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Thermodynamics and Interfacial Tension of Multicomponent Liquid-Liquid Interfaces

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Sternling and Scriven have shown that the derivative of interfacial tension with respect to solute concentration is an important parameter influencing the hydrodynamic stability at an interface across which mass transfer is taking place. This work is concerned with a molecular thermodynamic study of that derivative.

With surface thermodynamics and an extension of the solution theory of Schuchowitzky, an expression is derived which relates the interfacial tension to the solute concentration in terms of physically meaningful parameters. These in turn are related to molecular properties of the solute and solvent species.

New experimental data are reported for the interfacial tension of nine ternary systems; these consist of an aqueous phase and an organic phase where both phases are dilute solutions of an alcohol. The organic phases are hexane, benzene, and carbon tetrachloride and the alcohols are methanol, ethanol, and *n*-propanol.

The theoretical equations predict interfacial tensions which are in good agreement with the new experimental results and with experimental data of Vignes on aqueous-organic systems which are dilute solutions of organic acids.

In recent years researchers in chemical engineering (for example *4, 5, 6, 7, 9, 15, 19, 22, 24, 25, 26, 32, 42*) have shown a renewed interest in the role of surface and interfacial phenomena in situations involving the transfer of matter across liquid-liquid and liquid-vapor interfaces. Sternling and Scriven (*37*) have investigated the conditions under which the diffusive transport of material across an interface leads to hydrodynamic (Marangoni)

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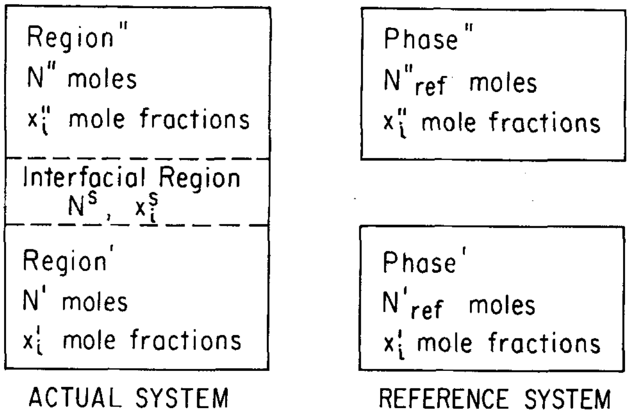

Fig. 1. Actual and reference systems.

instability. This instability is characterized by the onset of turbulent flows at the interface which have a pronounced effect on the rate of transport of material across the interface; it has been shown that the onset of Marangoni instability is strongly dependent on the variation of interfacial tension with composition. A summary of background material in the area of interfacial turbulence is available elsewhere (33).

The composition dependence of the interfacial tension can be investigated separately from considerations of mass transport insofar as this variable is a thermodynamic (equilibrium) property of the system. The objective of this paper is to describe the concentration dependence of interfacial tension by relating the interfacial tension to properties of the individual components of the system.

A few empirical and semiempirical methods are available for the calculation of interfacial tension in liquid-liquid systems (*1, 10, 14, 30*). These approaches generally suffer from a failure to relate the parameters which appear to fundamental properties of the individual components. The interpretation of the parameters which appear is difficult, and the extension of the methods to systems containing additional components is not possible (or at least not apparent). The method outlined here (see reference *34* for details) does not have this limitation.

In this work the regular solution equations of Schuchowitzky (*31*), Guggenheim (*16, 17*), and Belton and Evans (2) for the interfacial tension at a vapor-liquid interface are extended to include the interface between two liquids. Values are calculated for the derivative of the interfacial tension with respect to concentration of the third component in ternary systems where the two phases are water and a nonpolar organic solvent and the third component is a normal alcohol or an aliphatic acid. The theoretical results are compared with experimental data, and the relationship of the results to the phenomena of interfacial turbulence is considered briefly.

THERMODYNAMIC RELATIONSHIPS

The thermodynamic relationships presented are only valid under certain geometric and thermodynamic restrictions. The interface must be a plane separating the two regions and the two regions must be semi-infinite; that is their extent is to be large relative to the range of the intermolecular forces. As a result of these restrictions, some of the relations which follow are not directly applicable to small drops or molecular aggregates of less than say a hundred molecules or to thin films of less than about five molecular layers.

In addition several thermodynamic restrictions are made; no external fields, such as a gravitational field, may be present, and equilibrium only is considered.

