Estimation of Ternary Vapor-liquid Equilibrium

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Isothermal vapor-liquid equilibrium measurements were made at 50°C. for the ternary systems acetone-methanol-chloroform, acetone–methanol–carbon tetrachloride, and acetone–methanol–methyl acetate, by means of an improved vapor-recirculation type of apparatus. The complete range of concentrations was investigated, including six of the seven constituent binary systems. Chemical methods, supplemented by density and refractive-index measurements, were used for analysis.

Results are presented in the form of activity coefficients γ as a function of various concentrations. Binary and ternary constants for the three-suffix Margules equations were determined by plots of $(\log \gamma)/(1-x)^2$ as a function of the mole fraction x. Such equations have been found to represent both the binary and the ternary data adequately except in the system containing both methanol and carbon tetrachloride. For these mixtures a simplified four-suffix equation, including a single ternary constant, correlates binary and ternary equilibrium data.

The data indicate that reliable estimates of ternary equilibria can be based on the assumption that the ternary constant C^* is zero for mixtures in which all deviations from Raoult's Law are positive. This is interpreted as indicating that the probability of existence of trimolecular aggregates, two- or three-component, in ternary solutions is no greater than the average of probabilities of existence of trimolecular aggregates in the constituent binary systems.

Based on equations of the Margules type, a procedure is outlined for determining binary constants rapidly and for planning experiments whereby a ternary system may be completely investigated with the aid of very few measurements.

The composition changes that the accompany differential distillation of the three ternary mixtures are described qualitatively in terms of the shape of the vapor-pressure-composition surfaces.

In the design of azeotropic and extractive distillation equipment, reliable multicomponent vapor-liquid equilibria are necessary for the estimation of heat requirements and separation efficiencies. It would be most helpful to be able to predict equilibrium relationships from the properties of the pure compounds or, failing this, from a minimum of experimental data. Such information would be useful, for example, for the selection of a suitable third component to facilitate the separation of two close-boiling or azeotropic liquids by distillation. The use of empirical equations for extension or prediction of multicomponent vapor-liquid equilibria is useful for this purpose but is tedious even for the case of ternary mixtures.

A method for treating equilibria in ternary mixtures which would reduce the required experimentation and simplify the fitting of existing empirical equations to isothermal ternary data would appear to be of value. A method for predicting the constants in these empirical equations, preferably from the properties of the pure compounds or, alternatively, from data on the binary systems involved, would simplify calculations. Methods have been proposed for extending basic data and estimating values of constants in the equations for prediction of activity coefficients, but the literature does not presently contain sufficient thermodynamically reliable data to test these methods thoroughly. Experimental data have been published for several ternary and quarternary systems, but a complete test of equations for activity coefficients has usually not been possible because the whole range of compositions was not covered, because the experimental errors were too great, or because one of the pairs was ideal, leading to a degenerate case.

During this investigation isothermal data were determined for the systems acetone-methanol-chloroform, acetone-mtehanol–methyl acetate, and acetone-methanol–carbon tetrachloride at 50°C. The first system has both positive and negative deviations from Raoult's Law and none of its binary mixtures are ideal. The other two systems are of the type most frequently encountered: mixtures of organic liquids which exhibit only positive deviations from ideality. Again none of the binary mixtures are ideal. Wohl's Margules-type equations (*12* and *13*) were compared

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with the data. A systematic approach to experimentation and techniques facilitating the use of the equations were developed.

MATHEMATICAL REPRESENTATION OF ACTIVITY COEFFICIENTS

The equation describing the distribution of a component, i, at equilibrium between liquid and vapor phases and defining its activity coefficient, γ_i, is

$$\pi y_i z_i = \gamma_i P_i x_i \qquad (1)$$

Generally either π or the temperature is fixed; P_i and z_i are characteristic of the pure component. The liquid-phase mole fraction, x_i, may be chosen arbitrarily, and the activity coefficient, γ_i, is related to it by solutions of the equations

$$\ln \gamma_i = (1/RT)\,(\partial/\partial n_i) \sum_1^j n_j G^E \qquad (2a)$$

$$\sum_1^j x_i \, d(\ln \gamma_i) = 0 \qquad (2b)$$

Equation (2*b*) indicates a simple test for thermodynamic consistency of isothermal vapor-liquid equilibrium data.

Carlson and Colburn(*2*) gave methods of extending and predicting binary vapor-liquid equilibria. They pointed out the utility of end values of log γ_i at infinite dilution of component i as constants in the development of empirical equations applicable to binary mixtures. Wohl(*12* and *13*) presented a series of equations of varying complexity to describe activity coefficients as functions of concentration in binary, ternary, and quarternary mixtures using as constants the end values of log γ_i for the component binary pairs. The simplest of Wohl's equations to fit a wide variety of binary mixtures is the three-suffix Margules type expressed in mole fractions. In this case the excess free energy of mixing is assumed to be given by

$$G^E/2.3\,RT = x_1 x_2 (A_{21} x_1 + A_{12} x_2)$$

$$A_{12} = \lim_{x_1 \to 0} (\log_{10} \gamma_1) \qquad (3)$$

From Equation (3), by application of Equation (2), the equations for logarithms of activity coefficients are

$$\log_{10} \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})\, x_1] \qquad (4)$$

$$\log_{10} \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})\, x_2] \qquad (5)$$

These equations fitted each of the binary systems investigated in this study with the exception of mixtures of methanol and carbon tetrachloride, in which the deviations from ideal behavior were extremely large. The function (log γ) / (1-x)^2, hereafter called J, was used for evaluation of the data. From Equations (4) and (5)

$$J_1 = A_{12} + 2(A_{21} - A_{12})\, x_1 \qquad (6)$$

$$J_2 = A_{21} + 2(A_{12} - A_{21})\, x_2 \qquad (7)$$

At $x_1 = 0$, $J_1 = A_{12}$; at $x_2 = 0$, $J_2 = A_{21}$. Similarly, at $x_1 = 0.5$, $J_1 = A_{21}$ and $J_2 = A_{12}$. J is a linear function of x. The linearity of this function for binary systems described by Margules-type equations is also noted elsewhere(*8*).

In Equation (1) the quantities π, z_i, P_i, and temperature may be measured or calculated accurately. J is very sensitive to errors in measurement of concentrations and consequently is a good function with which to check adequacy of equilibrium experiments and accuracy of analyses. However, in the region $0.5 < x_i < 1.0$, J becomes very erratic even for good data. The most significant values of J_i are those observed in the region $0 < x_i < 0.5$.

For more complex binary mixtures, particularly those involving very large deviations from ideality, the four-suffix Margules binary equation of Wohl(*12*) may be useful. These equations, when plotted as J vs. x, result in curved lines, as for carbon-tetrachloride-methanol, as shoyn in Figures 19 and 20.

