Excess Thermodynamic Functions for Ternary Systems I. Acetone–Chloroform–Methanol at 50°C

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Extensive heat-of-mixing data taken with an isothermal titration calorimeter for the acetone–chloroform–methanol system at 50°C are reported, and a correlation of the results is presented. When combined with a correlation for the excess Gibbs free energy reported earlier, these results allow calculation of excess entropies.

The isothermal titration calorimeter described by Winterhalter and Van Ness (*9*) has been used without modification for measurement of heats of mixing for the system acetone–chloroform–methanol over the full composition range of the ternary system. Included are data for the constituent binaries; for ternary mixtures 15 runs were made by addition of a pure component to an initial mixture made up of known amounts of the other two components. The extent of coverage of the ternary composition diagram is indicated by the lines of Figure 1.

The chemicals employed were chromatoquality reagents supplied by Matheson Coleman & Bell; they were used as received with a minimum indicated purity of 99.8 mol %.

Data for Binary Systems

The experimental results for the three binary systems, acetone(1)–chloroform(2), acetone(1)–methanol(3), and chloroform(2)–methanol(3), are given in Table I (deposited with the ACS Microfilm Depository Service). These data are well correlated by equations of the form:

$$\frac{H^E}{x_i x_j RT} = A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_i x_j + (\psi_{ji}x_i + \psi_{ij}x_j)x_i^2 x_j^2 \quad (1)$$

The parameters in these equations as determined by least-squares fit with H^E(calculated) − H^E(experimental) as objective function are given in Table II. The last two rows of the table display the standard and the maximum deviations between calculated and measured values of H^E. We regard the standard deviations as realistic estimates of the absolute accuracy of the data. The experimental data and their correlating equations are displayed in Figures 2–4 as plots of $H^E/x_i x_j RT$ vs. x_i. Our results for these systems are consistent with, but more extensive and precise than, other published data (*2–8*).

Data for Ternary Mixtures

Since ternary mixtures are formed by addition of a pure component to a binary mixture, the measured values of H^E_{123} in any one run depend upon the value of H^E_{ij} for the initial bi-

Table II. Correlating Parameters in Equation 1 for Binary Systems
Pairs of components are listed in order *i, j*

	Acetone(1)–chloroform(2)	Acetone(1)–methanol(3)	Chloroform(2)–methanol(3)
A_{ij}	−2.7829	1.0362	−1.5466
A_{ji}	−1.8161	1.3636	3.8144
λ_{ij}	2.3607	0.1356	2.0991
λ_{ji}	0.6579	0.1650	14.6435
ψ_{ij}	1.1395	−0.3405	6.2152
ψ_{ji}	1.1395	−0.3405	26.4938
σ (J/mol)	1.4	0.5	4.1
Max dev (J/mol)	3.2	1.1	11.0

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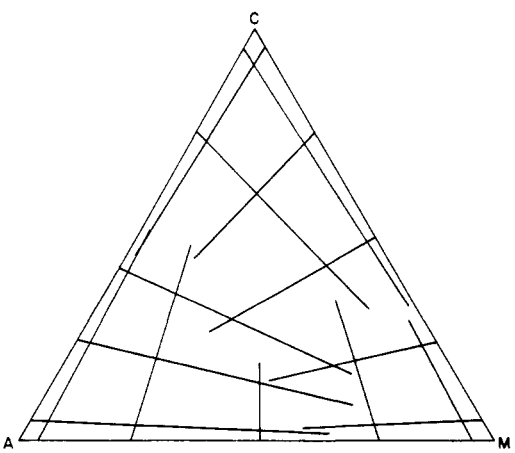

Figure 1. Lines showing compositions traversed during runs yielding heats of mixing for ternary mixtures

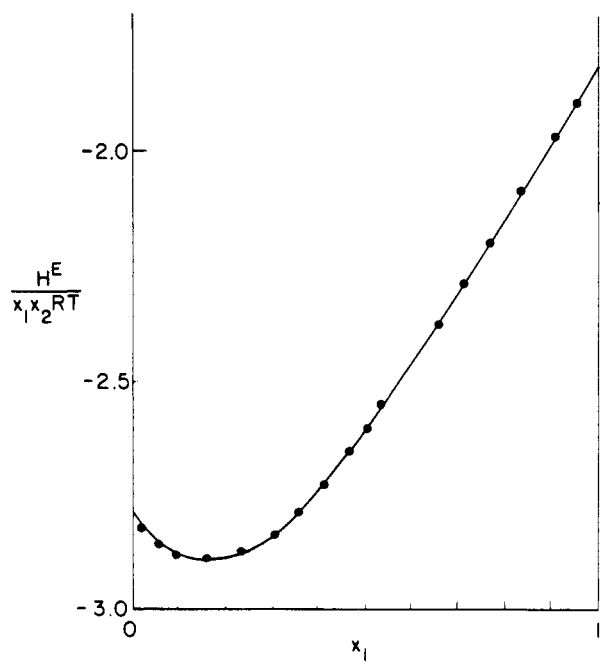

Figure 2. Correlation of H^E for binary system acetone(1)–chloroform(2) at 50°C
Points are experimental values; line represents Equation 1 with appropriate parameters from Table II

