Correlations for Ternary Liquid Equilibria

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MANY METHODS have been proposed for predicting the distribution of a solute between partially miscible solvents from a minimum of data. Empirical methods which are known as tie-line correlations for ternary systems may be useful for interpolation and extrapolation when the solubility data and some ternary liquid-liquid equilibrium data are available (*4, 6*). In addition, several methods for predicting ternary liquid equilibrium relationships by using activities of three components and mathematical procedures for estimating values of activity coefficients from binary and some ternary data have been proposed. The use of ternary activity coefficient equations is ordinarily limited to cases where the solubility curve of the ternary liquid system is known, because location of the triple intersection points of the constant activity curves on the triangular diagram is a difficult trial and error procedure.

In a regular ternary solution, phase relationships can be readily established with only three energy parameters for the interaction between different molecules or atoms (*1, 9*). Phase diagrams are simpler in the symmetrical type where two parameters are equal and the tie lines are parallel to the base of the triangle. Hand (*4*) presented an interesting method of plotting the ternary data in such a manner as to make the tie lines parallel to the base of the triangle as in a symmetrical type for regular ternary mixtures. This method suggests the possibility of correlating the ternary liquid equilibrium data with the theory of regular ternary mixtures.

TERNARY DATA METHODS IN SYMMETRICAL FORM

There are few liquid ternary systems in which the solubility curves are symmetrical in two of the components, or the tie lines are parallel to the base of the triangle. Hand (*4*) has indicated that the tie lines can be made horizontal by plotting with properly selected units for one of the immiscible liquids, and the distribution equation is expressed by the following relation

$$\frac{E'}{S' + KR'} = \frac{E''}{S'' + KR''} \tag{1}$$

where R, E, and S denote the mole or weight fractions of the diluent, the solute, and the solvent, respectively, and K is an empirical constant. The diluent-rich phase is designated by one prime, and the solvent rich phase by two primes. Examination of many data for systems described in the literature shows that the isothermal solubility curves (with horizontal tie lines plotted on triangular diagrams by changing the units) are not ordinarily symmetrical in two of the components, and that the value of K or $(E'S'' - E''S')/(E''R' - E'R'')$ is not always a constant over the entire range of compositions. In systems which comprise two partially miscible pairs of liquids and one miscible, the value of K becomes infinite at zero concentration of the diluent.

Let the respective concentrations of the solvent, the diluent, and the solute after a change of units be X_1, X_2, and X_3. Assume that the isotherm can be made symmetrical in X_1 and X_2 by using units in which the concentrations of each component are multiplied by some proper values. Then,

$$X_1' = X_2'' \qquad X_1'' = X_2' \qquad X_3' = X_3'' \tag{2}$$

$$X_1' = \frac{S'}{S' + aE' + bR'} \quad , \quad X_2' = \frac{bR'}{S' + aE' + bR'} \tag{3a}$$

$$X_1'' = \frac{S''}{S'' + cE'' + bR''} \quad , \quad X_2'' = \frac{bR''}{S'' + cE'' + bR''} \tag{3b}$$

where a, b, and c are the empirical coefficients. When either a and c is assumed to be a constant, the other may vary on changing the concentration of the solute.

The value of b corresponding to the value of K in Equation 1 is represented by

$$b = (S'S''/R'R'')^{1/2} \tag{4}$$

If the relative distribution ratio is designated by β,

$$\beta = E''R'/E'R'' \tag{5}$$

When c is assumed to be a constant, a may be expressed in terms of the ratios of one component to the other component in one phase as follows:

$$a = c\beta(X_2''/X_1'') \tag{6}$$

$$\frac{X_2''}{X_1''} = \frac{X_1'}{X_2'} = \left(\frac{R''S'}{R'S''}\right)^{1/2} \tag{7}$$

$$\frac{X_3''}{X_1''} = \frac{X_3'}{X_2'} = \frac{cE''}{S''} \tag{8}$$

Numerical values according to Equations 7 and 8, are convenient because these formulas are not dependent on use of weight or mole fractions in concentration units. Thus, when the compositions are plotted on a triangular graph as fractions in which concentrations of the diluent in each phase are multiplied by b, the solute in solvent-rich phase by a constant c, and the solute in diluent-rich phase by $c\beta(X_2''/X_1'')$, and then the total sum of concentrations in each phase after a change of units is brought back to unity, the solubility curve of the system will be symmetrical with respect to the solvent and the diluent, and the tie lines will be parallel to the base of the triangle.