In Wohl's nomenclature, recently revised(*13*), the three-suffix Margules ternary equation, written in mole fractions, is derived from

$$G^E/2.3\,RT = x_1 x_2 (x_1 A_{21} + x_2 A_{12}) + x_1 x_3 (x_1 A_{31} + x_3 A_{13}) + x_2 x_3 (x_2 A_{32} + x_3 A_{23}) + x_1 x_2 x_3 [\tfrac{1}{2} (A_{12} + A_{21} + A_{13} + A_{31} + A_{23} + A_{32}) - C^*] \qquad (8)$$

In this new method of representation Wohl has used a new ternary constant, C^*, that is independent of the numbering of components. It is related to the older definition of $C(12)$ by the equation

$$C^* - C = \tfrac{1}{2} (A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13}) \qquad (8a)$$

By use of Equation (2), it follows that

$$\log_{10}\gamma_1 = x_2^2 [A_{12} + 2x_1 (A_{21} - A_{12})] + x_3^2 [A_{13} + 2x_1 (A_{31} - A_{13})] + x_2 x_3 [\tfrac{1}{2} (A_{21} + A_{12} + A_{31} + A_{13} - A_{23} - A_{32}) + x_1 (A_{21} - A_{12} + A_{31} - A_{13}) + (x_2 - x_3)(A_{23} - A_{32}) - (1 - 2x_1)\, C^*] \qquad (9)$$

Log γ_2 and log γ_3 may be determined from Equation (14) by cyclic permutation of subscripts according to the scheme

$$\begin{tikzcd} & 1 \arrow[dr] & \\ 3 \arrow[ur] & & 2 \arrow[ll] \end{tikzcd}$$

Let R_2 be defined as $x_2/(x_2 + x_3)$, the mole fraction of component 2 on a one-free basis; then J_1 may be expressed as

$$J_1 \equiv (\log_{10} \gamma_1)/(1 - x_1)^2 = R_2^2 [A_{12} + 2x_1 (A_{21} - A_{12})] + (1 - R_2)^2 [A_{13} + 2x_1 (A_{31} - A_{13})] + R_2 (1 - R_2) [\tfrac{1}{2} (A_{21} + A_{12} + A_{31} + A_{13} - A_{23} - A_{32}) + x_1 (A_{21} - A_{12} + A_{31} - A_{13}) + (1 - x_1)(2R_2 - 1)(A_{23} - A_{32}) - (1 - 2x_1)\, C^*] \qquad (10)$$

As in binary systems, J_1 is a linear function of x_1 for R_2 constant. At $R_2 = 1$, Equations (4) and (9) as well as (6) and (10) are equivalent and describe the activity coefficient of component 1 in binary mixtures with component 2. At $R_2 = 0$ the activity coefficient of component 1 in binary mixtures with component 3 is obtained.

Equations (8), (9), and (10) fit the data of the first two ternary systems investigated with sufficient accuracy that use of more complicated equations was not required. The experimental data for the third ternary system were also fitted satisfactorily but the slightly more complicated four-suffix equations of Wohl(*13*) showed a statistically significant improvement, owing to the fact that the binary system methanol–carbon tetrachloride required the use of the four-suffix binary equations.

PLANNING OF EXPERIMENTS

Use of J as a correlating function, as shown in Equations (6) and (7), suggests a procedure for taking ternary vapor-liquid equilibrium data which will reduce appreciably the number of experiments required to investigate a system adequately. All compositions at constant R lie on a straight line on a ternary diagram such as Figure 1. From Equation (9) the ternary constant contributes most to the value of log γ_i in the region $x_i \doteq 0$, $x_j \doteq x_k \doteq 0.5$. One such region is found in Figure 1 for each of three components; these are the regions in which experimental ternary measurements should be concentrated once the binary data are fully known.

Chemical analysis for the dilute component should be accurate if the J value is to be significant; analytical accuracy need not be so great for the other compounds, although greater accuracy is required if these other compounds have very different molecular weights. Ternary equilibrium determinations in each of the regions 1, 2, and 3 of Figure 1, plus data on the three binary systems, are sufficient to evaluate all the constants in the equations. In their most general form the four-suffix equations contain three different ternary constants; consequently, three independent ternary determinations are required. A single ternary determinmination may be sufficient, however, if the binary systems are satisfied by the simpler three-suffix equations; even when the more involved equations are needed, the three C^* values may often be equal.

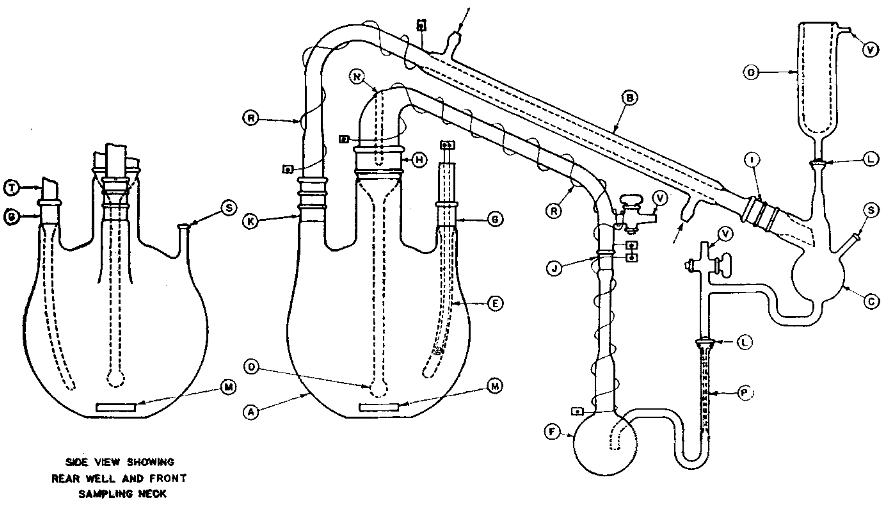

Fig. 2. Isothermal equilibrium apparatus.

