^{-1}$ | $x_1$ | $x_2$ | $H^E$/J mol$^{-1}$ |
|---|---|---|---|---|---|
| 0.0194 | 0.9806 | 28.0 | 0.4902 | 0.5098 | 1189.3 |
| 0.0501 | 0.9499 | 113.0 | 0.5418 | 0.4582 | 1232.2 |
| 0.0686 | 0.9314 | 177.6 | 0.5989 | 0.4011 | 1255.1 |
| 0.1066 | 0.8934 | 319.3 | 0.6482 | 0.3518 | 1249.2 |
| 0.1507 | 0.8493 | 472.8 | 0.6988 | 0.3012 | 1218.8 |
| 0.1999 | 0.8001 | 626.6 | 0.7511 | 0.2489 | 1147.6 |
| 0.2405 | 0.7595 | 739.1 | 0.7981 | 0.2019 | 1049.2 |
| 0.2475 | 0.7525 | 755.4 | 0.8494 | 0.1506 | 891.9 |
| 0.2919 | 0.7081 | 862.1 | 0.9007 | 0.0993 | 661.8 |
| 0.3432 | 0.6568 | 969.8 | 0.9327 | 0.0673 | 484.7 |
| 0.3936 | 0.6064 | 1060.2 | 0.9579 | 0.0421 | 318.1 |
| 0.4457 | 0.5543 | 1137.2 | 0.9858 | 0.0142 | 115.3 |

## Correlations for the Excess Properties

An excellent correlation of the reported $H^E$ data is achieved by the eight-parameter Margules equation

$$H^E/(x_1x_2RT) = A' - C'x_1x_2 + D'(x_1x_2)^2 - E'(x_1x_2)^3 \quad (1)$$

where $A' \equiv A_{21}'x_1 + A_{12}'x_2$; $C' \equiv C_{21}'x_1 + C_{12}'x_2$; $D' \equiv D_{21}'x_1 + D_{12}'x_2$; $E' \equiv E_{21}'x_1 + E_{12}'x_2$. Regression of the data to minimize the sum of squares of the differences between experimental and calculated values of $H^E$, all points weighted equally, leads to the following values of the parameters: $A_{21}' = 3.090\,40$, $A_{12}' = 0.282\,05$; $C_{21}' = 0.499\,64$, $C_{12}' = -13.335\,87$; $D_{21}' = -14.101\,70$, $D_{12}' = -66.704\,84$; $E_{21}' = -25.872\,04$, $E_{12}' = -104.790\,37$. The rms value of the deviations is 1.1 J mol$^{-1}$ and the maximum deviation is 2.1 J mol$^{-1}$. We could find no equation with a smaller number of parameters that provided a proper correlation of the data.

A comparable set of vapor/liquid equilibrium data, also at 50 °C, was reported recently by Villamañán et al. (*2*). A suitable correlation of these $P$-$x$ data resulted when the excess Gibbs energy of the liquid phase was represented by the six-parameter Margules equation. For present purposes, we require Margules equations for both $G^E$ and $H^E$ with the same number of terms. We have therefore refit the $P$-$x$ data of Villamañán et al. to provide parameters for the eight-parameter Margules equation, which may be written for $G^E$ as

$$G^E/(x_1x_2RT) = A - Cx_1x_2 + D(x_1x_2)^2 - E(x_1x_2)^3 \quad (2)$$

where $A \equiv A_{21}x_1 + A_{12}x_2$; $C \equiv C_{21}x_1 + C_{12}x_2$; $D \equiv D_{21}x_1 + D_{12}x_2$; $E \equiv E_{21}x_1 + E_{12}x_2$. The resulting parameter values are $A_{21} = 2.014\,13$, $A_{12} = 2.514\,24$; $C_{21} = 1.190\,13$, $C_{12} = 0.512\,24$; $D_{21} = 1.067\,64$, $D_{12} = -4.512\,92$; $E_{21} = -0.848\,90$, $E_{12} = -8.867\,91$. The rms value of the pressure deviations is 1.0 kPa, and the maximum deviation is 1.9 kPa.

Since $S^E = (H^E - G^E)/T$, we also have

$$S^E/(x_1x_2R) = A'' - C''x_1x_2 + D''(x_1x_2)^2 - E''(x_1x_2)^3 \quad (3)$$

where $A'' \equiv A_{21}''x_1 + A_{12}''x_2$, $C'' \equiv C_{21}''x_1 + C_{12}''x_2$, $D'' \equiv D_{21}''x_1 + D_{12}''x_2$, $E'' \equiv E_{21}''x_1 + E_{12}''x_2$, with each parameter $M_{ij}''$ related to the corresponding parameters in eq 1 and 2 by

$$M_{ij}'' = M_{ij}' - M_{ij}$$

The resulting parameter values for 50 °C are therefore $A_{21}'' = 1.076\,27$, $A_{12}'' = -2.232\,19$; $C_{21}'' = -0.690\,49$, $C_{12}'' = -13.848\,11$; $D_{21}'' = -15.169\,34$, $D_{12}'' = -62.191\,92$; $E_{21}'' = -25.023\,14$, $E_{12}'' = -95.922\,46$. The three excess properties at 50 °C as calculated from eq 1, 2, and 3 are plotted as functions of $x_1$ in Figure 1.