The variables which describe the system are chosen to be the temperature T, the pressure P, the interfacial area Ω, and the number of moles of each component N_i.

The properties of the actual system are referred to another system in which the two regions are homogeneous phases and have the same compositions that regions ' and '' in the actual system have at a large distance from the interface. The reference system however, unlike the actual system, has no physical interface. The reference system is characterized by the choice of two parameters, that is by the total number of moles in each phase N'_{ref} and N''_{ref} (or equivalently the total number of moles N_{ref} and a mathematical dividing surface). Figure 1 is a schematic representation of the actual and reference systems.

Extensive properties for the surface are defined as the difference between the value of the property for the actual system and the value of the property for the reference system. For example

$$\Delta N_i^s = N_i - N'_{\text{ref}}\, x_i' - N''_{\text{ref}}\, x_i'' \tag{1}$$

The properties may be made intensive by division by the area. For the surface composition or surface adsorption the special symbol Γ_i is used:

$$\Gamma_i = \Delta N_i^s/\Omega \tag{2}$$

Other extensive and intensive surface properties may be similarly defined. It should be emphasized that the values of these properties depend on the choice of reference system.

It is assumed that the surface area Ω depends only on T, P, and N_i^s, and that Ω is first-order homogeneous in N_i^s.

An additional assumption is that each molecule occupies a certain specific area irrespective of the other species. The equation used for the surface area is

$$\Omega = \sum_i \overline{\Omega}_i N_i^s \tag{3}$$

with the partial molal area of component i, $\overline{\Omega}_i$, taken to be independent of composition.

Since the compressibility of the liquid is small, the surface tension and the chemical potential in the standard state are essentially the same as those evaluated at the same temperature and at a pressure equal to the pure component vapor pressure.*

ACTIVITY COEFFICIENTS

The frequently used definition for chemical activity is through the relation

$$\mu_i = \mu_i^o + RT \ln a_i \tag{4}$$

where μ_i^o is the chemical potential in the standard state (to be chosen later).

If Equation (3) is introduced for the surface area, it is no longer possible to vary the area and the number of moles in the surface independently. Consequently it is convenient to define a fictitious chemical potential at the surface μ_i^*, such that the restriction of constant area does not appear. That is

$$\mu_i^* \equiv \left(\frac{\partial G}{\partial N_i^s}\right)_{T,\,P,\,N'_j,\,N''_j,\,N_k^s \atop k\neq i} \tag{5}$$

and since this is also

$$\mu_i^* = \left(\frac{\partial G}{\partial N_i^s}\right)_{T,\,P,\,N'_j,\,N''_j,\,N_k^s,\,\Omega \atop k\neq i} +$$

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* Noncondensable components dissolved in a liquid require a modified treatment in which the properties of the dissolved material are referred to a hypothetical liquid state. The hypothetical pure component surface tension may be estimated from Hildebrand's (*20*) correlation between surface tension and solubility parameter in conjunction with the solubility parameters and partial molal volumes evaluated by Prausnitz and Shair (*28*) from solubilities of gases in liquids.

$$\left(\frac{\partial G}{\partial \Omega}\right)_{T,\,P,\,N'_j,\,N''_j,\,N_j^s},\quad \left(\frac{\partial \Omega}{\partial N_i^s}\right)_{\substack{T,\,P,\,N'_j,\,N''_j,\,N_k^s\\ k\neq i}} \tag{6}$$

the previous relations yield

$$\mu_i^* = \mu_i + \sigma\bar{\Omega}_i \tag{7}$$

where σ is the interfacial tension.

This chemical potential may now be used to define a fictitious surface activity a_i^*, analogous to that for the bulk fluids

$$\mu_i^* = \mu_i^{*o} + RT \ln a_i^* \tag{8}$$

where μ_i^{*o} refers to some standard state. It must be emphasized that a_i^* is not a true activity and is not equal to the conventional activity a_i.