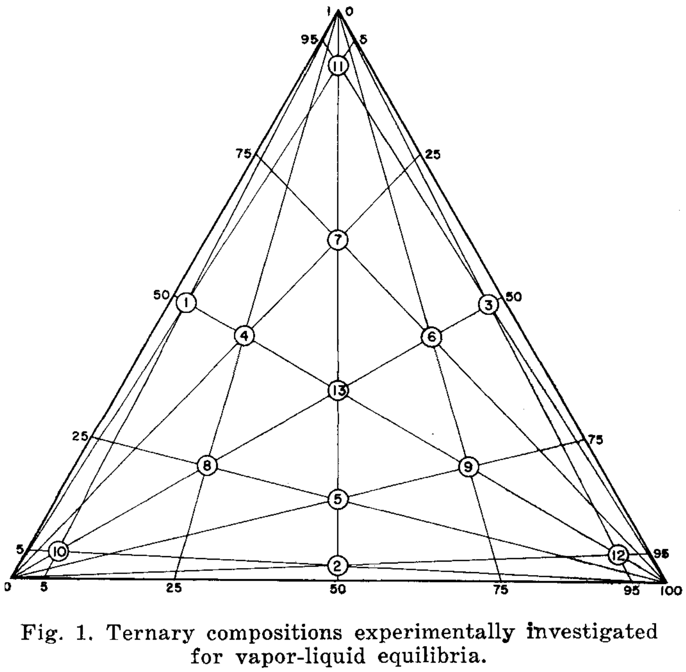

Fig. 1. Ternary compositions experimentally investigated for vapor-liquid equilibria.

For rapid comparison of data with calculated J values based on Equation (10), it is useful to know particular values of J_i at strategically chosen compositions. For example, at $x_1 = 0$ and $R_2 = \frac{1}{2}$, J_1 becomes

$$J_1 = \tfrac{1}{8}\,[3\,(A_{12} + A_{13}) + (A_{21} + A_{31}) - (A_{23} + A_{32}) - 2C^*] \quad (11)$$

for the three-suffix ternary Margules equation. The equivalent function for the other components are obtained by cyclic permutation of subscripts. Moreover, at $R_2 = \frac{1}{2}$, $x_1 = 0.5$, Equation (11) is altered to

$$J_1 = \tfrac{1}{4}\,[2\,(A_{21} + A_{31}) - \tfrac{1}{2}\,(A_{23} + A_{32})] \quad (12)$$

This latter equation does not include a term containing C^* and consequently the value of J is independent of C^* at $x = 0.5$. Thus it is clear that data taken at nearly equal mole fractions of the mole components give little information regarding ternary contributions to nonideality. Data plotted as J vs. x may be easily and sensitively checked for self-consistency and those taken at R = constant rapidly compared with the three- and four-suffix Margules equations. By use of Equations (11) and (12) from those data taken with x dilute and $R \doteq \frac{1}{2}$, C^* may be accurately

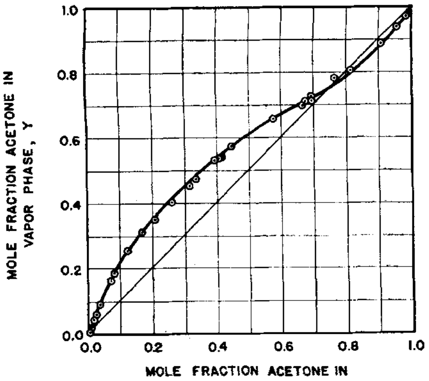

Fig. 3. Vapor-liquid equilibria for system acetone-methanol at 50°C.

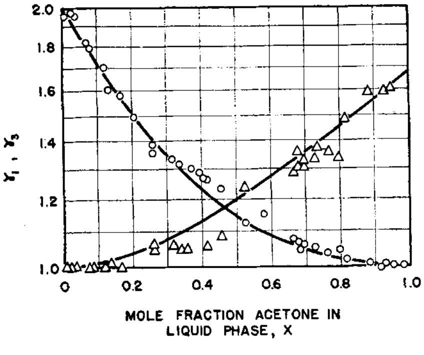

Fig. 4. Activity coefficients for binary system acetone-methanol at 50°C.

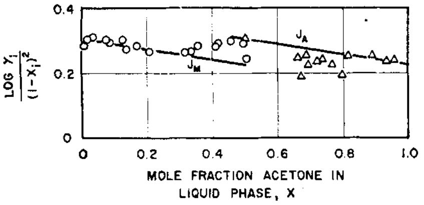

Fig. 5. Comparative plot of activity coefficients for acetone-methanol at 50°C. with three-suffix Margules equation.

and rapidly determined from the plot. Equations (11) and (12) give values of J calculated from ternary equations at the liquid-phase concentrations which are at the limits of the practical significance of the function. The J-plot procedure is equally applicable to three- and four-suffix equations of Wohl (13) in q or volume fractions. These modified equations, however, were not required to fit any of the systems investigated here.

EXPERIMENTAL PROCEDURE

A modification of the vapor-recirculation equilibrium still described by Jones, Schoenborn, and Colburn (5) was used for the equilibrium determinations. The present apparatus, shown in Figure 2, differs from the original model in two essentials. To provide better temperature control, the equilibrium chamber was surrounded by a water bath. Increasing the liquid-chamber volume to 3 liters increased the condensate volume and yet greatly reduced the condensate-to-liquid volume ratio. This permitted larger condensate samples to be taken for analysis and yet kept small the required time for attainment of equilibrium. In addition, several runs could be made at or very near the same composition with a given charge of components. The reprodicibility of successive samples provided an estimate of the accuracy of the experimental technique. Further, by starting with a binary charge and adding only the third component to change the composition between ternary determinations, successive experiments could be made at constant R.

A magnetic stirrer was used for agitation in the liquid chamber. This improved the rate of response to adjustments in total pressure. Both the liquid and condensate were sampled with a hypodermic syringe provided with a special long needle. The temperature of the liquid was compared with that of the water bath by means of a double-junction copper-constantan thermocouple. A small internal heater was useful for adjusting the vapor circulation rate to begin an experiment but was turned off after circulation had commenced. If the pressure became too high during operation, circulation promptly ceased; if the pressure was reduced below the equilibrium value, the circulation rate increased until the flash boiler flooded. The range of pressures over which steady circulation occurred was about 1 mm. Hg.

The pressure in the system was adjusted by introducing nitrogen into the condenser and was measured by means of a temperature-compensated mercury barometer. The temperature of the water bath was controlled and measured by standard apparatus.

For analysis of ternary mixtures, measurement of at least two independent properties is necessary. Chemical methods specific for acetone and methanol were supplemented by densities sensitive to the amount of chloroform, methyl acetate, or carbon tetrachloride present. A modification of the hydroxylamine hydrochloride method of Huckabay, Newton, and Metler (4) was used for acetone, and the acetyl chloride method proposed by Smith and Bryant (10) was used to determine methanol. Density was determined by the pycnometric method described by Langdon and Keyes (6). Refractive indexes were measured with a Bausch and Lomb dipping-type refractometer and were used instead of density for analyses of the acetone-chloroform and chloroform-methanol binary systems. In acetone analyses, results were reproducible to about 0.5 mole % of the acetone present in the sample and the methanol results were reproducible to about 1.0 mole % of the methanol present. Density and refractive-index measurement were reproducible to a precision equivalent to 0.1 mole % chloroform or carbon tetrachloride or 0.2 mole % methyl acetate. This high precision was possible because the two physical properties were found to be almost a linear function of the volume fraction of chloroform, carbon tetrachloride, or methyl acetate present. A calibration curve of deviations from additivity of density or refractive index when plotted vs. ideal volume fraction permitted precise determination of composition. To obtain complete analyses of ternary sample, check measurements were made by use of both chemical methods and density in practically all cases.