RELATIONS OF REGULAR TERNARY SOLUTION THEORY TO TERNARY LIQUID EQUILIBRIUM DATA

The symmetrical phase diagrams after a change of units are similar to those for symmetrical regular ternary mixtures. If all the empirical coefficients a, b, and c in Equations 3a and 3b are always constant, the system could be treated as the regular ternary mixtures. Very few systems satisfy the conditions for forming regular ternary mixtures in which the molecules are assumed to be alike in size and shape, and the empirical coefficients are not always constant, as has been stated for K in Equation 1. But it will be possible to obtain the empirical relationships between symmetrical phase diagrams for regular ternary solutions and those for actual ternary solutions.

A statistical study has been made of regular ternary solutions, and equilibrium equations have been deduced using the 0th order and quasi-chemical approximations by Bell (*1*). In the 0th approximation which corresponds to the limiting form taken by the first approximation when the coordination number, z, is made infinite, the conjugate phases in cases of the symmetrical type are obtained (*1*, *9*) from

$$\frac{x_3}{x_1} = \frac{(x_2/x_1 - 1)(w/kT)}{\ln(x_2/x_1)} - (x_2/x_1 + 1) \tag{9}$$

where x is mole fraction of components, and w/z is the interaction energy of a pair of nearest neighbors, one being of species 1 and the other of species 2; k is Boltzmann's constant and T the absolute temperature. The plait point of the binodal curve is given by

$$x_1 = x_2$$

and

$$(1 - x_3)(w/k\mathrm{T}) = 2 \tag{10}$$

If $x_3 = 0$, Equations 9 and 10 reduce to the equations for the binary system.

Values of w/kT may be obtained from the mutual solubility data of the nonconsolute components with $x_3 = 0$,

$$\frac{w}{kT} = \left[\frac{\ln x_2 - \ln x_1}{x_2 - x_1}\right]_0 = \left[\frac{(x_2/x_1 + 1)\ \ln(x_2/x_1)}{x_2/x_1 - 1}\right]_0 \tag{11}$$

where the subscript, 0, refers to the binary solutions of the diluent and the solvent.

To obtain the relation between values derived from the theory of regular ternary solutions and from symmetrical ternary liquid equilibrium data after a change of units, the experimental data in terms of X_3''/X_1'' are compared with the theoretical values of x_3/x_1 assuming $X_2''/X_1'' = x_2/x_1$. X_2''/X_1'' and x_2/x_1 change the values in a similar manner with increasing concentration of the third component until they become unity; values of w/kT are obtainable from mutual solubility data of the nonconsolute components in terms of X_2/X_1 for most binary nonelectrolyte liquid systems (*7*). Figure 1 shows the plots of E''/S'' against x_3/x_1 on double logarithmic coordinates in which values of x_3/x_1 are calculated from Equations 9 and 10, assuming $x_2/x_1 = X_2''/X_1''$. A linear relation is found to exist between $\log(E''/S'')$ and $\log(x_3/x_1)$, within their probable experimental accuracy, except a few systems where it seems plausible to correlate the data by two straight lines changing their slopes. Similar results are obtained between the function $\log(E''/S'')$ and $\log(x_3/x_1)$ according to the first approximation (*1*), showing little difference between the first approximation and the 0th approximation for the correlation of the data for isothermal liquid-liquid equilibria. Calculation according to the 0th approximation appears practical and less laborious. The relation shown in Figure 1 can be expressed by

$$\log(E''/S'') = n \log(x_3/x_1) + K_1 \tag{12}$$

where n and K_1 are empirical constants.

Since the existence of linear relation between $\log(E''/S'')$ and $\log(E'/R')$ has been found (*4*), a plot of values of E'/R' against x_3/x_1 on double logarithmic coordinates may give a straight line for the system which comprises two miscible, and one partially miscible pair of liquids. Therefore

$$\log(E'/R') = n' \log(x_3/x_1) + K_2 \tag{13}$$

However, when E'' is less than E' (E' will become less than E'' if the components of the diluent and the solvent are exchanged), the method expressed by Equation 12 seems preferable, because plots expressed by Equation 13 gave more instances in which data can not be correlated by a straight line having a definite slope.

