Vapor-Liquid Equilibrium:

Part IV. Reduction of P-x Data for Ternary Systems

Total pressure measurements taken for the ternary systems acetone-chloroform-methanol and chloroform-ethanol-*n*-heptane at 50°C are reduced by Barker's method and correlated by an equation similar to one proposed by Wohl (1953).

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SCOPE

The apparatus of Gibbs and Van Ness (1972) has been adapted to *P-x* measurements for ternary systems. Extensive data on the acetone-chloroform-methanol and chloroform-ethanol-*n*-heptane systems at 50°C are reported. Data reduction by Barker's method yields analytical expressions for the composition dependence of the excess Gibbs function for these systems. Through use of a general expression for G^E similar to one proposed by Wohl (1953), the precise expressions for binary systems discussed by Abbott and Van Ness (1974) in Part III are introduced into the equation for ternary systems, and all of the advantages of Barker's method are extended directly to ternary systems.

CONCLUSIONS AND SIGNIFICANCE

Parts I, II, and III of this series of papers have dealt with vapor-liquid equilibrium in binary systems and have demonstrated the reliability and advantages of correlations based on just *P-x* data. The possible methods of data reduction have been detailed, and the focus of attention has ultimately fallen on Barker's method, a one-step procedure that requires an analytical expression for G^E that is capable of reproducing the *P-x* relation within experimental accuracy. The advantages attending Barker's method for binary systems are of greater significance for multicomponent systems because the alternative methods of data reduction by numerical techniques become vastly more complex. The extension of Barker's method to multicomponent systems requires nothing more than an appropriate analytical expression for G^E. Having demonstrated in Part III the practicality of the method for highly nonideal binary systems, we here show that the extension to ternary systems is not only feasible, but simple and direct.

The apparatus for vapor-liquid equilibrium determination from total pressure measurements described by Gibbs and Van Ness (1972) has been modified by the addition of a third degassing chamber and piston injector so that data may be taken for ternary systems. We report here results for the systems acetone-chloroform-methanol and chloroform-ethanol-*n*-heptane at 50°C. Data for the six constituent binaries, also for 50°C, were given by Abbott and Van Ness (1974) in Part III of this series of papers. The acetone, chloroform, and methanol were chromatoquality reagents supplied by Matheson, Coleman, and Bell; the *n*-heptane was the pure grade of Phillips Petroleum Company; the reagent-quality ethanol came from U. S. Industrial Chemicals. Except for degassing, all reagents were used as received with a minimum indicated purity of 99.8 mole %.

For the acetone-chloroform-methanol system the raw data for ternary mixtures consist of 164 sets of P, x_1, x_2, x_3 values: 98 such sets are reported for the chloroform-ethanol-*n*-heptane system.*

TREATMENT OF DATA

Data reduction by Barker's method (Barker, 1953) is accomplished through use of an analytical expression for G^E as a function of x_1, x_2, and x_3 capable of producing a fit of the data to within the limits of experimental uncertainty. We have chosen to represent G^E for the ternary systems by an equation similar to that proposed by Wohl (1953):

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* Tables of the raw data for the ternary mixtures have been deposited as Document No. 02523 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 2 Park Ave. So., New York 10016 and may be obtained for $2.00 for microfiche or $5.00 or photocopies.

TABLE 1. RESULTS OF DATA REDUCTION FOR TWO TERNARY SYSTEMS AT 50°C. PURE-COMPONENT VAPOR PRESSURES, VIRIAL COEFFICIENTS, PARAMETERS FOR EQUATION (1), AND PRESSURE DEVIATIONS

	Acetone(1)-chloroform(2)-methanol(3)	Chloroform(1)-ethanol(2)-n-heptane(3)
P_1^{sat}, mm Hg	614.48	520.00
P_2^{sat}, mm Hg	520.00	221.61
P_3^{sat}, mm Hg	417.18	141.92
B_{11}, cm³/mol	−1,425	−1,030
B_{22}, cm³/mol	−1,030	−1,690
B_{33}, cm³/mol	−1,200	−2,310
B_{12}, cm³/mol	−785	−695
B_{23}, cm³/mol	−595	−970
B_{13}, cm³/mol	−1,030	−1,300
C_0	2.6610	4.7617
C_1	1.5388	−0.2640
C_2	3.1846	1.1721
C_3	2.4459	−0.8722
Root mean square ΔP, mm Hg	0.87	0.89
Max $\lvert\Delta P\rvert$, mm Hg	2.85	2.69