Large quantities of the pure components were required both for the vapor-liquid measurements and for the establishment of analytical methods. Baker and Adamson technical-grade chloroform was dried over phosphoric acid anhydride, then distilled batchwise at an 8-to-1 reflux ratio through a large-capacity, 24-theoretical-plate packed column. A heart fraction was collected having a boiling range of 0.2°C. Reagent-grade acetone and methanol were distilled in a similar manner. Technical-grade methyl acetate was dried over silica gel for 48 hrs. and a heart cut with a boiling range of 0.2°C. was collected. Technical-grade carbon tetrachloride was distilled batchwise in the fractionating column. The middle 60% of a batch was collected; the distillate temperature did not vary more than 0.1°C. during collection of the heart cut.

EXPERIMENTAL RESULTS

Vapor-liquid equilibrium determinations were made on the three ternary systems acetone-methanol-chloroform, acetone-methanol–carbon tetrachloride, acetone-methanol–methyl acetate and on six of the seven constituent binary systems. All activity coefficients were corrected slightly for nonideality of the vapor phase by the method described by Mertes and Colburn (7).*

The acetone (1)-methanol (3) binary system is common to all the ternary groups. Figures 3 to 5 show, in order, the x-y diagram, curves of $\log_{10}\gamma$ vs. x, and J plots for this system. End values were computed from the J plots by the method of least squares. The values compare favorably with the results of Uchida et al. (11).

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*Experimental data may be obtained as document 4510 from the Photoduplication Service, American Documentation Institute, Library of Congress, Washington 25, D.C., for $1.75 for microfilm or $2.50 for photoprints.

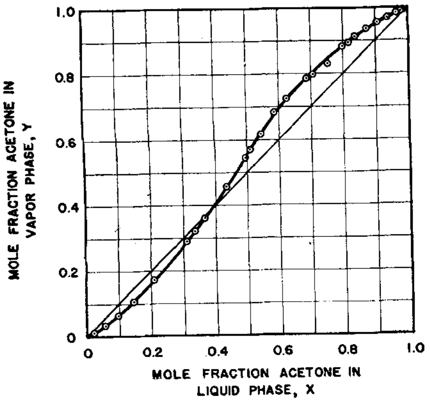

Fig. 6. Vapor-liquid equilibria for acetone-chloroform at 50°C.

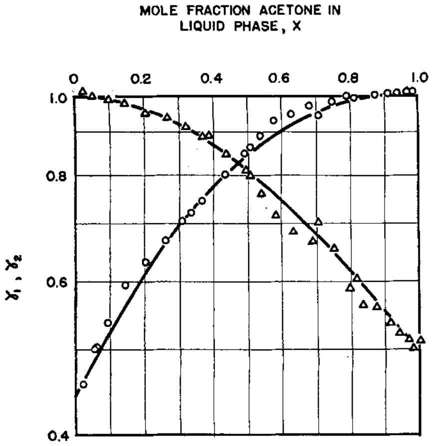

Fig. 7. Activity coefficients for system acetone-chloroform at 50°C.

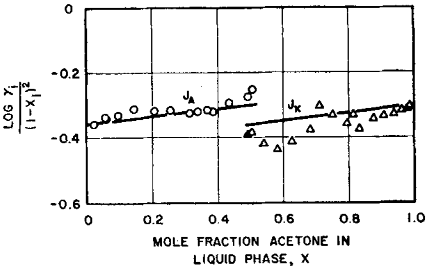

Fig. 8. Comparative plot of activity coefficients for acetone-chloroform at 50°C. with three-suffix Margules equation.

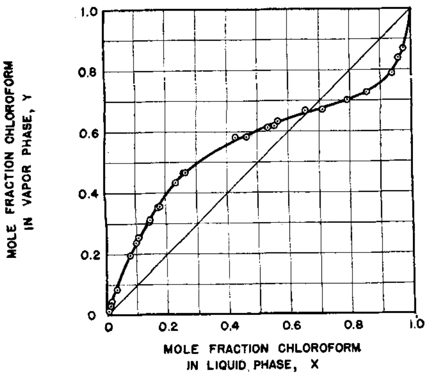

Fig. 9. Vapor-liquid equilibria for chloroform-methanol at 50°C.

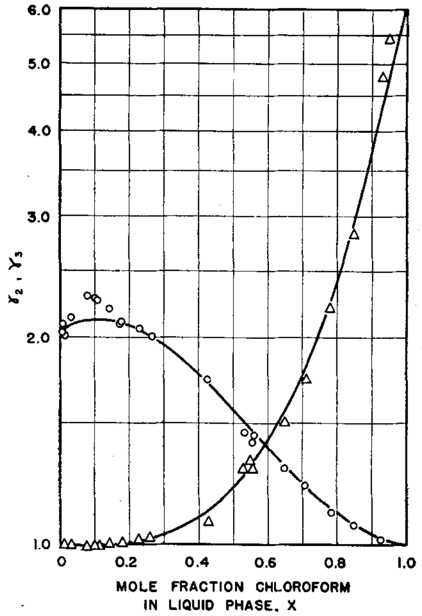

Fig. 10. Activity coefficients for chloroform-methanol at 50°C.

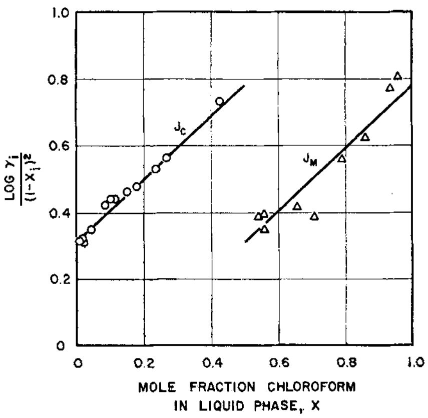

Fig. 11. Comparative plot of activity coefficients for chloroform-methanol at 50°C. with three-suffix Margules equation.

The system acetone (1)-chloroform (2) shows negative deviations from ideality; Figures 6 to 8 represent the results.

Figures 9 to 11 show the characteristics of the system chloroform (2)-methanol (3), which is interesting because of the great asymmetry of the log γ–x curves.

