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Interfacial Tensions of Binary and Ternary Two-Phase Liquid Systems

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A theory is developed to enable prediction of interfacial tension in unsymmetrical, regular, binary liquid systems from solubility data. This is also shown to be applicable to nonregular aqueous binary systems by using solubility parameters and molar volumes calculated from mutual solubilities as substitutes for true molar volumes and the solubility parameters obtained from energies of vaporization.

The theory is extended to include unsymmetrical, regular, ternary liquid systems, and is shown to be applicable to systems consisting of perfluoro-*n*-hexane and other nonpolar organic liquids. The theory is not adequate for aqueous ternary systems.

In several previous theoretical studies of interfacial tension in binary liquid systems, the theory of *strictly regular* solutions has been used as a basis (*2, 3, 8*). Strictly regular systems occur when both components possess identical molar volumes and both liquid phases are regular, which results in temperature-solubility curves which are symmetrical about a critical solution composition $x_{1CS} = x_{2CS} = 0.5$. Since real binary systems are in general neither symmetrical nor completely regular, these previous theoretical models cannot be directly applied in the prediction of interfacial tensions in actual systems. In the development which follows the assumption of identical molar volumes is not made and thus the theory may be applied directly to real binary systems and, as will be shown, even to nonregular aqueous systems. It is also extended to real, regular ternary systems of any degree of immiscibility of the nonconsolutes and for all concentrations of the distributed component. This work is then complementary to that of Shain and Prausnitz (*11*), who treated the initial change of interfacial tension with concentration of a polar distributed component for completely insoluble liquid pairs at infinite dilution of the distributed component. The complete details of the present development are available elsewhere (*9*).

BINARY TWO-LIQUID PHASE SYSTEMS

The theoretical development is based upon the following assumptions, which are similar to those used by Kahlweit (*8*):

1. The system consists of two components present in two coexisting liquid phases at equilibrium.
2. The solutions possess a lattice structure of the same configuration in both phases.
3. Both the bulk phases and the interface layer between them can be described by regular solution theory (*6, 7*).

The lattice structure of assumption 2 is inherently incompatible with the desire to remove all restrictions on relative liquid volumes, since presumably only molecules of a limited ratio of molecular size may be accommodated in a single lattice. Hildebrand and Scott (*7*) have further shown that the lattice concept, together with such other frequently used structure theories as the hole theory, is an unlikely model for liquids generally, perhaps especially for solutions which are so random as to be described by the regular solution theory of assumption 3. Nevertheless, the concept of a lattice for a regular solution has recently been used to good advantage in consideration of interfacial tension (*8, 11*). The lattice struc-

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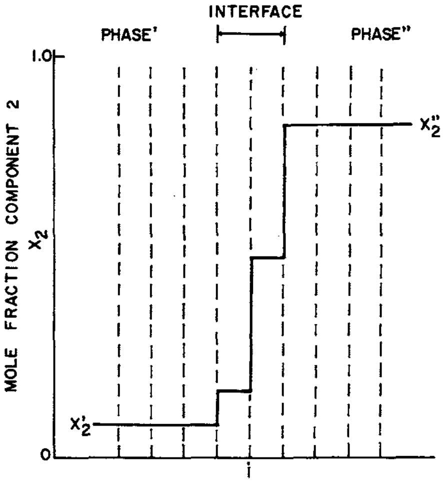

Fig. 1. Stepwise change of concentration in the interface.

ture is used here only as a means of getting started, and is ultimately abandoned in favor of a continuously differentiable change of solution properties with passage from the bulk of one liquid to the bulk of the other (*3*).

In the following, subscripts will be used to indicate the component and superscripts the phase being referenced. Thus x_1'' represents the mole fraction of component 1 in the component 2-rich phase.

The interface between phases, finite in thickness, is considered to be a region in which all of the system properties vary as one passes from the interior (or bulk) of phase ′ to phase ″ in a direction normal to the phase boundary. In the bulk phase regions, the solution properties do not change from point to point. The simplest way for the compositions to vary as one moves through the interface, normal to the phase boundary, is by finite step changes. This is shown schematically in Figure 1, where the concentration of component 2 is plotted vs. network plane number, the network planes being parallel to the interface. The i^{th} and $(i+1)^{\text{th}}$ network planes have associated with them a composition of component 2, $x_{2(i)}$ and $x_{2(i+1)}$, respectively. Each molecule, in every network plane, has associated with it a volume contribution and a surface contribution to the total free energy of mixing. These contributions arise from the fact that in a nonuniform system the total free energy at any point is not only a function of the concentration at that point, but also depends upon the concentration gradient. The volume contribution per molecule is

$$g^M{}_{vi} = G^M\,(x_{2(i)})/N \qquad (1)$$

where G^M is the free energy of mixing per mole associated with a homogeneous, binary, regular solution of composition $x_{2(i)}$. The free energy of mixing is of the form