$$g = g_{12} + g_{23} + g_{13} + (C_0 - C_1x_1 - C_2x_2 - C_3x_3)\,x_1x_2x_3 \qquad (1)$$

where $g \equiv G^E/RT$. Success in the application of Equation (1) to ternary data depends upon having first an excellent fit of g_{12}, g_{23}, and g_{13} to the data for the constituent binaries. Once this is accomplished, addition of the equations for the binaries [represented by $g_{12} + g_{23} + g_{13}$ in Equation (1)] produces results that require relatively simple expressions for the ternary term [represented by $(C_0 - C_1x_1 - C_2x_2 - C_3x_3)x_1x_2x_3$ in Equation (1)].

All of the constituent binaries were treated by Abbott and Van Ness (1974) in Part III, and the correlations of binary data summarized by Table 3 of that paper were used to provide the g_{ij} terms of Equation (1). Thus only the C_n's in Equation (1) are determined from the ternary data.

When Equation (15) of Part III is written for a multicomponent system, it becomes

$$P = \sum_i \frac{x_iP_i^{sat}}{\Phi_i} \exp\left[g - \sum_{k\neq i} x_k\left(\frac{\partial g}{\partial x_k}\right)_{x_{l\neq k,i}}\right] \qquad (2)$$

where

$$\Phi_i = \exp\left[\frac{(B_{ii} - V_i^L)(P - P_i^{sat}) + \frac{1}{2}P\sum_j\sum_k y_jy_k(2\delta_{ji} - \delta_{jk})}{RT}\right]$$

In the regression of ternary data, Barker's method provides values of the C_n's in Equation (1) that minimize the sum of squares of the differences between experimental values of P and the corresponding values given by Equation (2). Each term on the right-hand side of Equation (2) represents a partial pressure, y_1P, y_2P, or y_3P; thus the vapor composition is found by division of these terms by P. The Φ_i's represent factors which take into account the vapor-phase nonidealities (through the two-term virial equation) and the effect of pressure on liquid-phase fugacities. Since the y's are not known initially, these factors are determined through an iterative process.

Results of the application of Barker's method to the data for the two ternary systems reported here are summarized in Table 1. The pure-component vapor pressures and the virial coefficients are the same as reported in Part III. The C_n's represent only the ternary parameters in Equation

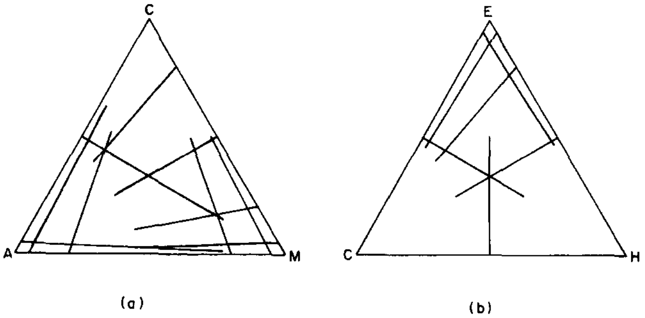

Fig. 1. Lines showing the compositions traversed during runs yielding vapor pressures:
(a) acetone(A)-chloroform(C)-methanol(M)
(b) chloroform(C)-ethanol(E)-n-heptane(H).

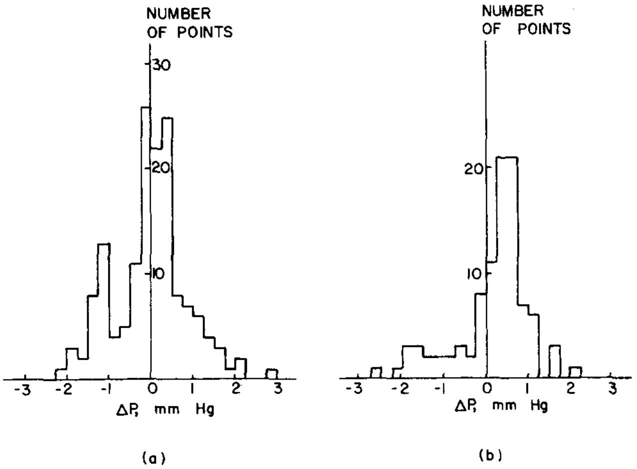

Fig. 2. Distributions of pressure deviations between values calculated by Equation (1) and experimental values (ternary data only):
(a) acetone-chloroform-methanol
(b) chloroform-ethanol-n-heptane.