The data used for the carbon tetrachloride–methanol system are those of Scatchard, Wood, and Mochel(*9*), who recommended a four-suffix equation for representing the excess free energy.

Table 1 lists the Margules constants for each of the systems.

Observed vapor-liquid equilibrium compositions for the ternary systems acetone-methanol-chloroform (A-M-C or 1-3-2), acetone-

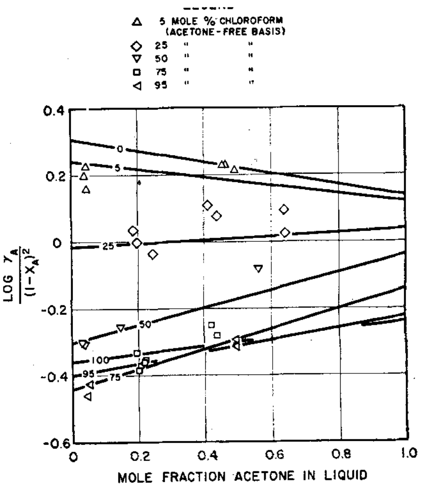

Fig. 12. Comparative plots of activity coefficients for acetone in the ternary system acetone–methanol–chloroform at 50°C. with three-suffix Margules ternary equation.

TABLE 1—MARGULES CONSTANTS FOR CONSTITUENT BINARY SYSTEMS

System	End values, A_{ij} Three-suffix Margules	Four-suffix Margules	Azeotropic composition
Acetone (1) Chloroform (2)	$A_{12} = -0.36$ $A_{21} = -0.30$		$x_1 = 0.38$
Acetone (1) Methanol (3)	$A_{13} = 0.305$ $A_{31} = 0.225$		$x_1 = 0.81$
Chloroform (2) Methanol (3)	$A_{23} = 0.31$ $A_{32} = 0.78$		$x_2 = 0.66$
Acetone (1) Methyl acetate (2′)	$A_{12'} = 0.065$ $A_{2'1} = 0.050$		$x_1 = 0.78$
Methyl acetate (2′) Methanol (3)	$A_{2'3} = 0.465$ $A_{32'} = 0.445$		$x_3 = 0.32$
Acetone (1) Carbon tetrachloride (2″)	$A_{12''} = 0.41$ $A_{2''1} = 0.31$		$x \doteq y$ in range $0.89 < x_1 < 1.0$
Methanol (3) Carbon tetrachloride (2″)	$A_{2''3} = 0.765$ $A_{32''} = 1.10$	$A_{2''3} = 0.891$(9) $A_{32''} = 1.132$(9) $D_{2''3} = 0.483$(9)	$x_3 = 0.45$(*9*)

TABLE 2—EXPERIMENTALLY OBSERVED TERNARY CONSTANTS FOR THE SYSTEM ACETONE-CHLOROFORM-METHANOL

Run	Dilute Component	C^*
145	Acetone (1)	0.61
121		0.63
122		0.59
141	Chloroform (2)	0.37
142		0.53
117		0.53
120		0.43
132	Methanol (3)	0.37
133		0.34
144		0.52
	Mean:	0.49
	Standard deviation of mean:	0.10

methanol–carbon tetrachloride (A-M-CT or 1-3-2″), and acetone-methanol–methyl acetate (A-M-MA or 1-3-2′) are also on file.* Multiple equilibrium determinations were made at each of the points 1 to 13 of Figure 1 for the systems A-M-C and A-M-MA. About a third of the data on each system were taken near regions 1 to 3 of Figure 1. For the system A-M-CT, determinations were made only at points 1 to 3.

J plots for each component of the A-M-C system are presented in Figures 12 to 14. Curves for the three-suffix Margules equations with $C^* = 0.5$ are plotted. Values of C^* were calculated from the three-suffix Margules equations by use of data from individual runs in the region $R = \frac{1}{2}\, x$ dilute. The results are shown in Table 2. Calculation of three different ternary constants, C^*_1, C^*_2, C^*_3, for use in the four-suffix Margules equation of Wohl was also carried out, but the resulting values did not differ significantly from each other or from the single C^* average listed in the table.

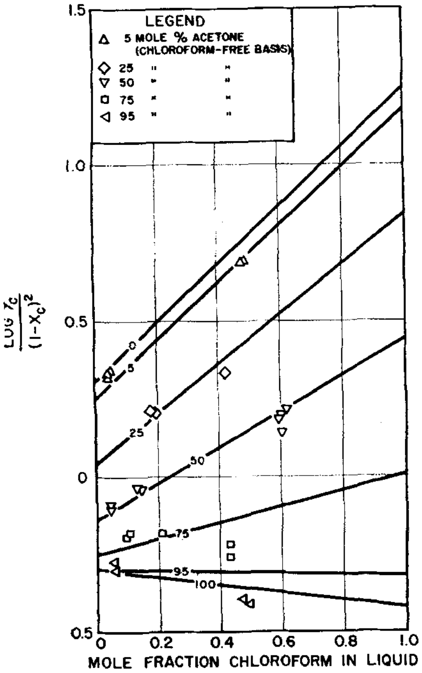

Fig. 13. Comparative plots of activity coefficients for chloroform in the ternary system acetone–methanol–chloroform at 50°C. with three-suffix Margules ternary equation.

TABLE 3—EXPERIMENTALLY OBSERVED TERNARY CONSTANTS FOR THE SYSTEM ACETONE—METHYL ACETATE—METHANOL

Run	Dilute Component	C^*
52	Acetone (1)	−0.16
53		−0.16
69		−0.02
70		0.00
59	Methyl acetate (2′)	−0.05
60		0.00
61		+0.04
62		+0.11
57	Methanol (3)	+0.14
58		+0.12
82		+0.04
	Mean:	0.00
	Standard deviation of mean:	0.09

For the system A-M-MA, *J* plots are shown as Figures 15 to 17. The lines correspond to the three-suffix Margules equation with $C^* = 0$. Values of C^* were calculated from individual runs as indicated in Table 3. Again a single ternary constant was found adequate to describe the system.

J plots for the system A-M-CT are presented in Figures 18 to 20. The lines are calculated from the four-suffix Margules equation with $C^* = 0$. Calculations of C^* from each of the six experiments are summarized in Table 3. The two sets of C^* values correspond to the three- and the four-suffix equations. Based on the latter, the average value of C^* is not significantly different from zero. This is in agreement with data from other ternary systems and the slightly more complicated equations are therefore preferred. Whenever one or more of the binary systems require the use of four-suffix equations, the multicomponent equations should also be of the four-suffix variety, but the ternary effects may be no more complicated in these cases than they are for systems with simpler binary component systems.