The activity coefficients γ_i', γ_i'', and γ_i^* are defined by

$$\gamma_i' \equiv \frac{a_i}{x_i'};\quad \gamma_i'' \equiv \frac{a_i}{x_i''};\quad \gamma_i^* \equiv \frac{a_i^*}{x_i^s} \tag{9}$$

The standard state is chosen as having N_i' moles of pure component i in region ′, N_i'' moles of pure component i in region ″, and N_i^s moles of pure component i in the transition region at the temperature and pressure of the system. That is

$\gamma_i' = 1$, $\gamma_i'' = 1$, and $\gamma_i^* = 1$ when

$$x_i' = x_i'' = x_i^s = 1 \tag{10}$$

For this standard state

$$\mu_i^{*o} = \mu_i^o + \sigma_i\tilde{\Omega}_i^o \tag{11}$$

where σ is the surface tension and $\tilde{\Omega}_i^o$ the molar surface area of pure component i at the temperature and pressure of the system (σ_i is zero when a liquid-liquid interface is considered).

Equation (7) may now be solved for the surface tension to yield

$$\sigma = \frac{\mu_i^* - \mu_i}{\bar{\Omega}} = \frac{\sigma_i\tilde{\Omega}_i^o}{\bar{\Omega}_i} - \frac{RT}{\bar{\Omega}_i}\ln\left(\frac{a_i}{a_i^*}\right) \tag{12}$$

where

$$a_i = \gamma_i'x_i' = \gamma_i''x_i'' \text{ and } a_i^* = \gamma_i^*\, x_i^s \tag{13}$$

Equation (12) must be satisfied for all components simultaneously. There are n such equations for an n-component system. If the compositions x_i' (or x_i'') are specified and expressions for γ_i' (or γ_i'') in terms of the compositions x_i', x_i'', and x_i^s are known, then the n Equations (12) and the equation

$$\sum_i x_i^s = 1 \tag{14}$$

can be solved for the $n + 1$ unknowns x_i^s and σ.

The activity coefficients γ_i', γ_i'', and γ_i^* are related to the thermodynamic excess functions of mixing providing that the states which are mixed are the previously chosen standard states which include the surface region:

$$\left.\begin{aligned} RT \ln \gamma_i' &= \left(\frac{\partial\, \Delta G^E{}_{\text{mix}}}{\partial N_i}\right)_{\substack{T,\,P,\,N'_k,\,N''_j,\,N_j^s\\ k\neq i}} \\ RT \ln \gamma_i'' &= \left(\frac{\partial\, \Delta G^E{}_{\text{mix}}}{\partial N_i}\right)_{\substack{T,\,P,\,N'_j,\,N''_k,\,N_j^s\\ k\neq i}} \end{aligned}\right\} \tag{15}$$

and

$$RT \ln \gamma_i^* = \left(\frac{\partial\, \Delta G^E{}_{\text{mix}}}{\partial N_i^s}\right)_{\substack{T,\,P,\,N'_j,\,N''_j,\,N_k^s\\ k\neq l}} \tag{16}$$

Since it is assumed that the bulk fluid regions are not influenced by each other or by the adjacent transition region, the restrictions on the compositions of the coexisting phases in the derivatives in Equation (15) may be dropped.

The excess free energy of mixing is related to the other excess functions by

$$\Delta G^E{}_{\text{mix}} = \Delta U^E{}_{\text{mix}} + P\,\Delta V^E{}_{\text{mix}} - T\,\Delta S^E{}_{\text{mix}} \tag{17}$$

The basic thermodynamics can be carried no further than this last relation. A physical model is required for the determination of each of the three excess properties on the right-hand side of Equation (17) as a function of composition and of molecular properties.

REGULAR SOLUTIONS

The regular solution theory as applied to surface tension in liquid-vapor systems has been developed by Schuchowitzky (*31*), Guggenheim (*16*), and Belton and Evans (3). The approach may be generalized to include liquid-liquid interfaces. Both the surface and the bulk liquid phases are considered regular, so that

$$\left.\begin{aligned} &\Delta S^E{}_{\text{mix}} = 0 \quad \text{and also} \quad \Delta V^E{}_{\text{mix}} = 0 \\ &\text{and therefore} \\ &\qquad \Delta G^E{}_{\text{mix}} = \Delta U^E{}_{\text{mix}} \end{aligned}\right\} \tag{18}$$

The results obtained may be considered as a first approximation, and as Hildebrand (*20*) points out, an estimation of free energy terms is generally less in error than estimates of the other thermodynamic functions.