$$G^M = \Delta H^M - T\Delta S^M \qquad (2)$$

or

$$G^M = \frac{(\delta_1-\delta_2)^2\,x_2\,(1-x_2)\,V_1V_2}{(1-x_2)\,V_1 + x_2V_2} + RT[x_2 \ln x_2 + (1-x_2)\ln(1-x_2)] \qquad (3)$$

where δ is defined as

$$\delta = \left(\frac{\Delta U^V}{V}\right)^{0.5} \qquad (4)$$

The surface contribution per molecule due to interactions between adjacent network planes i and $(i+1)$ is (*1*, *8*, *9*):

$$g^M{}_{o,i,i+1} = \frac{1}{2}\left(\frac{Z-Z'}{Z}\right)\frac{\bar V}{\bar N}\{[x_{1(i+1)} - x_{1(i)}]^2\,\delta_1{}^2 + [x_{2(i+1)} - x_{2(i)}]^2\,\delta_2{}^2 + 2[x_{1(i+1)} - x_{1(i)}][x_{2(i+1)} - x_{2(i)}]\delta_1\delta_2\} \qquad (5)$$

The total free energy of the nonhomogeneous mixture may be obtained by summing all of the surface and volume contributions per molecule and multiplying by the number of molecules. If A is the surface area of the interface and a the distance between network planes, this summation is

$$G^M = A\left(\frac{AN}{\bar V}\right)\sum_i\,(g^M{}_{vi} + g^M{}_{o,i,i+1}) \qquad (6)$$

If the surface contributions are all both multiplied and divided by a^2, if Equations (1) and (5) are substituted into Equation (6), and if the distance a is allowed to become very small, the finite summation of Equation (6) can be changed to an integration over the distance coordinate ξ in a direction normal to the interface, from ξ' in phase ′ to ξ'' in phase ″:

$$\mathbf{G}^M = \frac{A}{\bar V}\int_{\xi'}^{\xi''}\left\{G^M[x_2(\xi)] + \frac{1}{2}\left(\frac{Z-Z'}{Z}\right)\bar V a^2 \left[\left(\frac{dx_1}{d\xi}\right)^2\delta_1{}^2 + \left(\frac{dx_2}{d\xi}\right)^2\delta_2{}^2 + 2\left(\frac{dx_1}{d\xi}\right)\left(\frac{dx_2}{d\xi}\right)\delta_1\delta_2\right]\right\} d\xi \qquad (7)$$

In this case, concentration is a continuously differentiable function of distance ξ (see Figure 2). Because the sum of the mole fractions at any point equals unity

$$\frac{dx_1}{d\xi} = -\frac{dx_2}{d\xi} \qquad (8)$$

This may be substituted into Equation (7), which then becomes

$$\mathbf{G}^M = \frac{A}{\bar V}\int_{\xi'}^{\xi''}\left\{G^M\,[x_2(\xi)] + K\left(\frac{dx_2}{d\xi}\right)^2\right\} d\xi \qquad (9)$$

where

$$K = \frac{1}{2}\left(\frac{Z-Z'}{Z}\right)\bar V a^2\,(\delta_1-\delta_2)^2 \qquad (10)$$

The homogeneous free energy of mixing G^M may be plotted as a function of x_2 at a temperature below the

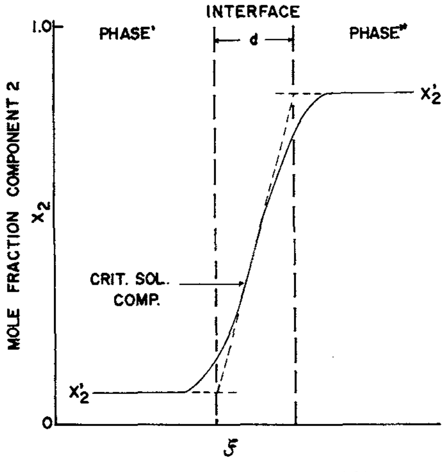

Fig. 2. Continuous change of concentration in the interface.

critical solution temperature. For such a temperature, two liquid phases are in equilibrium and the free energy of mixing curve is of the form shown in Figure 3. A straight line can be drawn so that it is tangent to the free energy curve at two separate points corresponding to the two coexisting phase compositions. The criteria for two phases at equilibrium are that

$$\left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} = \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2''} \tag{11}$$

and

$$G^M(x_2'') = G^M(x_2') + \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} (x_2'' - x_2') \tag{12}$$

Equilibrium will be established only when the total free energy of the system is at a minimum. Therefore, the integral of Equation (9) must be minimized, and it must also satisfy the condition of conservation of mass:

$$\int_{\xi'}^{\xi''} x_2(\xi)\, d\xi = \text{constant} \tag{13}$$

Hence

$$d\left\{\frac{A}{\overline{V}}\int_{\xi'}^{\xi''}\left\{ G^M[x_2(\xi)] + K\left(\frac{dx_2}{d\xi}\right)^2 + \lambda\, x_2(\xi)\right\} d\xi\right\} = 0 \tag{14}$$