Additional data from the literature allow development of correlations that incorporate the temperature dependence of the parameters. The assumption that $H^E$ is linear in $T$ and

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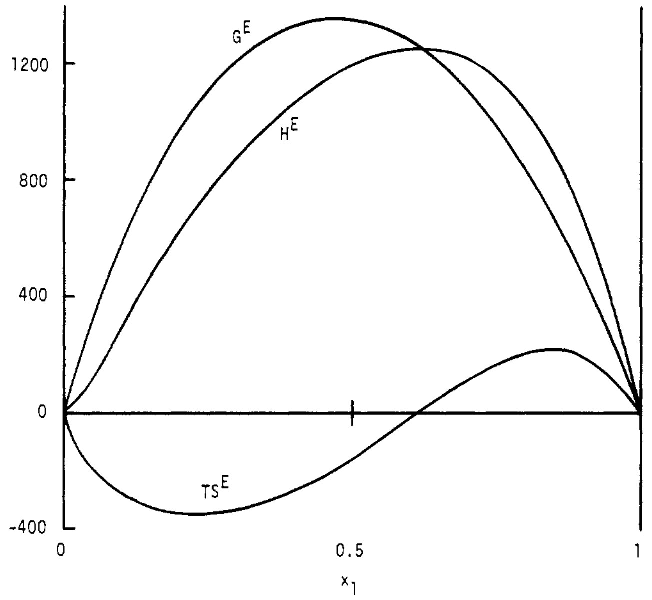

**Figure 1.** Excess properties (J mol$^{-1}$) as functions of composition for acetonitrile (1)/water (2) at 50 °C.

imposition of the Gibbs/Helmholtz equation lead to the relations (*3*)

$$M_{ij}' = M_{ij0}/T + M_{ij2} \tag{4}$$

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

where $M_{ij}'$ and $M_{ij}$ represent parameters in eq 1 and 2, and $M_{ij0}$, $M_{ij1}$, and $M_{ij2}$ are constants. The $H^E$ data at 50 °C reported in Table I and the data sets of Morcom and Smith (*4*) at 5 and 25 °C are fitted simultaneously by eq 1 with parameters given by eq 4. This establishes the constants $M_{ij0}$ and $M_{ij2}$. The overall rms deviation of the fit is 2.9 J mol$^{-1}$. These constants, when combined with the parameter values already listed for $G^E$ at 50 °C allow calculation of the constants $M_{ij1}$ by application of eq 5. Values of all constants so determined are as follows: $A_{210} = 2074.744$, $A_{211} = -23.55573$, $A_{212} = -3.31414$; $A_{120} = -3623.278$, $A_{121} = 79.96047$, $A_{122} = 11.46288$; $C_{210} = 30960.00$, $C_{211} = -642.7379$, $C_{212} = -94.86155$; $C_{120} = -32072.63$, $C_{121} = 593.0406$, $C_{122} = 85.37009$; $D_{210} = 154674.6$, $D_{211} = -3302.486$, $D_{212} = -488.8976$; $D_{120} = -127937.1$, $D_{121} = 2273.964$, $D_{122} = 325.8105$; $E_{210} = 283642.7$, $E_{211} = -6044.612$, $E_{212} = -894.0664$; $E_{120} = -177824.3$, $E_{121} = 3075.908$, $E_{122} = 438.6363$.

## Discussion

Equations 1–5 should provide appropriate values of the excess properties $H^E$, $G^E$, and $S^E$ over a considerable range of temperature. Thus we should be able to predict with reasonable accuracy the vapor/liquid equilibrium relations for the water/acetonitrile system over a temperature range from 0 to 100 °C. One can make both BUBL $T$ calculations (given $x$ and $P$, calculate $y$ and $T$) and BUBL $P$ calculations (given $x$ and $T$, calculate $y$ and $P$) as described by Van Ness and Abbott (*3*) and compare the results with VLE data from the literature. The necessary activity coefficient values are calculated from the correlation of $G^E$ represented by eq 2 and 5, and fugacity coefficients come from the correlation of Hayden and O'Connell (*5*). Vapor pressures of the pure species are given by Antoine equations with coefficients from Boublik et al. (*6*).

The results of such calculations are certainly in qualitative agreement with data appearing in the data collection of Gmehling et al. (*7*). Multiple data sets are available only at atmospheric pressure; no two of these are in agreement with each other, and none is in good quantitative agreement with predictions based on the correlation given here. In all probability the correlation is to be preferred to the available experimental *Pxy* and *Txy* data sets at temperatures where it is applicable.

## Glossary

| | |
|---|---|
| $A'$, $A_{12}'$, $A_{21}'$ | parameters in eq 1 |
| $A$, $A_{12}$, $A_{21}$ | parameters in eq 2 |
| $A''$, $A_{12}''$, $A_{21}''$ | parameters in eq 3 |
| $C'$, $C_{12}'$, $C_{21}'$ | parameters in eq 1 |
| $C$, $C_{12}$, $C_{21}$ | parameters in eq 2 |
| $C''$, $C_{12}''$, $C_{21}''$ | parameters in eq 3 |
| $D'$, $D_{12}'$, $D_{21}'$ | parameters in eq 1 |
| $D$, $D_{12}$, $D_{21}$ | parameters in eq 2 |
| $D''$, $D_{12}''$, $D_{21}''$ | parameters in eq 3 |
| $E'$, $E_{12}'$, $E_{21}'$ | parameters in eq 1 |
| $E$, $E_{12}$, $E_{21}$ | parameters in eq 2 |
| $E''$, $E_{12}''$, $E_{21}''$ | parameters in eq 3 |
| $G^E$ | excess Gibbs energy |
| $H^E$ | excess enthalpy |
| $M_{ij}'$ | generic parameter, eq 1 |
| $M_{ij}$ | generic parameter, eq 2 |
| $M_{ij}''$ | generic parameter, eq 3 |
| $M_{ij0}$, $M_{ij1}$, $M_{ij2}$ | constants, eq 4 and 5 |
| $R$ | universal gas constant |
| $S^E$ | excess entropy |
| $T$ | absolute temperature, K |

**Registry No.** Acetonitrile, 75-05-8.

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