It now remains to estimate $\Delta U^E{}_{\text{mix}}$, the change in total energy of mixing. The assumption of regularity implies that the molecules of the liquid and surface regions are distributed at random so that the probability of a pair interaction is proportional to the product of the mole fractions for unlike pairs or of half that product for like pairs. For molecules of differing molal volume it may be preferable to use volume fractions as does Hildebrand (*20*) or area fractions as suggested by Langmuir (*23*). For simplicity in the following equations the mole fraction is used. Area fractions are introduced at a later stage in the development.

The interaction energy ϵ_{ij} is defined as the average potential energy of interaction of a pair of molecules, one of species i and one of species j. Coordination numbers r, p, and q are defined where r is equal to the average number of interacting neighbors for surface-to-surface interactions, p for surface-to-liquid interactions, and q for interactions in the bulk liquid. The coordination numbers are taken to be constant and to satisfy the relation

$$r + 2p = q \tag{19}$$

Figure 2 illustrates the meanings of r, p, and q for a schematic two-dimensional lattice configuration. As an indication of their order of magnitude

for a cubic lattice:

$$\frac{r}{q} = \frac{4}{6} = 0.667,\quad \frac{p}{q} = \frac{1}{6} = 0.167$$

for a hexagonal close-packed lattice:

$$\frac{r}{q} = \frac{6}{12} = 0.500;\quad \frac{p}{q} = \frac{3}{12} = 0.250$$

At constant temperature it will be assumed that only the configurational energy terms need be considered. The pair-by-pair interactions for the pure component standard states are subtracted from the corresponding interactions for the actual system. These interactions include liquid′-liquid′, liquid″-liquid″, surface-surface, surface-liquid′, and surface-liquid″ interactions. The resulting expressions for the activity coefficients are

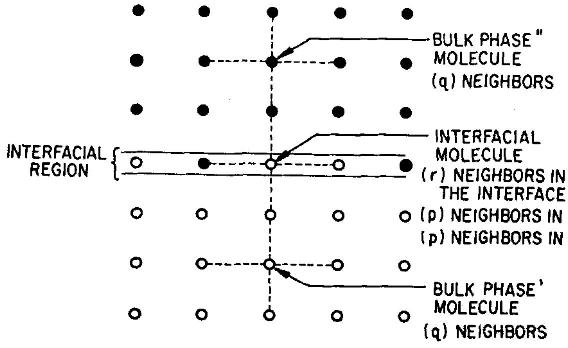

Fig. 2. Liquid-liquid interface.

$$\left.\begin{aligned} RT\ln\gamma_k' &= F_k(x_i') + O(N^s/N) \\ RT\ln\gamma_k'' &= F_k(x_i'') + O(N^s/N) \end{aligned}\right\} \quad (20)$$

and

$$RT\ln\gamma_k^* = \frac{r}{q}F_k(x_i^s) + \frac{p}{q}F_k(x_i') + \frac{p}{q}F_k(x_i'') \quad (21)$$

where the function $F(x_i)$ represents

$$F_k(x_i) = \sum_{\substack{i \\ i\neq k}} A_{ki}x_i^2 + \sum_{\substack{i \\ i>j \\ i\neq k}} (A_{ki} + A_{kj} - A_{ij})x_ix_j \quad (22)$$

with

$$A_{ij} = -N_o\,(\epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij})\,\frac{q}{2} \quad (23)$$

The term of order (N^s/N) in Equations (20), even though already small, exaggerates the influence of the surface on the bulk fluid phase. It implies that a molecule far removed from the surface feels the influence of the surface in proportion to the number of molecules in the surface region. The decrease in the intermolecular forces with increasing distance is so rapid that molecules further than a few molecular layers from the interface experience a vanishingly small influence from the interface.

For the case of a binary liquid-vapor system Guggenheim (*16, 17*) has noted that the regular solution expressions for the activity coefficients fail to satisfy the Gibbs-Duhem relation and are therefore thermodynamically inconsistent. The situation for liquid-liquid systems is completely analogous. This inconsistency is probably a result of ignoring the influence of the interface in calculating the bulk properties in Equation (20) but including the influence of the bulk solution on the interfacial properties in Equation (21).