This standard problem of variational calculus results in the Euler differential equation of the following form, where I corresponds to the integrand of Equation (14) (this form is used because I is not explicitly dependent upon ξ).

$$I - \frac{\partial I}{\partial\left(\frac{dx_2}{d\xi}\right)}\left(\frac{dx_2}{d\xi}\right) = \text{constant} \tag{15}$$

Substitution of the integrand of Equation (14) into Equation (15) yields

$$G^M\,[x_2(\xi)] + \lambda\, x_2 - K\left(\frac{dx_2}{d\xi}\right)^2 = \text{constant} \tag{16}$$

Since Equation (16) must apply to the homogeneous phases as well as to the interface, one may solve for the parameter λ. In each homogeneous phase

$$\frac{dx_2'}{d\xi} = 0, \quad \frac{dx_2''}{d\xi} = 0 \tag{17}$$

Hence, from Equation (16)

$$G^M(x_2'') + \lambda x_2'' = G^M(x_2') + \lambda x_2' \tag{18}$$

Now by using the basic relationship for equilibrium, Equations (11) and (12) with Equation (18), one obtains

$$\lambda = -\left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} = -\left.\frac{\partial G^M}{\partial x_2}\right|_{x_2''} \tag{19}$$

Equation (16) may now be written

$$K\left(\frac{dx_2}{d\xi}\right)^2 = G^M[x_2(\xi)] - G^M(x_2') - \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} [x_2(\xi) - x_2'] \tag{20}$$

Therefore Equation (9) becomes

$$G^M = \frac{A}{\overline{V}}\int_{\xi'}^{\xi''}\left\{2G^M[x_2(\xi)] - G^M(x_2') - \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} [x_2(\xi) - x_2']\right\} d\xi \tag{21}$$

By using the basic definition of interfacial tension, Kahlweit (8) has shown that the total free energy of a two-phase regular system can be related to the interfacial tension and the homogeneous free energy of mixing. This relationship may be written as

$$G^M = A\left\{\frac{1}{\overline{V}}\int_{\xi'}^{\xi''}\left[G^M(x_2') + \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} [x_2(\xi) - x_2']\right] d\xi + \sigma\right\} \tag{22}$$

By equating the total free energies of mixing given by Equations (21) and (22) and by rearranging, one has for the interfacial tension

$$\sigma = \frac{2}{\overline{V}}\int_{\xi'}^{\xi''}\left\{G^M[x_2(\xi)] - G^M(x_2') - \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} [x_2(\xi) - x_2']\right\} d\xi \tag{23}$$

The integration of Equation (23) requires a functional relationship between composition and distance. Although this is unknown, it can nevertheless be approximated as a linear function (3). Other functions might be used, as suggested by Cahn and Hilliard (3), with parameters adjustable to minimize the total free energy, but anything other than the linear function enormously increases the complexity of the mathematics. In Figure 2, a line is drawn tangent to the unknown curve at the critical solution concentration. This may be somewhat arbitrary, but at least it is known that as the temperature approaches the critical solution temperature, only the critical solution composition is always intermediate between the two bulk phase compositions.

An effective interface thickness d can therefore be defined as

$$d = \frac{(x_2'' - x_2')}{\left.\frac{dx_2}{d\xi}\right|_{x_2 = x_{2CS}}} \tag{24}$$

It is now possible to change the variable of integration of Equation (23) to mole fraction of component 2:

$$\sigma = \frac{2d}{\overline{V}(x_2'' - x_2')}\int_{x_2'}^{x_2''}\left\{G^M(x_2) - G^M(x^{2'}) - \left.\frac{\partial G^M}{\partial x_2}\right|_{x_2'} (x_2 - x_2')\right\} dx_2 \tag{25}$$

Geometrically, this integral represents the area between the curve of the homogeneous energy of mixing and the

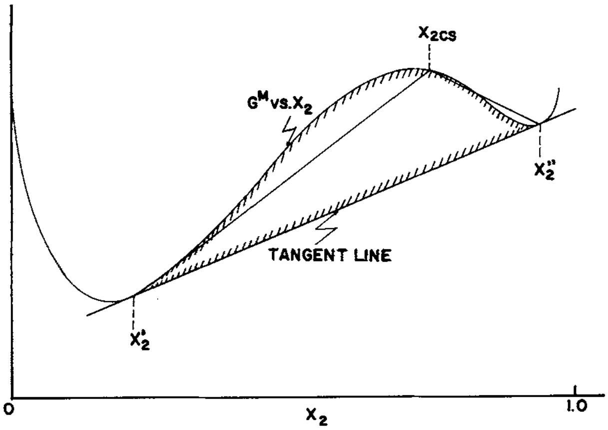

Fig. 3. Free energy of mixing vs. composition.