nary mixture. These H_{ij}^E values were determined from the correlations provided by Equation 1. The 123 experimental values of H_{123}^E for the ternary system acetone(1)–chloroform(2)–methanol(3) are given in Table III (deposited with the ACS Microfilm Depository Service). These data are adequately correlated by an equation of the form:

$$H_{123}^E = H_{12}^E + H_{13}^E + H_{23}^E + x_1x_2x_3\Delta_{123} \quad (2)$$

where

$$\Delta_{123}/RT = C_0 - C_1x_1 - C_2x_2 - C_3x_1^2 - C_4x_2^2 - C_5x_1x_2 - C_6x_1^3 - C_7x_2^3 - C_8x_1^2x_2 - C_9x_1x_2^2 \quad (3)$$

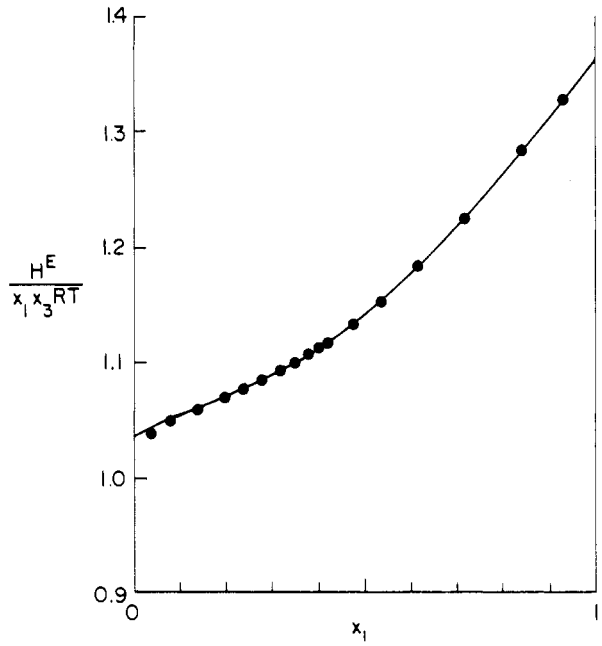

Figure 3. Correlation of H^E for binary system acetone(1)–methanol(3) at 50°C

Points are experimental values; line represents Equation 1 with appropriate parameters from Table II

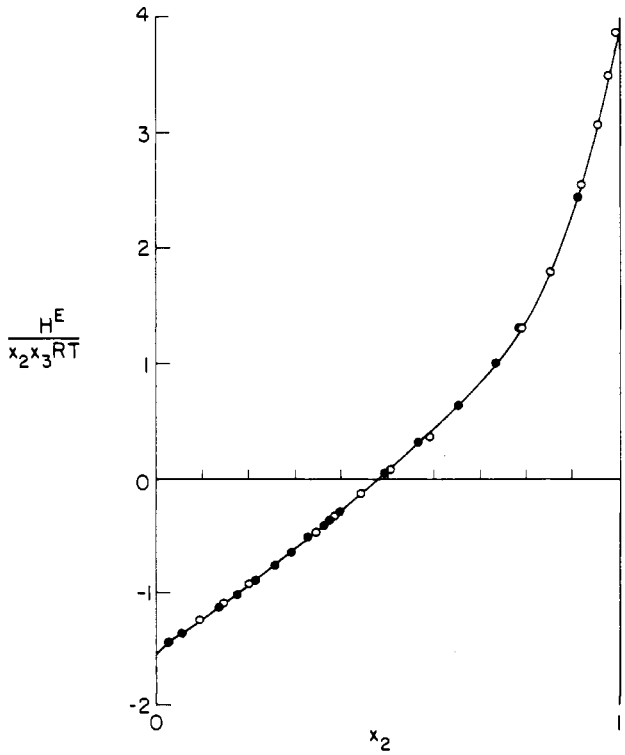

Figure 4. Correlation of H^E for binary system chloroform(2)–methanol(3) at 50°C

Points are experimental values; line represents Equation 1 with appropriate parameters from Table II. Open and closed circles distinguish between two sets of data taken by two different operators