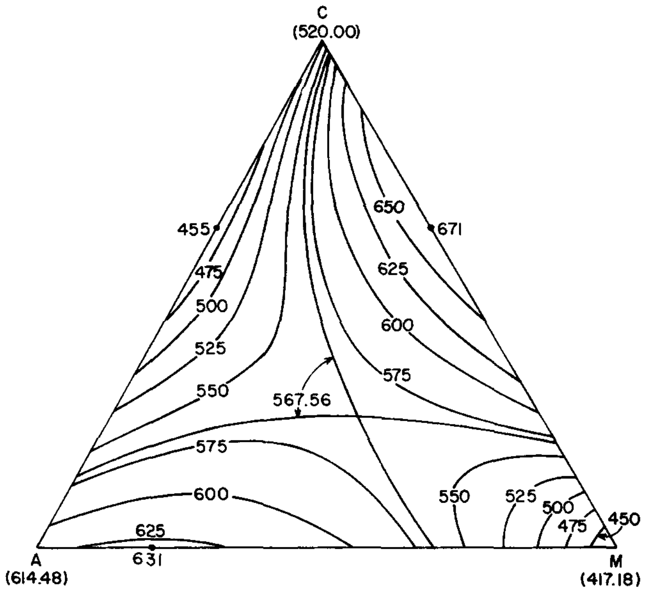

Fig. 3. Isobars (P in mm Hg) for the acetone(A)-chloroform(C)-methanol(M) system at 50°C.

(1). The binary correlations required in Equation (1) are provided by Table 3 of Part III. Thus the correlation of all data by means of Equation (1) for the acetone-chloroform-methanol system requires a total of 13 parameters and for the chloroform-ethanol-*n*-heptane system, 16 parameters. This straightforward correlational procedure produces equations which represent the data for these two highly nonideal systems to within the limits of experimental uncertainty, all that is required for the application of Barker's method.

The experimental data were taken in runs that proceeded along lines of constant mole ratio x_i/x_j, and those represented by the data are shown in Figure 1. The histograms of Figure 2 give an indication of the quality of fit to the data provided by the correlations. For both systems the root mean square ΔP is less than 0.9 mm Hg, and the maximum deviation is less than 3 mm Hg. In each case more than 70% of the measurements lie within ± 1 mm Hg.

Given an equation for G^E/RT as a function of liquid composition, one can readily determine both lines of constant G^E and lines of constant P for display on triangular diagrams with a grid representing liquid composition. Such diagrams for both systems are shown in Figures 3 through 6. For the acetone-chloroform-methanol system a saddle point appears on each diagram.

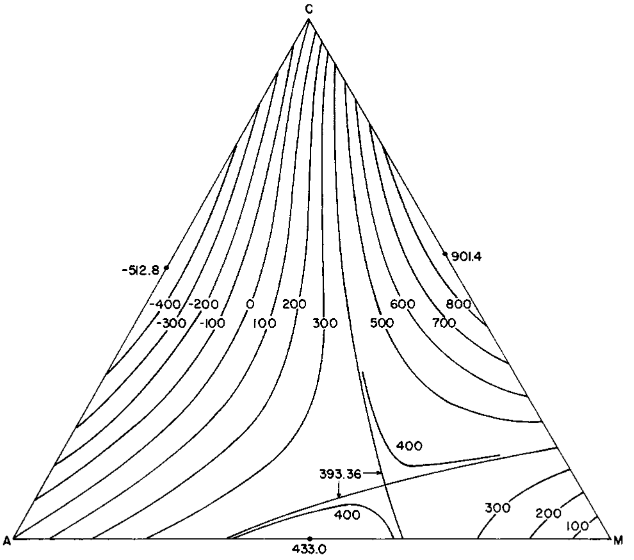

Fig. 4. Lines of constant G^E (*J/mol*) for the acetone(A)-chloroform(C)- methanol (M) system at 50°C.