Coefficient b is sometimes a variable. When plots of corresponding values of $1/b$ against x_2/x_1 are made, curves similar to hyperbolas are obtained. If such curves are assumed to be represented by hyperbolas approximately, values of b may be obtained from values of x_2/x_1 by

$$b = b_0[p + q\{(x_2/x_1) - (x_2/x_1)_0\}]/[p + (q - b_0)\{(x_2/x_1) - (x_2/x_1)_0\}] \tag{14}$$

where the subscript 0 refers to values for the binary solutions of the solvent and the diluent which correspond to the zero concentration of the solute, $E = O$; and p and q are the empirical constants which are defined from two conjugate ternary liquid equilibrium data and mutual solubility of solvent and diluent. Plots (Figure 2) of $bb_0/(b - b_0)$ against $1/\{(x_2/x_1) - (x_2/x_1)_0\}$, for several systems show that Equation 14 holds over the entire range of compositions within their probable experimental accuracy. Ratios of the concentrations of two components in each phase, can be evaluated from these three data by the following relations:

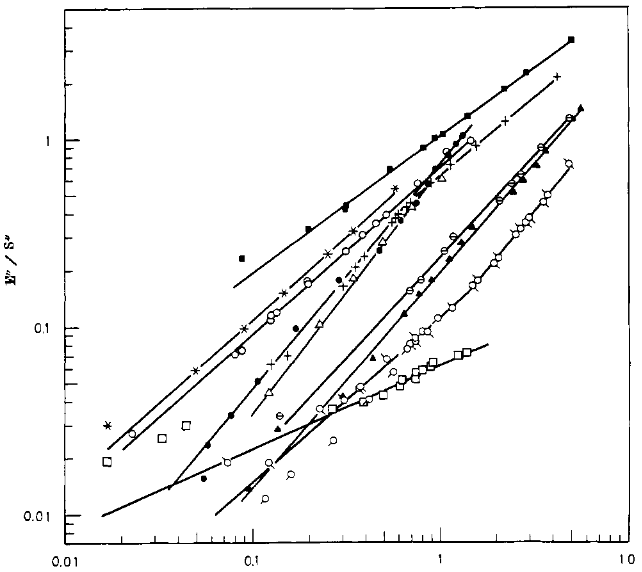

Figure 1. Plot of double logarithmic coordinates for several systems shows the existence of a simple relation between the actual and the symmetrical, regular ternary solutions for values of solute-solvent ratio in the solvent-rich phase

(See Figure 2 for legend)

$$R''/S'' = x_2/x_1b \tag{15}$$

$$S'/R' = bx_2/x_1 \tag{16}$$

Since a linear relation between $\log \beta$ and $\log(x_2/x_1)$ has been found empirically for most systems (*6*),

$$\log \beta = m \log(x_2/x_1) + K_3 \tag{17}$$

isothermal ternary phase equilibria for the system will be established by algebraic Equations 12 or 13, 15, 16, and 5

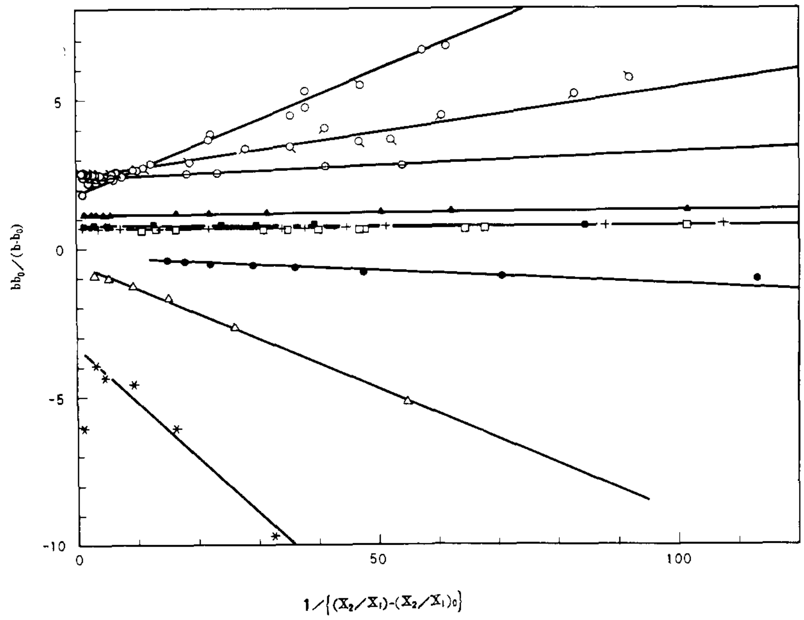

Figure 2. Plot for several systems describes the existence of hyperbolic relation between 1/b and x_2/x_1 approximately