straight line drawn tangent to the curve at the two phase compositions (Figure 3). Division of the area by the difference in compositions ($x_2'' - x_2'$) results in an average difference in free energy between points on the curve and corresponding points on the tangent line. This average is

$$\overline{\Delta G^M} = \frac{1}{(x_2'' - x_2')} \int_{x_2'}^{x_2''} \left\{ G^M(x_2) - G^M(x_2') - \frac{\partial G^M}{\partial x_2}\bigg|_{x_2'} (x_2 - x_2') \right\} dx_2 \quad (26)$$

and therefore

$$\sigma = \frac{2d}{\overline{V}} \overline{\Delta G^M} \quad (27)$$

One can solve for the interfacial thickness d by substituting x_{2CS} for x_2 in Equation (20), by solving for $\partial x_2/\partial \xi$ at x_{2CS}, and by using this to calculate d from Equation (24). As a result

$$d = \frac{K^{1/2}(x_2'' - x_2')}{\left[G^M(x_{2CS}) - G^M(x_2') - \frac{\partial G^M}{\partial x_2}\bigg|_{x_2'} (x_{2CS} - x_2') \right]^{1/2}} \quad (28)$$

The denominator of Equation (28) is a very cumbersome expression. However, by approximating the curve of free energy of mixing by two straight lines joining the free energy of mixing at the critical solution composition with the values at the two bulk phase compositions (the two dashed lines of Figure 3), the approximate $\overline{\Delta G^M}$ can be calculated by dividing the area within the triangular region by ($x_2'' - x_2'$). Hence

$$\left[G^M(x_{2CS}) - G^M(x_2') - \frac{\partial G^M}{\partial x^2}\bigg|_{x_2'} (x_{2CS} - x_2') \right]^{1/2} \doteq (2\overline{\Delta G^M})^{1/2} \quad (29)$$

Now Equation (28) can be written approximately

$$d \doteq \frac{K^{1/2}(x_2'' - x_2')}{(2\overline{\Delta G^M})^{1/2}} \quad (30)$$

and from Equation (27)

$$\sigma \doteq \frac{(2K\overline{\Delta G^M})^{1/2}(x_2'' - x_2')}{\overline{V}} \quad (31)$$

The calculation of interfacial tension through Equation (31) requires that K be evaluated. The distance a between network planes in Equation (10) depends upon the type of lattice structure that one chooses to represent the system. In general, a is proportional to $(\overline{V}/N)^{1/3}$. By combining the proportionality constant with the term containing the coordination numbers Z and Z', there is obtained from Equation (10)

$$K^{1/2} = \frac{k\overline{V}^{5/6}\,|(\delta_1 - \delta_2)|}{2^{1/2}N^{1/3}} \quad (32)$$

and therefore

$$\sigma \doteq \frac{k|(\delta_1 - \delta_2)|(x_2'' - x_2')(\overline{\Delta G^M})^{1/2}}{N^{1/3}V^{1/6}} \quad (33)$$

$\overline{\Delta G^M}$ can be obtained from Equation (44) by putting m, b, x_3, V_3, and δ_3 equal to 0. The parameter k might be expected to vary with the nature of the components, but would be expected to remain fairly constant for systems of similar components. As will be shown, it has the same value, 0.846, for a great variety of binary liquid pairs.

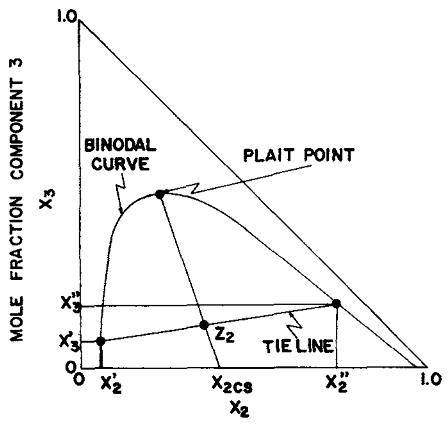

Fig. 4. Ternary equilibrium phase diagram.

TERNARY TWO-LIQUID PHASE SYSTEMS

Components 1 and 2 are taken to be partially miscible, while component 3 may be either completely miscible with both 1 and 2 or partially miscible with one of them. The mole fractions of the bulk phases are represented as the points at the ends of the equilibrium tie lines plotted in any convenient coordinate system (Figure 4) for example. The equation of a typical tie line in this figure will be

$$x_3 = mx_2 + b \quad (34)$$

where

$$m = (x_3'' - x_3')/(x_2'' - x_2') \quad (35)$$

and

$$b = (x_2''x_3' - x_3''x_2')/(x_2'' - x_2') \quad (36)$$

The same basic assumptions as for the case of two components are made: a lattice structure and the applicability of regular solution theory. In general, although substantially more complex, the development parallels that for two components. In fact, all of the following ternary equations reduce to their binary counterparts in the absence of a third component.