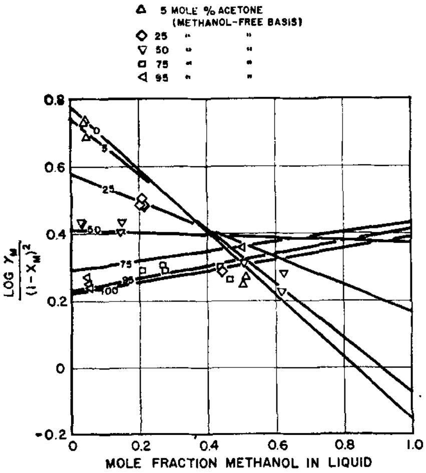

Fig. 14. Comparative plots of activity coefficients for methanol in the ternary system acetone–methanol–methyl acetate at 50°C. with three-suffix Margules ternary equation.

TABLE 4—EXPERIMENTALLY OBSERVED TERNARY CONSTANTS† FOR THE SYSTEM ACETONE-CARBON TETRACHLORIDE-METHANOL

Run	Dilute component	C^* Three-suffix	C^* Four-suffix
1	Carbon	−0.13	+0.07
2	tetrachloride (2″)	−0.28	−0.09
3	Acetone (1)	+0.26‡	+0.38‡
4		−0.17	+0.05
5	Methanol (3)	−0.07	+0.17
6		−0.13	+0.06
	Mean:	−0.16	+0.05
	Standard deviation of mean:	0.04	0.04

†Assuming $C^*_1 = C^*_2 = C^*_3 = C^*$ in the four-suffix equation of Wohl (*13*).

‡This value omitted from average, based on statistical rules.

This is in accord with a recent study by Carlson(*1*), who examined published data for twelve different ternary systems and concluded that $C^* = 0$ is satisfactory for all systems of which the deviations from ideal behavior are either zero or uniformly positive.

DISCUSSIONS OF RESULTS

Figures 21 to 23 are isothermal plots for the three ternary systems. In each case the isobars were calculated by use of the appropriate Margules equations.

In each system a steep gradient of vapor pressure is evident in the region of high methanol concentrations. The cause of this positive deviation from ideality probably is the decomposition of methanol aggregates brought about by dilution with either one of the other components. The methanol–carbon tetrachloride binary system is very strongly nonideal and causes very large vapor pressures over the whole range of compositions in the A-M-CT system. Figure 23 shows that the isobars for this system are nearly symmetrical about a line representing equal amounts of methanol and carbon tetrachloride. The A-M-MA system is dominated to a lesser degree by the methanol–methyl

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*See footnote on page 404.

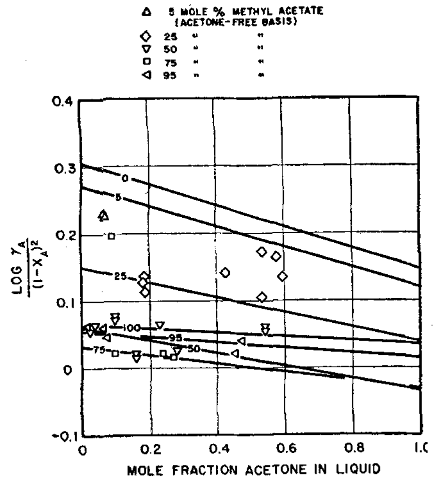

Fig. 15. Comparative plots of activity coefficients for acetone in the ternary system acetone–methanol–methyl acetate at 50°C. with three-suffix Margules ternary equation.

acetate binary system; the mixtures of methanol and acetone show only moderate positive deviations from ideality.

The extent of positive deviations from ideality of binary mixtures of acetone, methyl acetate, and carbon tetrachloride, respectively, with methanol is in inverse relation to their ability to accept protons in the formation of hydrogen bonds. In the order listed, they show decreasing ability to form aggregates with methanol and, consequently, are decreasingly compatible with it in mixtures.

The replacement of one chlorine of carbon tetrachloride by hydrogen, resulting in chloroform, makes a very large change in the deviations from ideal behavior in ternary systems with acetone and methanol. Chloroform and acetone have a strong tendency to form hydrogen-bonded aggregates in their binary mixtures. This results in negative deviations from Raoult's Law. Methanol, on the other hand, shows moderate positive deviations from ideality when mixed with either acetone or chloroform. Hydrogen bonds are formed also in these cases, but positive deviations result from the decomposition of methanol aggregates. This is particularly noticeable (Figure 9) in the activity of dilute methanol in chloroform.

In spite of positive deviations in the A-M and M-C binary systems, ternary mixtures nearly equimolar in acetone and chloroform, regardless of methanol concentration, exhibit a vapor-pressure depression relative to the methanol-containing binary systems that may be partially attributed to the formation of ternary aggregates (Figure 21). The excess free energy of the A-M-C- system is successfully represented by an equation in the third powers of mole fraction, suggesting that aggregates no more complex than trimolecular are responsible for the deviations observed. In addition, the value and the positive sign of C^* observed experimentally for this system enter Equation (13) in such a way as to lower the excess free energy. From this it seems likely that ternary aggregate of acetone, chloroform, and methanol exist in the molar ratio 1:1:1. It appears unlikely that significant negative values of C^* in Equation (13) will occur in any ternary system.

The Margules equations successfully predict that, owing to the strongly positive deviations in the methanol–carbon tetrachloride system, the activity coefficients of acetone in ternary solutions should fall outside the region between the two binary lines on Figure 18. Slightly negative deviations are predicted for a limited range of compositions. Apparently, even though acetone is "repelled" or made abnormally active by the presence of either methanol or carbon tetrachloride molecules alone, when these latter substances are present together they repel each other so strongly that a few molecules of acetone find ample free space in the solutions. Probably the partial entropy of acetone is therefore abnormally large, owing to this greater degree of freedom to occupy free volume in the liquid, resulting in a decreased free energy without necessarily involving energy effects.