If the molecular layer underlying the surface layer is presumed to have a composition closer to x_i^s rather than x_i' or x_i'', the inconsistency is removed. Equation (21) becomes

$$\left.\begin{aligned} RT\ln\gamma_k^* &= \frac{r+2p}{q}F_k(x_i^s) \\ \text{or}\quad RT\ln\gamma_k^* &= F_k(x_i^s) \end{aligned}\right\} \quad (24)$$

The surface activity coefficient γ_k^* is thus given by an expression equivalent to that for the bulk fluid phases, region ', and region ", except that the local concentrations x_i^s replace the bulk concentration variables. Equation (24) reflects the fact that γ_k^* should depend only on local conditions. The reason for changing Equation (21) to Equation (24) is to retain thermodynamic consistency without significantly changing the regular solution model.

THE INTERFACIAL TENSION AT INFINITE DILUTION IN TERNARY LIQUID-LIQUID SYSTEMS

The quantity of interest in influencing the stability of a liquid-liquid interface during mass transfer is the derivative of the interfacial tension with respect to the changing composition of the transferring third component.

The total differential of the interfacial tension at constant temperature and pressure is given by the basic relation for a three-component system:

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad (25)$$

The reference system and dividing surface may be chosen such that the adsorption of the principal components, components 1 and 2, will be identically zero. This defines the adsorption of the third component relative to components 1 and 2:

$$\Gamma_{3(2,1)} \equiv \Gamma_3 \quad \text{for the above convention} \quad (26)$$

The derivative of the interfacial tension is therefore

$$\frac{d\sigma}{dx_3'} = -\Gamma_{3(2,1)}\frac{d\mu_3}{dx_3'} \quad (27)$$

$$T, P = \text{constant}$$

The relative adsorption of component 3 defined by Equation (26) may be shown to be (*34*)

$$\Gamma_{3(2,1)} = \frac{\left[x_3^s - \frac{(x_2''x_1^s - x_1''x_2^s)}{(x_2''x_1' - x_2'x_1'')}x_3' - \frac{(x_1'x_2^s - x_2'x_1^s)}{(x_2''x_1' - x_2'x_1'')}x_3''\right]}{\tilde{\Omega}} \quad (28)$$

This result in conjunction with Equation (27) is independent of the choice of reference system and dividing surface. Computational convenience prompted the particular choice made above.

Equation (28) still contains the unknown surface compositions x_i^s, and its use in Equation (27) requires an estimate to be made for these quantities. Simplifications in Equation (28) can be made by restriction to systems which are limited by the following assumptions:

1. The principal components, components 1 and 2, have negligible mutual solubility:

$$x_1'' \cong 0 \quad \text{and} \quad x_2' \cong 0 \quad (29)$$

component 1 (phase ') being the highly polar material, water, and component 2 (phase ") being a nonpolar organic solvent.

2. Both phases are infinitely dilute in component 3:

$$x_3' \cong 0; \quad x_3'' \cong Kx_3'; \text{ so that also } x_3'' \cong 0 \quad (30)$$

K is the distribution coefficient for component 3.

3. Component 3 is a polar organic material such as an alcohol or organic acid. Because it has an affinity for both phase ' and phase " it is strongly adsorbed at the interface; that is

$$x_3^s >> x_3'; \quad x_3^s >> x_3'' \quad (31)$$

Equation (28) is now simplified to

$$\Gamma_{3(2,1)} \cong \frac{x_3^s}{\Omega} \quad (32)$$

and Equation (27) for the derivative of the interfacial tension becomes

$$\frac{d\delta}{dx_3'} = -\frac{x_3^s}{\overline{\Omega}}\cdot\frac{RT}{x_3'} \quad (33)$$

$$T, P = \text{constant}$$

where the relation

$$\frac{d\mu_3}{dx_3'} = \frac{RT}{x_3'} \quad \text{as} \quad x_3' \to 0 \quad (34)$$

$$T, P = \text{constant}$$

has been used.

If the interfacial tension for the two-component system of components 1 and 2 alone is considered as known, the surface composition x_3^s can be found from Equations (12) and (13). Solving for x_3^s one gets

$$x_3^s = \frac{\gamma_3' x_3'}{\gamma_3^\circ} \exp\left\{\frac{\sigma_o \bar{\Omega}_3}{RT}\right\} \tag{35}$$

where σ_o is the interfacial tension in the absence of the third component. Substitution of Equation (35) in Equation (33) gives

$$\frac{d\sigma}{dx_3'} = -\left(\frac{RT}{\tilde{\Omega}}\right) \frac{\gamma_3'}{\gamma_3^\circ} \exp\left\{\frac{\sigma_o \bar{\Omega}_3}{RT}\right\} \tag{36}$$

$$T, P = \text{constant}, \quad x_3' \to 0$$

Equation (36) is the basic working relationship for the interfacial tension gradient at infinite dilution.