As one moves normal to the interface from the interior of phase ′ to the interior of phase ″, the concentrations of all three components change. Only one condition is certain:

$$x_1 + x_2 + x_3 = 1.0 \quad (37)$$

The total free energy of mixing for a continuously changing concentration in the interface is analogous to Equation (7):

$$\mathbf{G}^M = \frac{A}{\overline{V}} \int_{\xi'}^{\xi''} \left\{ G^M[x_1(\xi), x_2(\xi)] + \frac{1}{2}\left(\frac{Z - Z'}{Z}\right)\overline{V}a^2 \left[\left(\frac{dx_1}{d\xi}\right)^2 \delta_1^2 + \left(\frac{dx_2}{d\xi}\right)^2 \delta_2^2 + \left(\frac{dx_3}{d\xi}\right)^2 \delta_3^2 + 2\left(\frac{dx_1}{d\xi}\right)\left(\frac{dx_2}{d\xi}\right)\delta_1\delta_2 + 2\left(\frac{dx_1}{d\xi}\right)\left(\frac{dx_3}{d\xi}\right)\delta_1\delta_3 + 2\left(\frac{dx_2}{d\xi}\right)\left(\frac{dx_3}{d\xi}\right)\delta_2\delta_3 \right] \right\} d\xi \quad (38)$$

For a regular ternary mixture, the homogeneous free energy of mixing is given by Equation (2) in which

$$\Delta H^M = \frac{(\delta_1-\delta_2)^2x_1x_2V_1V_2 + (\delta_1-\delta_3)^2x_1x_3V_1V_3 + (\delta_2-\delta_3)^2x_2x_3V_2V_3}{x_1V_1 + x_2V_2 + x_3V_3} \quad (39)$$

and

$$\Delta S^M = -R(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3) \qquad (40)$$

Reduction of G^M and the partial derivatives to a function of only one composition requires that the relationship among concentrations of all the components as one moves through the interface be known. Since this relationship is both unknown and with present knowledge impossible to determine, the concentrations in the interface are arbitrarily assumed to follow the tie line equation [Equation (34)]. Actually, there are an infinite number of possible concentration paths that could be used, but all except Equation (34) cause great complications in the mathematics of the development. Aside from its simple linear nature, the choice of the tie line path implies that the mole fraction of any component cannot be greater in the interface than it is in the bulk phase in which its concentration is highest; neither can a component mole fraction be less in the interface than in the bulk phase in which its concentration is lowest. Such situations could conceivably occur in ternary systems in which a component is strongly adsorbed at the interface. It cannot arise in the case of only two components, since this would imply that identical solution concentrations exist at two points in the system separated by points of dissimilar concentration.

Thus, the homogeneous free energy of mixing can be reduced to a function only of x_2 by using the restrictions of Equations (34) and (37). These restrictions also yield relationships among the partial derivatives of Equation (38), and as a result

$$\mathbf{G}^M \doteq \frac{A}{\bar{V}} \int_{\xi'}^{\xi''} \left\{ G^M[x_2(\xi)] + K\left(\frac{d\,x_2}{d\xi}\right) \right\} d\xi \qquad (41)$$

where the approximate equality implies the tie line restriction, and

$$K = \frac{1}{2}\left(\frac{Z - Z'}{Z}\right) \bar{V} a^2 \, [(\delta_1 - \delta_2) + m(\delta_1 - \delta_3)]^2 \qquad (42)$$

These are the three-component analogs of Equation (9) and (10).

One can now use the procedure described previously for binary mixtures to minimize the total free energy of mixing and equate the resulting integral to Equation (22), which must be evaluated along a tie line. Equation (22) has been shown to be valid for three-component systems whose component concentrations in the interface are related by a tie line (9). Since there is no critical solution composition for a ternary tie line, some other intermediate composition z_2 must be used for evaluating the interface thickness d. This z_2 must be identical with x_{2CS}, the critical solution composition for a binary system of components 1 and 2 in the absence of 3, and it must also equal x_{2pp} at the plait point if one exists. Therefore, for a ternary tie line, z_2 is arbitrarily chosen as the component 2 concentration at the point of intersection of the tie line with a straight line joining x_{2CS} with x_{2pp}, as in Figure 4. Then, by following the procedure described for two components and by replacing x_{2CS} with z_2, one obtains

$$\sigma \doteq \frac{k|(\delta_1 - \delta_2) + m(\delta_1 - \delta_3)|(x_2'' - x_2')(\overline{\Delta G^M})^{1/2}}{N^{1/3}\bar{V}^{1/6}} \qquad (43)$$