	System *R* *E* *S*	Temp., ° C.	Reference
○	$n\text{-}C_7H_{16}–C_6H_5CH_3–NH_3$	20	5
ϙ	$H_2O–C_2H_5OH–C_6H_6$	25	14
Ծ	$H_2O–C_2H_5OH–C_6H_6$	25	3
Q	$H_2O–C_2H_5OH–C_6H_6$	25	13
⊖	$H_2O–CH_3COOH–C_6H_6$	25	4
▲	$H_2O–CH_3COOH–C_6H_5CH_3$	25	16
■	$C_6H_6–1,4\text{-}C_4H_8O_2–H_2O$	25	2
+	$CH_2Cl\cdot CHCl_2–CH_3COCH_3–H_2O$	25	12
□	$C_6H_6–n\text{-}C_4H_9OH–H_2O$	25	15
●	$H_2O–2\text{-}C_3H_7OH–C_6H_6$	25	11
△	$H_2O–CH_3COOH–C_2H_5OC_2H_5$	25	8
✳	$H_2O–CH_3OH–n\text{-}C_4H_9OH$	15	10

over the entire range of compositions from values of b_0 and w/kT, which are obtained from the binary data for the diluent and the solvent, and those of the empirical constants p, q, m, n, or n', K_1 or K_2 and K_3 which are defined from two conjugate ternary liquid equilibrium data by Equations 14 and 12 or 13 and 17.

The method of plotting data according to Equations 12 or 13, 14, and 17 may be useful for the correlation of ternary liquid equilibrium data, especially when the concentrations of two parts in each phase can be easily determined. Because phase diagrams from two pairs of tie-line data and mutual solubility of the diluent and the solvent can be established by this method, the application of these correlations by using activities of three components will greatly reduce the work in the prediction of ternary liquid equilibria, even if the data of ternary solubility curve are not available. The calculation of the theoretical values of x_3/x_1 from x_2/x_1 can be simplified by using a chart correlated with the values of x_3/x_1 and x_2/x_1.

EXAMPLE OF CALCULATION

A typical example is given to show the application of equations and methods of extension of ternary liquid equilibrium data. Although the water-2-propanol-benzene system at 25° C., given as an example, is one of the "solutropic system," phase diagrams were established by the same procedure not only for ordinary systems, but also for those containing two partially miscible pairs. In the extension of limited data by these equations very consistent data are required for the evaluation of empirical constants; otherwise discontinuity on the solubility curve near the plait point may occur. Even if the extrapolation to the plait point were unsatisfactory by using consistent data far from the plait point, the interpolation of these data would be accurate enough to use for practical purposes.

Such values estimated by interpolation of the experimental data of Olsen and Washburn (*11*) as shown in Table I were used for the basic data on the calculation of phase equilibria. According to Equations 4 and 7, numerical values of b and $X_2''/X_1'' = x_2/x_1$ for these data are calculated as shown in Table I. Using values of b and x_2/x_1, p and q are defined from Equation 14 as

$$p = -0.01274 \qquad q = -0.2657$$

From Equation 11

$$\frac{w}{2.303\,kT} = \frac{1.001026 \times \log 0.001026}{-0.998974} = 2.995$$

Values of x_3/x_1 corresponding to values of x_2/x_1 between 0.001026 and 1.0 may be obtained by Equations 9 and 10; only three values corresponding to the given data are shown in Table I. Values of n and K_1 are obtained by Equation 12, and values of m and K_3, by Equation 17 as follows: $n = 1.146$, $K_1 = -0.1402$; $m = -0.9287$, $K_3 = -0.0082$
At the plait point, $x_2/x_1 = 1$.
According to Equation 10

$$x_3/x_1 = w/kT - 2 = 4.8962$$

Denoting values at the plait point by subscript p,

$$\log(E_p/S_p) = 1.146 \log 4.8962 - 0.1402 = \log 4.4702$$

Also

$$1/(1/1b_0 - 1/b_p) = -0.01274/(1 - 0.001026) - 0.2657 = 1/(-3.5920)$$

$$1/b_p = 4.2749$$

By Equation 15

$$R_p/S_p = 1/b_p$$

Table I. Equilibrium and Some Calculated Weight Fractions for the Water(*R*)–2-propanol(*E*)–Benzene(*S*) System at 25° C.