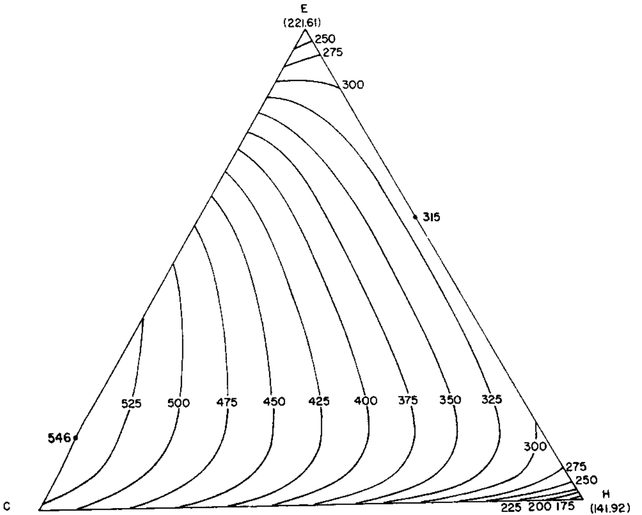

Fig. 5. Isobars (*P* in mm Hg) for the chloroform(C)-ethanol(E)-*n*-heptane(H) system at 50°C.

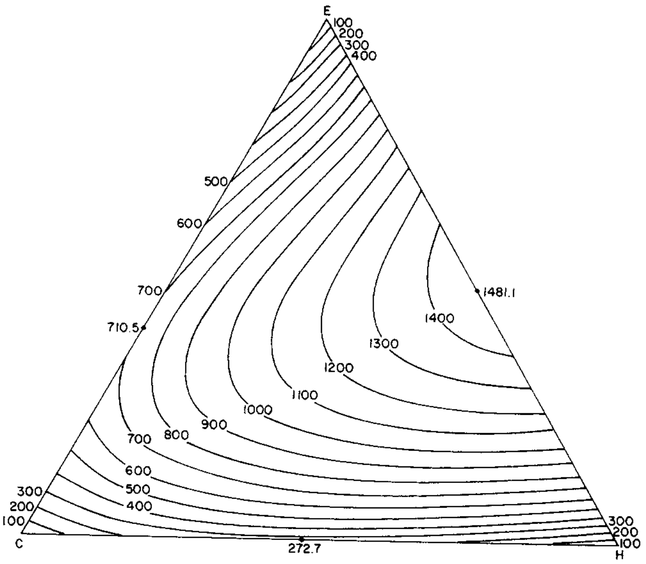

Fig. 6. Lines of constant G^E (*J/mol*) for the chloroform(C)-ethanol(E)-*n*-heptane(H) system at 50°C.

DISCUSSION

The form of the final term of Equation (1) is quite arbitrary; it lends flexibility without complexity. One wonders, first, what it contributes in comparison with the rest of the equation, and, second, whether a much simpler expression might not be adequate. We have therefore made two comparisons: (a) Values of P and the y's have been calculated at each experimental liquid composition from Equation (2) with $C_0 = C_1 = C_2 = C_3 = 0$ in Equation (1); (b) these calculations have been repeated with

$$C_0 = \frac{1}{2} \sum_{i \neq j}\sum A_{ij} \quad \text{and} \quad C_1 = C_2 = C_3 = 0$$

where the A_{ij} are the first two parameters in the Margules equations which represent the g_{ij} terms for the constituent binaries in Equation (1). The expression for C_0 is that proposed by Wohl (1953).

Comparison of pressures calculated for these two variants of Equation (1) with experimentally measured values yield the following results:

Acetone-chloroform-methanol

Case (a): Ave $\Delta P = -2.25$ and root mean square $\Delta P = 3.63$ mm Hg

Case (b): Ave $\Delta P = 8.76$ and root mean square $\Delta P = 11.97$ mm Hg

Chloroform-ethanol-*n*-heptane

Case (a): Ave $\Delta P = -29.83$ and root mean square $\Delta P = 38.81$ mm Hg

Case (b): Ave $\Delta P = -1.35$ and root mean square $\Delta P = 3.28$ mm Hg

In no case is the representation of pressure bias-free or within the limits of experimental accuracy. However, for each system one case produces surprisingly good results. Unfortunately, it is not the same case for the two systems, and in each instance we must conclude that the agreement is fortuitous. With respect to vapor composition, comparisons can be made only with values of the y_i's calculated with Equation (1) and best-fit values for the C_n's. Here the root mean square Δy is 0.01 or less in both case (a) and (b) for acetone-chloroform-methanol and in case (b) for ethanol-chloroform-n-heptane. For the latter system case (a) gives a root mean square Δy of about 0.04.