The quantity $\overline{\Delta G^M}$ must be evaluated from Equation (26) in which the integral is a line integral for a particular tie line. Equation (26) can be integrated by using Equation (2) with Equations (34), (37), (39), and (40) to obtain G^M as a function of x_2 only, and by substituting for $\partial G^M/\partial x_2|_{x_2'}$ by means of Equation (12). The result is valid for binary systems and ternaries whose concentrations in the interface can be related by a tie line. For such systems

$$\overline{\Delta G^M} = \frac{C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_7}{(x_2'' - x_2')[V_2 - V_1 + m(V_3 - V_1)]} + \frac{Q}{(x_2'' - x_2')} - \frac{G^M(x_2'') + G^M(x_2')}{2} \qquad (44)$$

in which

$$C_1 = -(\delta_1 - \delta_2)^2 V_1 V_2 (m + 1) X \qquad (44a)$$

$$C_2 = (\delta_1 - \delta_2)^2 V_1 V_2 (1 - b) Y \qquad (44b)$$

$$C_3 = -(\delta_1 - \delta_3)^2 V_1 V_3 m(m + 1) X \qquad (44c)$$

$$C_4 = (\delta_1 - \delta_3)^2 V_1 V_3 (m - 2mb - b) Y \qquad (44d)$$

$$C_5 = (\delta_1 - \delta_3)^2 V_1 V_3 b(1 - b) \ln W \qquad (44e)$$

$$C_6 = (\delta_2 - \delta_3)^2 V_2 V_3 m X \qquad (44f)$$

$$C_7 = (\delta_2 - \delta_3)^2 V_2 V_3 b Y \qquad (44g)$$

$$W = \frac{[V_2 - V_1 + m(V_3 - V_1)]x_2'' + V_1 + b(V_3 - V_1)}{[V_2 - V_1 + m(V_3 - V_1)]x_2' + V_1 + b(V_3 - V_1)} \qquad (44h)$$

$$X = \frac{(x_2''^2 - x_2'^2)}{2} - \frac{[V_1 + b(V_3 - V_1)](x_2'' - x_2')}{V_2 - V_1 + m(V_3 - V_1)} + \left[\frac{V_1 + b(V_3 - V_1)}{V_2 - V_1 + m(V_3 - V_1)}\right]^2 \ln W \qquad (44i)$$

$$Y = (x_2'' - x_2') - \left[\frac{V_1 + b(V_3 - V_1)}{V_2 - V_1 + m(V_3 - V_1)}\right] \ln W \qquad (44j)$$

$$Q = \frac{RT}{2} \left\{ \left[x_2''^2 \ln x_2'' - x_2'^2 \ln x_2' - \frac{(x_2''^2 - x_2'^2)}{2} \right] - \frac{1}{(m + 1)} \left[x_1''^2 \ln x_1'' - x_1'^2 \ln x_1' - \frac{(x_1''^2 - x_1'^2)}{2} \right] + \frac{1}{m} \left[x_3''^2 \ln x_3'' - x_3'^2 \ln x_3' - \frac{(x_3''^2 - x_3'^2)}{2} \right] \right\} \qquad (44k)$$

A Fortran program for the computations of Equations (43) and (44) is available (9).

APPLICATIONS

For regular solutions (6, 7)

$$\ln \gamma_j = \frac{V_j}{RT} (\delta_j - \bar{\delta})^2; \quad j = 1, 2, 3 \qquad (45)$$

where

$$\bar{\delta} = \frac{x_1 V_1 \delta_1 + x_2 V_2 \delta_2 + x_3 V_3 \delta_3}{x_1 V_1 + x_2 V_2 + x_3 V_3} \qquad (46)$$

At equilibrium the activities of each component in both phases are identical:

$$a_j' = a_j'' = \gamma_j' x_j' = \gamma_j'' x_j''; \quad j = 1, 2, 3 \qquad (47)$$

For truly regular solutions, the δ's may be computed through Equation (4), which gives thermodynamic values. For real mixtures, however, even such as those of hydrocarbons and fluorocarbons which come very close to the theoretical model for regular solutions, the δ's so computed are not compatible with observed solubilities (5). Further, if true molar volumes are used, no values of δ for each component can be found from any source which will permit Equation (47) to be satisfied. It is therefore necessary to assign values of δ differences other than the thermodynamic values, and values of V other than the true values if Equation (47) is to be in agree-

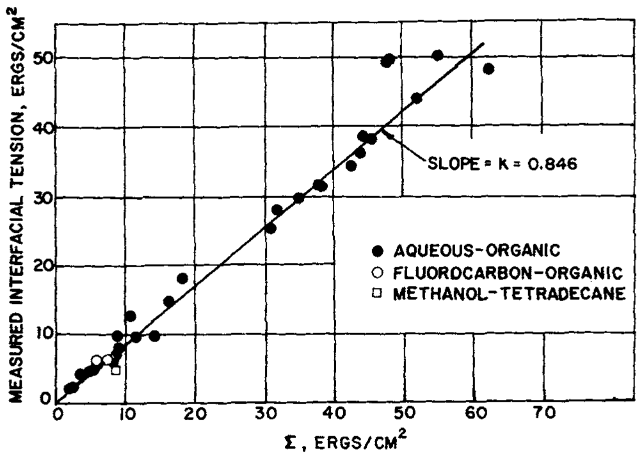

Fig. 5. Measured interfacial tension vs. Σ for binary systems.

ment with observed solubilities. In what follows Equation (47) is used to obtain these from observed solubility data and the values of v (rather than V) so determined are called pseudo molar volumes. These yield consistent results when substituted into Equation (3) and plotted in the manner of Figure 3.