The distillation characteristics of the three ternary systems are of interest because of their extremely nonideal behavior. The triangular plots of total vapor pressure can be used to bring out some general features of this behavior. With reference to Figure 22, for the A-M-MA system, for example, the location of the calculated ternary azeotropic composition is shown by the small circle inside the diagram. The binary azeotropes are located on each of the three sides of the triangle. The dashed lines (called "path lines") on the figure show the predicted gradual change of the liquid residue away from the azeotropes in a differential batch distillation. These lines were constructed by drawing straight tie lines on the triangle, each joining a pair of compositions representing liquid and vapor phases in equilibrium. If a liquid mixture is differentially distilled in apparatus having an

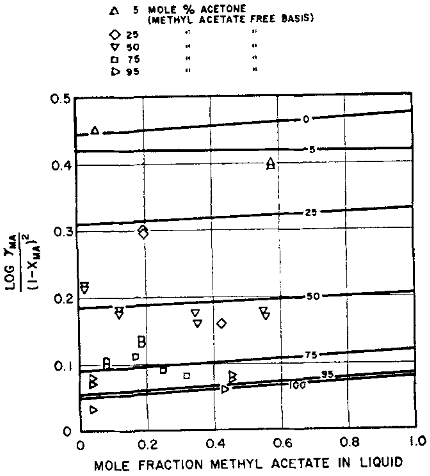

Fig. 16. Comparative plots of activity coefficients for methyl acetate in the ternary system acetone–methanol–methyl acetate at 50°C. with three-suffix Margules equation.

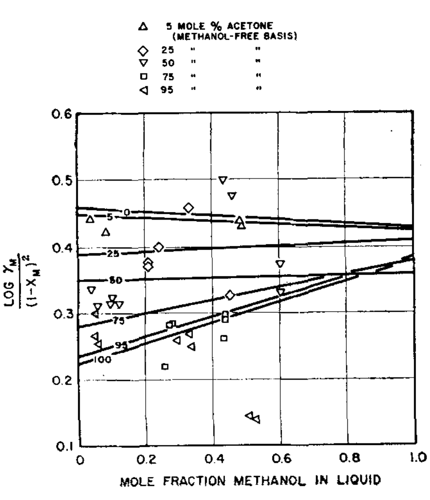

Fig. 17. Comparative plots of activity coefficients for methanol in the ternary system acetone–methanol–methyl acetate at 50°C. with three-suffix Margules equation.

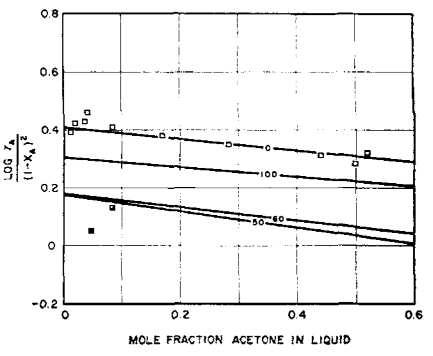

Fig. 18. Activity coefficients for acetone in the system acetone–methanol–carbon tetrachloride at 50°C.; lines are four-suffix ternary Margules equation.

efficiency equivalent to one theoretical plate, the residue will move for a short distance along the tie line through its original composition but in a direction away from the vapor end of the tie line. The path lines on Figure 22 therefore are constructed so that the tie lines are their tangents.

When the path lines are nearly straight, as they are near the bottom of the triangle or in the corners, the liquid and the equilibrium vapor are greatly different in composition, and vice versa. The path lines form a family of curves radiating from the dotted lines that join the three binary azeotropes to the ternary azeotrope. These dotted lines are called "characteristic lines" of the system because they cannot be crossed by any path line. A liquid whose initial composition falls on a dotted line at any point other than the azeotropic point will move along the dotted line to the nearest binary azeotrope. When it reaches this limiting composition, the residue will not change, but if a trace amount of one pure component is added to this residue it will move in a direction toward one of the pure-component vertices of the triangle, provided the azetrope has a minimum boiling point. The characteristic lines and the sides of the triangle are therefore path lines of singular characteristics.

In a ternary system with two binary azeotropes a characteristic line will join the two corresponding points on the sides of the triangle. Any possible ternary azeotrope will lie on this characteristic line. If the third binary pair is nonideal but does not have an azeotrope, owing to a large difference in the vapor pressures of the pure components, a ternary azeotrope still may exist. This may be the situation of the A-M-CT system, shown by Figure 23, in which it is not clear from the data whether a binary azeotrope exists or not. (Along the acetone–carbon tetrachloride side binary mixture containing more than about 90% acetone have very nearly equal liquid and vapor compositions. It does not appear to be essential that three binary azeotropes be present in a ternary system in order to have a multicomponent azeotrope; two binary azeotropes would appear to be sufficient if the third system is sufficiently nonideal.

The A-M-C system has mixed deviations from ideal behavior, owing to negative deviations in the A-C binary system (a maximum-boiling azeotrope) and positive deviations in the A-M and M-C binary pairs (minimum-boiling azeotropes). This results in an inflection point of invariant composition called by Ewell and Welch (*3*) a "saddle point," which is neither maximum- nor minimum-boiling with respect to other possible ternary compositions. Figure 21 shows the location of this saddle. The residue in a differential batch distillation tends to move across this saddle-shaped surface in a general down-hill direction, as indicated by the path lines on Figure 21.

CONCLUSIONS

Ternary vapor-liquid equilibria of nonideal liquid mixtures exhibiting only positive deviations from ideality can be predicted in many cases from data on the binary pairs alone by use of the appropriate Margules equation. Selection of the three- or four-suffix forms of the Margules equation is determined by the most complicated binary system involved, usually the one with the highest activity coefficients. Mixtures having uniformly positive deviations from ideality in the binary pairs may frequently be represented by $C^* = 0$, as indicated by two ternary systems described here and confirmed by an extensive evaluation of literature data by Carlson(*1*). Only one ternary system including both positive and negative deviations has apparently been investigated to date: the system A-M-C investigated here. This system ap-

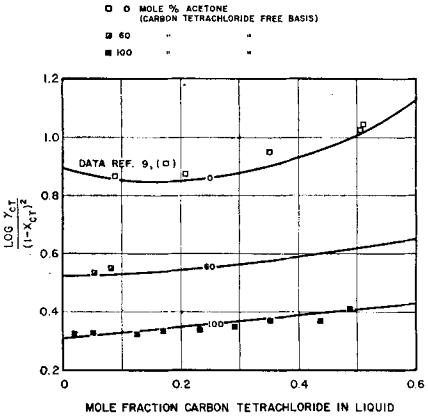

Fig. 19. Activity coefficients for carbon tetrachloride in the system acetone–methanol–carbon tetrachloride at 50°C.; lines are four-suffix ternary Margules equation.

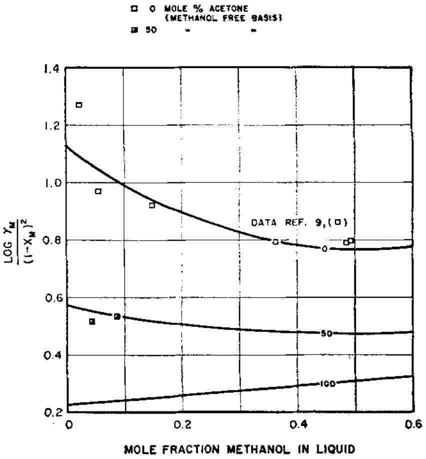

Fig. 20. Activity coefficients for methanol in the system acetone–methanol–carbon tetrachloride at 50°C.; lines are four-suffix ternary Margules equation.