Table IV. Correlating Parameters in Equation 3

Based on data for ternary mixtures of acetone(1)–chloroform(2)–methanol(3)

C_0 =	0.2936	C_5 =	−54.1833
C_1 =	7.1692	C_6 =	6.2136
C_2 =	29.7189	C_7 =	37.7718
C_3 =	−13.0018	C_8 =	34.3746
C_4 =	−56.0785	C_9 =	62.1298

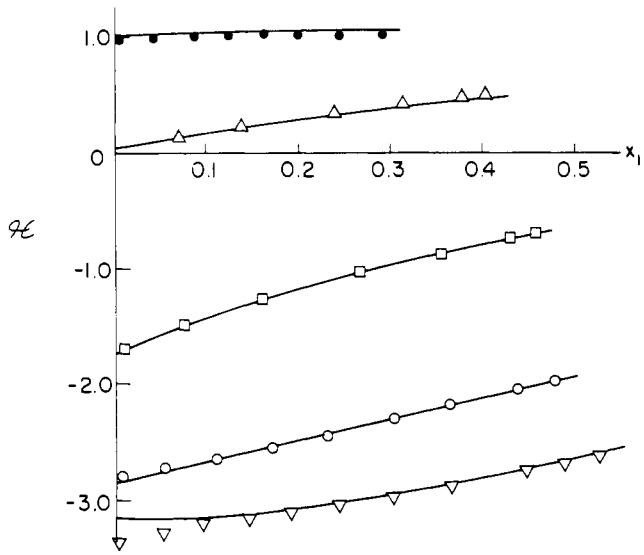

Figure 5. Correlation of results for ternary mixtures formed by addition of acetone(1) to initial binary mixtures of chloroform(2)–methanol(3)

Function plotted is $\mathcal{H} = [H_{123}^E - (1 - x_1)H_{23}^E(\text{initial})]/x_1(1 - x_1)RT$. Points are experimental values, and lines represent correlation provided by Equations 2 and 3. ●, x_2/x_3 = 0.0517; △, x_2/x_3 = 0.326; □, x_2/x_3 = 0.992; ○, x_2/x_3 = 3.03; ▽, x_2/x_3 = 21.9

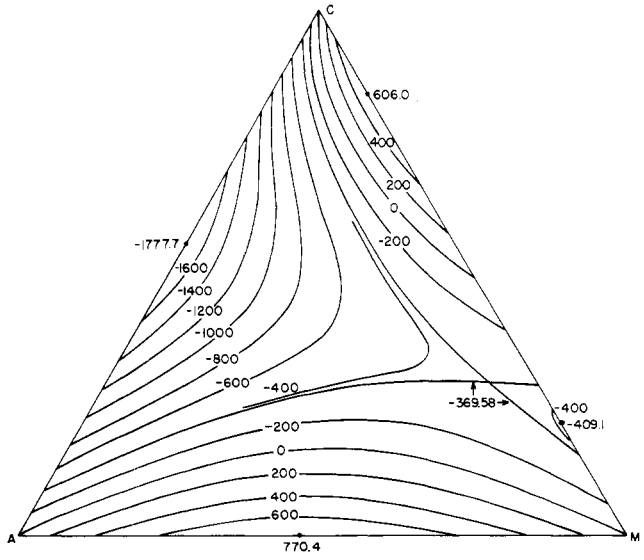

Figure 6. Lines of constant H^E in J/mol calculated from correlation of Equations 2 and 3 with parameters of Tables II and IV

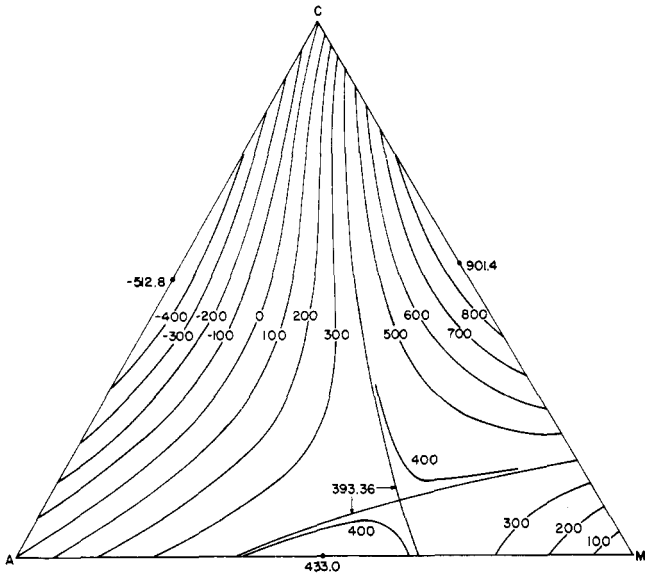

Figure 7. Lines of constant G^E in J/mol calculated from correlation for G^E given earlier (*1*)