BINARY SYSTEMS

If it is assumed that the arithmetic average of the pseudo molar volumes is identical with the arithmetic average of the actual molar volumes, then

$$v_1 + v_2 = V_1 + V_2 \tag{48}$$

From this

$$v_1 = \frac{V_1 + V_2}{1 + \beta}, \quad v_2 = \frac{\beta(V_1 + V_2)}{1 + \beta} \tag{49}$$

in which $\beta = v_2/v_1$ is calculated from the activity coefficient equations, replacing V's with v's, with measured solubilities:

$$\beta = \frac{(x_1''x_2' + x_1'x_2'')[\ln(x_2''/x_2')]/[\ln(x_1''/x_1') + 2x_1'x_2''}{2x_2'x_2''[\ln(x_2''/x_2')]/[\ln(x_1''/x_1')] + x_1'x_2'' + x_2'x_1''} \tag{50}$$

Further

$$|\delta_1 - \delta_2| = \left\{ \frac{RT \ln (x_2''/x_2')}{\dfrac{\beta(V_1 + V_2)}{1 + \beta} \left(\dfrac{x_1'^2}{x_2'^2\beta^2 + 2x_1'x_2'\beta + x_1'^2} - \dfrac{x_1''^2}{x_2''^2\beta^2 + 2x_1''x_2''\beta + x_1''^2} \right)} \right\}^{1/2} \tag{51}$$

Equation (33) may be tested by plotting the measured interfacial tension against values of

$$\sum = \frac{|\delta_1 - \delta_2|(x_2'' - x_2')(\overline{\Delta G^M})^{1/2}}{N^{1/3}\bar{V}^{1/6}}$$

where

$$\sigma = k\Sigma \tag{52}$$

and Σ is calculated from pseudo molar volumes and the solubility parameter differences. If the theory is valid, a single straight line should result, at least for similar systems, whose slope is the value of k for the systems.

Donahue and Bartell (*4*) have compiled a list of interfacial tensions and corresponding mutual solubilities for many aqueous systems. Despite the fact that such systems are far from regular, it is nevertheless possible to use their solubility data to calculate $\overline{\Delta G^M}$ and Σ. In addition, solubilities and interfacial tensions have been measured for some additional systems, including several containing perfluoro-*n*-hexane with other organics (*9, 10*).

A graph of these data appears in Figure 5. A single straight line fits all the data very well, including both the aqueous and fluorocarbon systems. The scattering at high values of σ is due largely, it is felt, to uncertain mutual solubilities for these highly insoluble liquids. It is also noteworthy that the fluorocarbon systems and methanol-tetradecane deviate considerably from the correlation of Donahue and Bartell (*4*), although they fall in with the others in Figure 5.

TERNARY SYSTEMS

In these cases, because regular solution theory in general fails to predict the phase diagrams, measured equilibrium compositions for each tie line in a system are used to compute consistent solubility parameters and pseudo molar volumes. Since it is the δ differences and not absolute values of δ that are needed, δ_1 may be taken from the tables of Hildebrand and Scott (*6*) or even chosen arbitrarily. Since within a given ternary system the results must be consistent with those for the binary immiscible pair 1 — 2, v_1 and v_2 may be taken from Equations (48) to (50) and kept constant throughout. This leaves v_3, δ_2, and δ_3 to be obtained for each ternary tie line. Equations (45) and (47), when separately solved simultaneously for each component, provide

$$\ln\left(\frac{x_j''}{x_j'}\right) = \frac{V_j}{RT}(\bar{\delta}' - \bar{\delta}'')(\bar{\delta}' + \bar{\delta}'' - 2\delta_j), \quad j = 1, 2, 3 \tag{53}$$

These three relationships, together with the definition of $\bar{\delta}$ written with v's rather than V's [Equation (46)], permit computation of v_3, δ_2, and δ_3 by a trial-and-error procedure. Different values are obtained for each tie line within a given system.

This method was used to compute $\overline{\Delta G^M}$ and Σ for the ternary systems perfluoro-*n*-hexane(1)—benzene(2)—*n*-hexane(3), and perfluoro-*n*-hexane(1)—carbon disulfide (2)—*n*-hexane(3), where Σ is taken from Equation (43):

$$\sum = \frac{|\delta_1 - \delta_2 + m(\delta_1 - \delta_2)|(x_2'' - x_2')(\overline{\Delta G^M})^{1/2}}{N^{1/3}\bar{V}^{1/6}}$$

A plot of Σ vs. measured interfacial tensions (*9, 10*) is shown in Figure 6. Besides the fact that the graph is linear, it is noteworthy that the line is the same as that for the binary systems in Figure 5.

Detailed data on interfacial tensions in three aqueous systems were also obtained (*9, 10*), and only a few points for these are shown in Figure 6: Points A3 and A4: 1,1,2-trichloroethane(1)—water(2)—acetone(3). Point C3: benzene(1)—water(2)—acetone(3). Point D1: benzene(1)—water(2)—methanol(3).