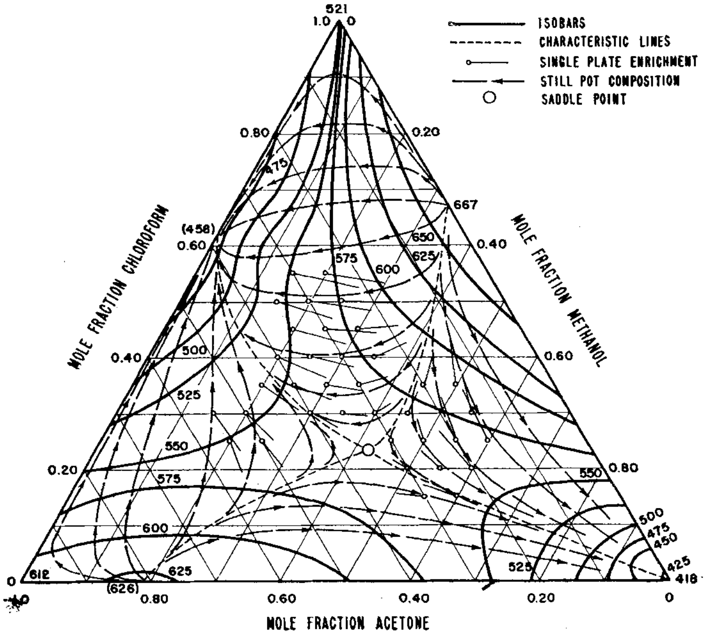

Fig. 21. Vapor pressures at 50°C. for system acetone–methanol–chloroform. Tie lines showing single-plate enrichment are drawn with small circle at the end representing the equilibrium liquid composition.

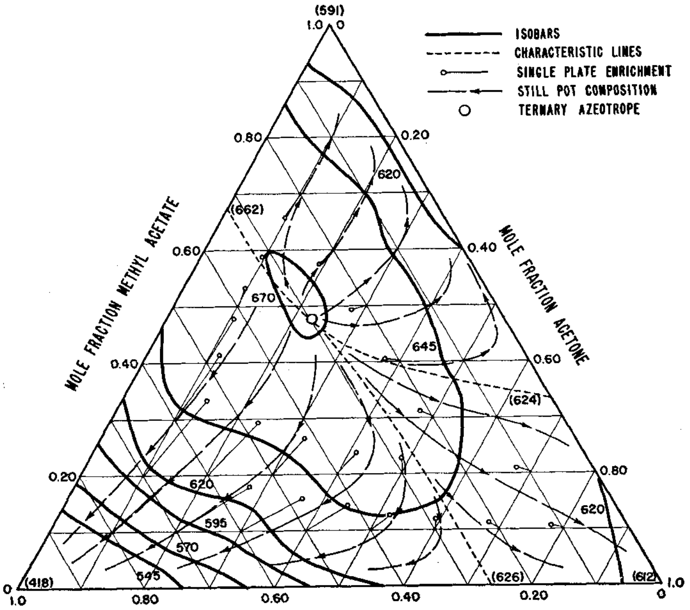

Fig. 22. Vapor pressures at 50°C. for system methanol–acetone–methyl acetate. Tie lines showing single-plate enrichment are drawn with small circle at the end representing the equilibrium vapor composition.

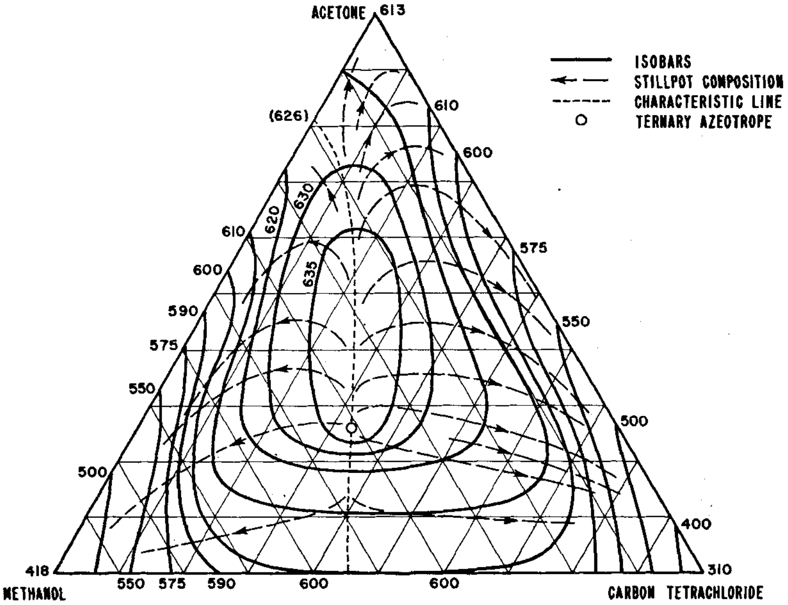

Fig. 23. Vapor pressures at 50°C. for system methanol–acetone–carbon tetrachloride.

pears to require a value of C^* that is significantly different from zero in order to be accurately described by the three-suffix Margules equation, but whether this behavior will also be found in other mixtures having both negative and positive deviations simultaneously is not yet known.

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NOTATION

A_{ij} = logarithm to base ten of activity coefficient of component i at infinite dilution in binary mixtures with j
C^* = ternary constant in three- or four-suffix modified ternary Margules equation. Also, coefficient of term in equation for excess free energy of mixing expressing effect of triple aggregates of unlike compounds
D = constant in four-suffix Margules equation for description of complex binary mixtures
G^E = Gibbs's free energy per mole of mixture in excess of that of an ideal mixture of the same composition
$J_i = \log \gamma_i/(1-x_i)^2$
P_i = vapor pressure of pure component i
q = arbitrary multiplier to x, originally molecular volume in liquid phase
R = gas constant
$R_2 = x_2/(x_2+x_3)$; $R_3 = x_3/(x_3+x_1)$; $R_1 = x_1/(x_1+x_2)$
T = absolute temperature, °K.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
z = correction factor for nonideality of vapor phase, ratio of fugacity to partial pressure of component in vapor mixture
γ = activity coefficient, ratio of thermodynamic activity to mole fraction in the liquid phase
π = total pressure

Subscripts

1 refers to component 1, the most volatile in the pure state
2 refers to component 2
3 refers to component 3, the least volatile
i refers to any component
j refers to any component including i
k refers to any component except i or j

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