TABLE 2. RESULTS OF DATA REDUCTION FOR THE BINARY SYSTEMS REPORTED BY SEVERNS ET AL. (1955)

	Acetone(1)-chloroform(2)	Acetone(1)-methanol(2)	Chloroform(1)-methanol(2)
Type of Margules equation*	4-suffix	3-suffix	5-suffix
P_1^{sat}, mm Hg	612	612	521
P_2^{sat}, mm Hg	521	418	416
A_{12}	−0.8713	0.6124	0.7694
A_{21}	−0.5138	0.6168	2.1224
α_{12}	0.1809	—	—
α_{21}	0.1809	—	—
λ_{12}	—	—	−0.2890
λ_{21}	—	—	1.6087
Root mean square ΔP, mm Hg	0.86	1.57	1.28
Max $\lvert\Delta P\rvert$, mm Hg	1.69	3.33	2.65
Root mean square Δy	0.007	0.010	0.010
Max $\lvert\Delta y\rvert$	0.016	0.023	0.020
No. of data points	29	34	22

* See Equations (5) and (6) of Part III.

We conclude that for the highly nonideal ternary systems considered here Barker's method for the reduction of P-x data can be successfully applied provided an adequate expression for the ternary term of Equation (1) is included.

Although no data are reported in the literature for the chloroform-ethanol-n-heptane system (Wichterle et al., 1973), data for acetone-chloroform-methanol at 50°C are given by Severns et al. (1955), and we have made a detailed analysis of their results. Their data were taken with a recirculating still, and measured values of P, x, and y were reported. In order to treat their data on the same basis as our own, we fit their P vs. x data for the three binary systems by Barker's method to exactly the same G^E vs. x expressions reported in Part III. The same virial coefficients were used, but the pure-component vapor pressures were those reported with their data. As a result of preliminary fits, one data point for the acetone-methanol system and three data points for the chloroform-methanol system were found to deviate from the correlation by several times the root mean square deviation, and these points were eliminated from the data set. The results of this treatment of the data of Severns et al. for the three binary systems are given in Table 2, which is directly comparable to Table 3 of Part III. In addition, the deviations ΔP and Δy_1 between calculated and experimental pressures and vapor compositions are displayed in Figure 7. The experimental pressures, which are reported just to the nearest mm Hg, are seen to be well correlated by the equations used. The comparison of the correlating equations with our own results is shown in Figure 8. The deviations Δy_1 in Figure 7 show varying degrees of nonrandom behavior, least for acetone-chloroform and greatest for chloroform-methanol, indicating that the requirements of thermodynamic consistency