For none of these ternaries could a straight line be drawn in Figure 6, even though the data for the 1-2 binaries are handled well in Figure 5. Neither does the empirical extension of the Donahue-Bartell correlation suggested by Treybal (*12*) apply. The measured interfacial tensions of the aqueous ternaries are lower than those predicted with k from the binary correlation, and it is not unreasonable to believe that this could be caused

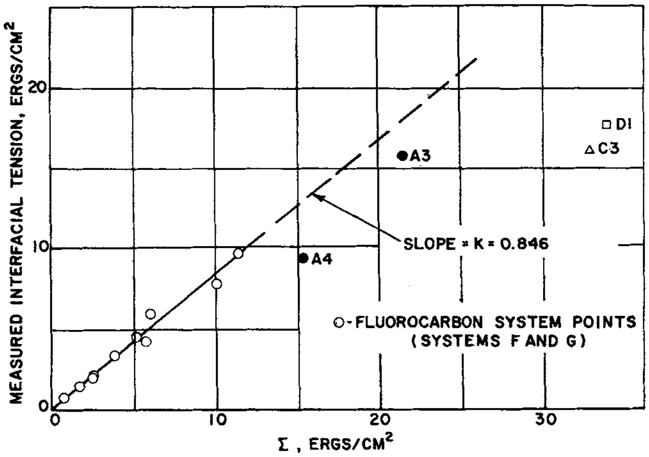

Fig. 6. Measured interfacial tension vs. Σ for ternary systems.

by an adsorption of one of the components at the interface. This in turn indicates that for these systems it is likely that the component concentrations in the interface layer do not follow the tie line path assumed in the development.

SUMMARY

1. Kahlweit's theoretical development for interfacial tensions of symmetrical, binary, regular systems is extended to unsymmetrical systems.

2. By computing molar volumes and solubility parameters consistent with measured solubilities, it is shown that interfacial tensions for nonregular, unsymmetrical, binary systems (including aqueous systems) can now be computed from solubility data alone through Equation (52) with $k = 0.846$.

3. The theory is extended to include unsymmetrical, ternary, regular systems whose component concentrations in the interface can be described by equilibrium tie lines. The ternary equations all reduce to their binary counterparts in the absence of a third component.

4. The theory is verified for ternary systems containing fluorocarbons and nonpolar organics, and for these systems interfacial tensions can now be computed from equilibrium solubility data alone. The same value of k (0.846) applies.

5. The theory fails for aqueous ternary systems, and it is suggested that this is the result of adsorption of a component at the interface. At present, such adsorption cannot be predicted.

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NOTATION

A = interfacial area, sq. cm.
a = distance between network planes, cm.; also activity [Equation (47)]
b = intercept of a tie line with the x_3 axis, Figure 4
d = interface thickness, cm.
G^M = Gibbs free energy of mixing for homogeneous solutions, cal./g.-mole
$\mathbf{G}^M$ = total Gibbs free energy of mixing for a two-phase system, cal.
$\overline{\Delta G^M}$ = quantity defined by Equation (26), cal./g.-mole
$g_o{}^M$ = surface contribution to the free energy of mixing, cal./molecule
$g_v{}^M$ = volume contribution to the free energy of mixing, cal./molecule
ΔH^M = enthalpy of mixing of homogeneous solutions, cal./g.-mole
I = integrand
K = parameter defined by Equation (42)
k = parameter defined by lattice type (or simple proportionality constant)
m = slope of a tie line, Figure 4
N = Avagadro's number, molecules/g.-mole
R = universal gas constant, cal./(g.-mole) (°K.)
ΔS_M = entropy of mixing of homogeneous solutions, cal./(g.-mole) (°K.)
T = absolute temperature, °K.
ΔU^V = internal energy of vaporization, cal./g.-mole
V = molar volume, cc./g.-mole
$\overline{V}$ = average molar volume, cc./g.-mole
v = pseudo molar volume, cc./g.-mole
x = concentration, mole fraction
Z = coordination number, or total of nearest neighbors to a molecule
Z' = number of nearest neighbors in the same network plane
z = intermediate concentration, mole fraction

Greek Letters

β = pseudo molar volume ratio, v_2/v_1
γ = activity coefficient
δ = solubility parameter, (cal./cc.)$^{1/2}$
$\overline{\delta}$ = volume fraction average solubility parameter, (cal./cc.)$^{1/2}$
λ = parameter
ξ = distance normal to the interface, cm.
σ = interfacial tension, cal./sq. cm.; to convert to ergs/sq. cm. or dynes/cm., multiply by 4.18×10^7

Subscripts

$i, i + 1$ = network planes i and $i + 1$, respectively
1, 2, 3 = components 1, 2, and 3
CS = critical solution
pp = plait point

Superscripts

$'$ = component 1 rich phase
$''$ = component 2 rich phase

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