E''	R''	S''	E'	R'	S'	$1/b$	X_2''/X_1''	x_3/x_1
0	0.0007	0.9993	0	0.9985	0.0015	0.6829	0.001026	0
0.386	0.044	0.570	0.279	0.710	0.011	2.2321	0.03458	0.9433
0.419	0.061	0.520	0.285	0.702	0.013	2.5169	0.04661	1.0979

Accordingly,

$$(1 - S_p)/S_p = (E_p + R_p)/S_p = 4.4702 + 4.2749 = 8.7451$$

$$S_p = 0.1026, \qquad E_p = 0.4586$$

At the other value of x_2/x_1—for instance, $x_2/x_1 = 0.01$—

$$x_3/x_1 = \frac{0.99 \times 2.995}{2} - 1.01 = 0.4725$$

In the way described above,

$$\log(E''/S'') = \log 0.3067$$

$$bb_0/(b - b_0) = 1/(-0.5931) \qquad 1/b = 1.2760$$

From Equation 15,

$$R''/S'' = 0.01 \times 1.276 = 0.01276 \qquad (1 - S'')/S'' = 0.3195,$$

$$S'' = 0.7579, \qquad E'' = 0.2324$$

From Equation 16,

$$S'/R' = 0.01/1.276 = 0.00784$$

By Equation 17

$$\log \beta = 0.9287 \times 2 - 0.0082 = 1.8492 = \log(1/0.01415)$$

$$E'/R' = (E''/S'')/(R''/S'')\beta = (0.3067 \times 0.01415)/0.01276 = 0.3401$$

$$(1 - R')/R' = 0.3480, \qquad R' = 0.7419, \qquad \text{and } E' = 0.2523$$

Similarly, compositions in the conjugate phases are evaluated from any other value of x_2/x_1. These results are shown in Figure 3. Except for the disagreement on the solubility curve near the plait point, which is of little importance in the design of extraction processes from a practical point of view, the agreement of calculated values with experimental data is good, and the phase diagram can be represented satisfactorily by these equations.

NOMENCLATURE

a = $c\beta X_2''/X_1''$
b = $(S'S''/R'R'')^{1/2}$
c = constant
E = mole (or weight) fraction of solute
K, K_1, K_2, K_3, p, q = empirical constants
k = Boltzmann's constant
m, n, n' = empirical coefficients
R = mole (or weight) fraction of diluent
S = mole (or weight) fraction of solvent
T = absolute temperature
w/z = interaction energy of a pair of nearest neighbors, one, of species 1; other, of species 2
X = mole (or weight) fraction of the component after unit change
x = mole fraction of component for symmetrical ternary regular mixtures
z = coordination number
β = relative distribution ratio

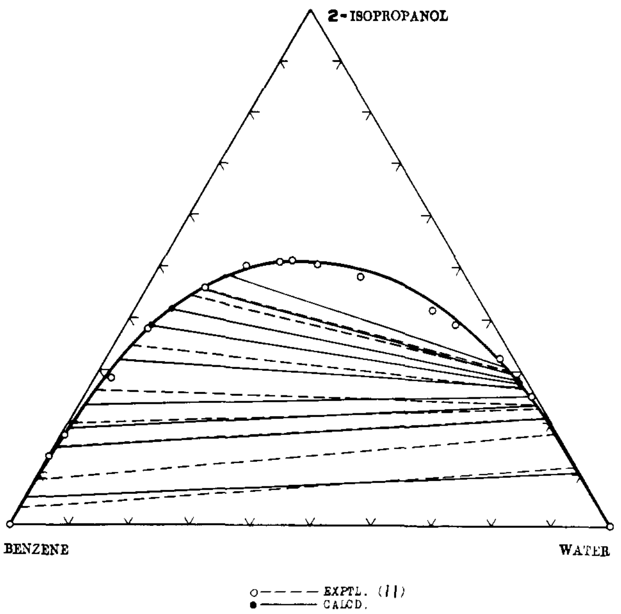

Figure 3. Calculated and experimental equilibria for the water–2-propanol–benzene system at 25° C. weight fraction

Subscripts

1 = solvent
2 = diluent
3 = solute
0 = values for binary solutions of solvent and diluent with $E = 0$
p = values at plait point

Superscripts

$'$ = raffinate phase
$''$ = extract (solvent) phase

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