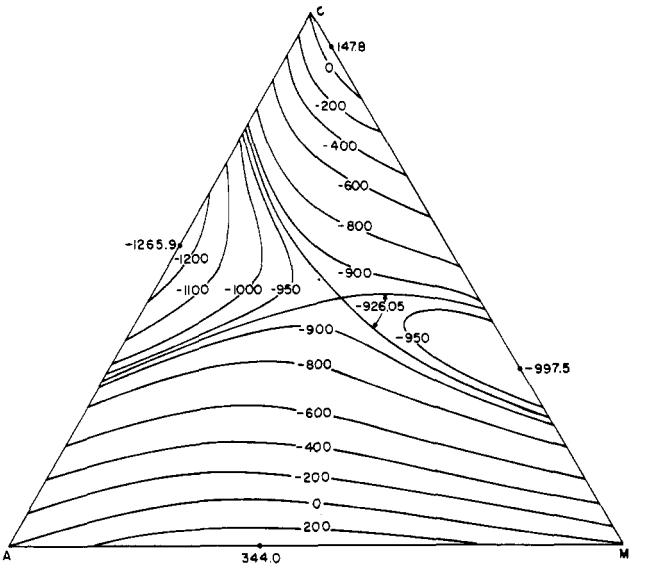

Figure 8. Lines of constant TS^E in J/mol calculated from correlations for H^E given here and for G^E given earlier (*1*)

In Equation 2 H^E_{12}, H^E_{13}, and H^E_{23} represent the correlations for the constituent binaries as given by Equation 1 in which all terms are evaluated at the actual mole fractions of the ternary mixture. The quantity Δ_{123}/RT incorporates all of the parameters determined solely from data taken for the ternary mixtures and is expressed as a function of composition by Equation 3. The parameters C_0 through C_9 determined by a least-squares fit of the 123 experimental data points for ternary mixtures are given in Table IV. The standard deviation between calculated and experimental values of H^E_{123} is about 10 J/mol, and the maximum deviation is about 30 J/mol. Figure 5 illustrates the quality of the fit provided by Equation 2 for the five runs in which pure acetone was added to initial binary mixtures of chloroform and methanol. The function plotted

$$[H^E_{123} - (1 - x_1)H^E_{23}(\text{initial})]/x_1(1 - x_1)RT \text{ vs. } x_1$$

is an analog for these runs of the plot of H^E_{ij}/x_ix_jRT vs. x_i commonly made for binary systems and illustrated by Figures 2–4.

A correlation was published earlier (*1*) for G^E for the ternary system considered here. This correlation and the one for H^E allow calculation of excess entropies from $TS^E_{123} = H^E_{123} - G^E_{123}$. In Figures 6–8 we show on triangular diagrams lines representing constant values for all three functions, H^E_{123}, G^E_{123}, and TS^E_{123}, as determined from these correlations.

Discussion

Since the correlations of our data by Equation 1 for the three binary systems represent the data within the precision of the experimental measurements, we do not expect that these correlations can be significantly improved. However, we have serious reservations with respect to the ultimate efficacy of Equations 2 and 3 in the correlation of data for such highly nonideal ternary mixtures as those considered here. Even with the use of 10 constants specific to ternary mixtures, the correlation does not do full justice to the data. Nevertheless, after many attempts by various means to achieve an improved correlation, we have reluctantly determined to publish the present correlation as an interim result, while continuing our efforts to improve upon it. Any such improvement must come as a result of an innovative procedure, for we have already tried the various schemes and equations extant in the literature, as well as many others that have come to mind.

Nomenclature

A_{ij}, A_{ji} = parameters in Equation 1
$C_0, \ldots, C_9$ = parameters in Equation 3
G^E = excess Gibbs free energy
H^E = excess enthalpy or heat of mixing
R = universal gas constant
S^E = excess entropy
T = absolute temperature
x_i, x_j = mole fractions of components i and j

Greek letters

Δ_{123} = function defined by Equation 3
λ_{ij}, λ_{ji}, ψ_{ij}, ψ_{ji} = parameters in Equation 1
σ = standard deviation

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Supplementary Material Available. Tables I and III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JCED-75-403.