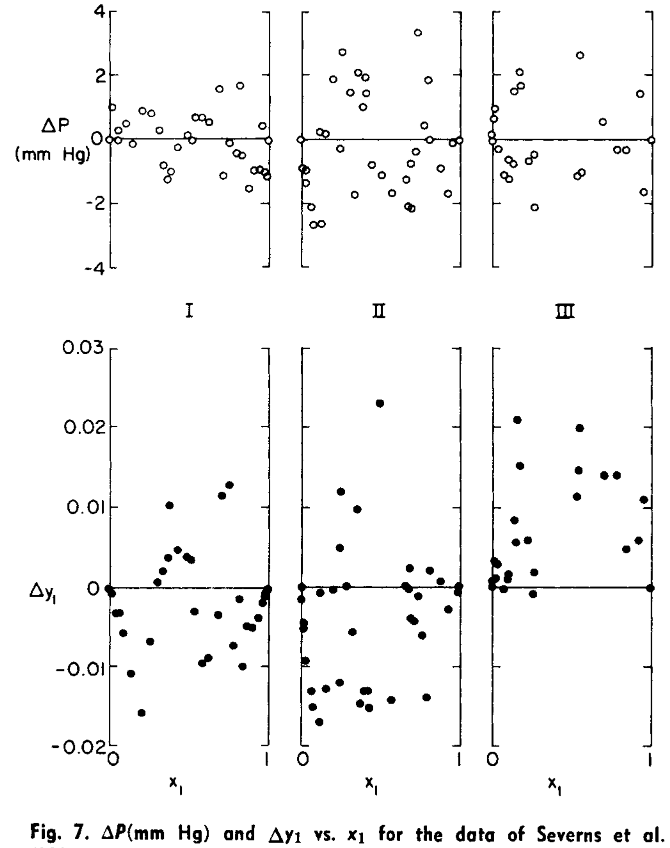

Fig. 7. ΔP(mm Hg) and Δy_1 vs. x_1 for the data of Severns et al. (1955) at 50°C. (I) acetone-chloroform, (II) acetone-methanol, (III) chloroform-methanol.

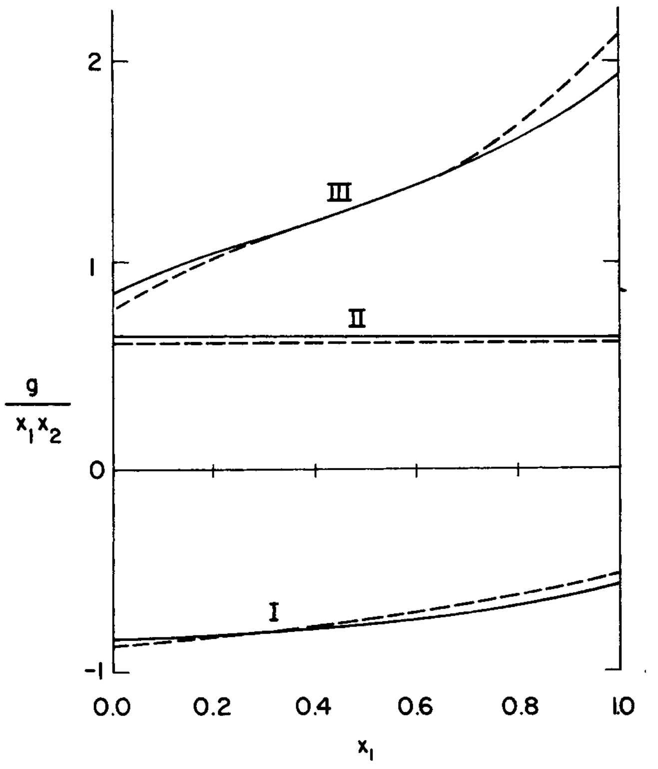

Fig. 8. Comparison of the correlations g/x_1x_2 vs. x_1 at 50°C of the data of Severns et al. (1955) [dashed lines] with those of Abbott and Van Ness (1974) [solid lines]. (I) acetone-chloroform, (II) acetone-methanol, (III) chloroform-methanol.

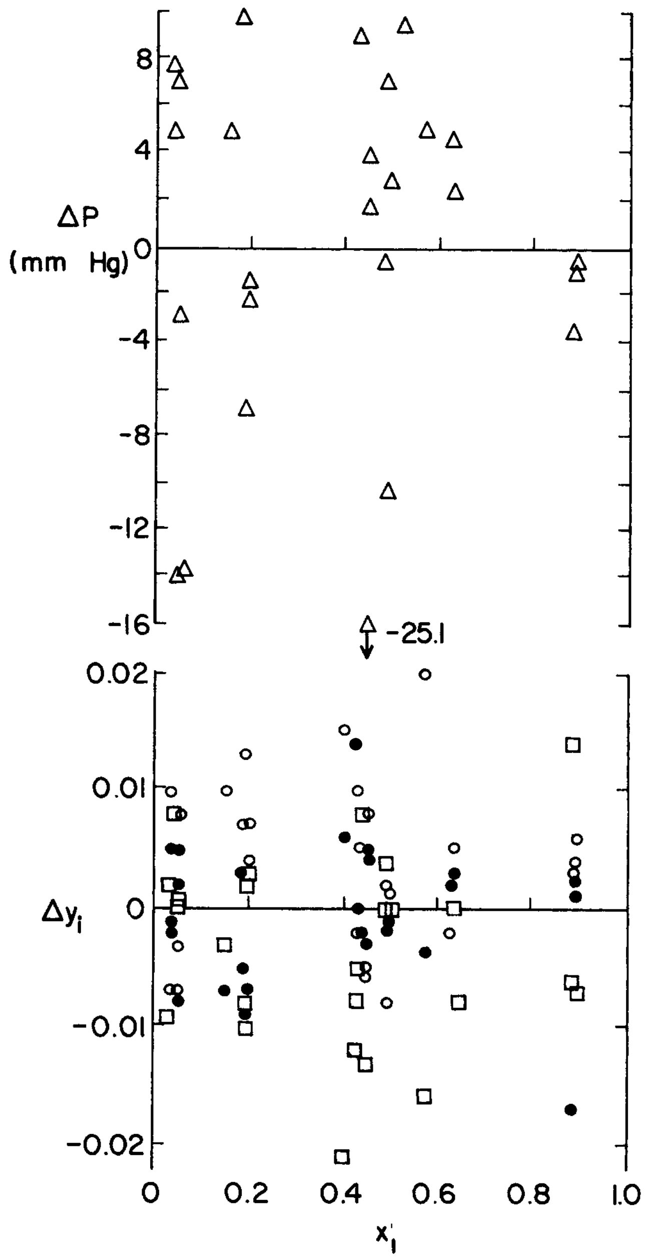

Fig. 9. ΔP(mm Hg) and Δy_i vs. x_1 representing differences between the present correlation of ternary data for the acetone(1)-chloroform(2)-methanol(3) system at 50°C and the experimental values of Severns et al. (1955).

are not fully met by the data. Nevertheless, the data of Severns et al. for the three binary constituents of the acetone-chloroform-methanol system appear to be of reasonable reliability and are not significantly at odds with the results presented in Part III.

If we presume that the data of Severns et al. for the ternary system are of comparable reliability to those for the constituent binaries, then we can with some confidence use their results to assess our own ternary data. The table of data for the ternary system provided by Severns et al. contains several inconsistencies ($\Sigma x_i \neq 1 \pm 0.005$) and obvious typographical errors. On this basis we rejected five data points, leaving a total of 26 experimental sets of measurements (P, x, and y). For each of the 26 liquid compositions, values of P and the vapor compositions were calculated from the correlation represented by Equation (1) with the parameters given in Table 1 of this paper and in Table 3 of Part III. The results were compared with the experimental values of Severns et al. by calculation of the deviations ΔP, Δy_1, Δy_2, and Δy_3. These deviations are plotted as a function of x_1 in Figure 9. The root mean square ΔP is 8.2 mm Hg; however, the average ΔP is less than -0.1 mm Hg, showing that our equation provides an essentially bias-free correlation of the pressures measured by Severns et al. With respect to vapor composition the overall root mean square Δy (all three y_i's) is 0.0076, and the average Δy is necessarily zero. Comparison of Figure 9 with Figure 7 shows that the range of the ternary Δy deviations between our calculated y's and the experimental y's of Severns et al. is no greater than the range of the binary Δy deviations based entirely on the data of Severns et al. We must conclude that our calculated results fall well within the range of uncertainty of the experimental values reported by Severns et al.

The extension from binary to ternary systems of the technique of determining reliable VLE relationships from just P-x data and their reduction by Barker's method appears to be straightforward, as is demonstrated by the results presented here for the two ternary systems acetone-chloroform-methanol and chloroform-ethanol-n-heptane.

ACKNOWLEDGMENT

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NOTATION

A_{ij} = binary parameters in Margules equations
B_{ij} = second virial coefficient
C_0, C_1, C_2, C_3 = empirical parameters in Equation (1)
G^E = excess Gibbs function, liquid phase
g = G^E/RT
g_{ij} = represents an expression for g for ij binary
P = vapor pressure in general
P_i^{sat} = vapor pressure of pure i
R = universal gas constant
T = absolute temperature
x_i = mole fraction of i, liquid phase
y_i = mole fraction of i, vapor phase
δ_{ij} = $2B_{ij} - B_{ii} - B_{jj}$
Φ_i = fugacity correction factor
ΔP, Δy_i = differences between calculated and experimental values

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