THE AVERAGE PARTIAL MOLAL AREA

The area per mole appearing in the denominator of Equation (36) is the average of the partial molal areas of the individual components. Since component 3 is present in negligibly small amounts

$$\tilde{\Omega} = \bar{\Omega}_1 x_1^s + \bar{\Omega}_2 x_2^s \tag{37}$$

The mole fractions x_1^s and x_2^s must be found from solution of the equations corresponding to Equation (12) with the interfacial tension eliminated and with

$$a_1 \cong 1; \quad a_2 \cong 1 \tag{38}$$

That is

$$\frac{RT \ln \gamma_1^\circ x_1^s}{\bar{\Omega}_1} = \frac{RT \ln \gamma_2^\circ x_2^s}{\bar{\Omega}_2} \tag{39}$$

In accordance with Langmuir (23), let γ_1° and γ_2° be represented by an expression of the form of Equation (24) but with area fractions in place of mole fractions:

$$\left.\begin{aligned} RT \ln \gamma_1^\circ &= \frac{A_{12}(x_2^s \bar{\Omega}_2)^2}{(x_1^s \bar{\Omega}_1 + x_2^s \bar{\Omega}_2)^2} \\ RT \ln \gamma_2^\circ &= \frac{A_{21}(x_1^s \bar{\Omega}_1)^2}{(x_1^s \bar{\Omega}_1 + x_2^s \bar{\Omega}_2)^2} \end{aligned}\right\} \tag{40}$$

with

$$\bar{\Omega}_2 A_{12} = \bar{\Omega}_1 A_{21} \tag{41}$$

In the above expressions the cross-sectional molal area is used rather than a molecular surface area; the relation between the areas is a simple proportionality.

Since A_{12} must be much greater than RT for phase separation to have occurred, Equation (39) is equivalent to

$$x_2^s \bar{\Omega}_2 \cong x_1^s \bar{\Omega}_1 \tag{42}$$

Equation (42) and the relation $x_1^s + x_2^s = 1$ determine

$$\left.\begin{aligned} x_1^s &\cong \frac{\bar{\Omega}_2}{\bar{\Omega}_1 + \bar{\Omega}_2} \\ x_2^s &\cong \frac{\bar{\Omega}_2}{\bar{\Omega}_1 + \bar{\Omega}_2} \end{aligned}\right\} \tag{43}$$

The surface compositions of components 1 and 2 are approximately in inverse proportion to their partial molal areas.

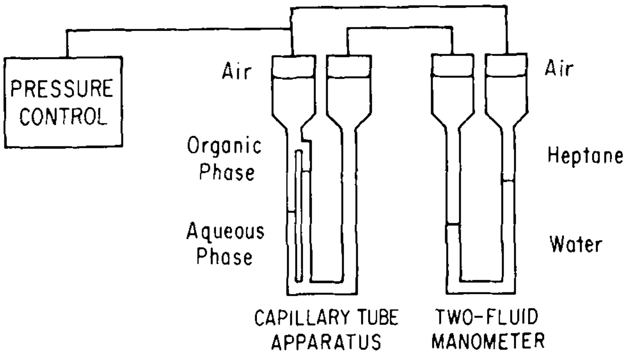

Fig. 3. Measurement of interfacial tension.

Errors in the approximations leading to Equations (43) are of minor significance, since the surface fractions as given by this relation are only to be used in averaging the partial molal areas. The average area per mole is therefore given by the harmonic mean

$$\tilde{\Omega} = \frac{2\bar{\Omega}_1\bar{\Omega}_2}{\bar{\Omega}_1 + \bar{\Omega}_2} \tag{44}$$

THE SURFACE ACTIVITY COEFFICIENT

The activity coefficient of component 3 in phase or phase $''$ cannot be expected to follow relationships as simple as the regular solution equations. This is because of the complicating effects of association of the polar solvent and of complex formation between the solvent and solute. Nevertheless the regular solution equations can provide a basis for the calculation of the fictitious activity coefficient of component 3 at the interface. The reason this is possible is that the very same effects which complicate the calculation of free energy contributions in the bulk fluid phases serve to simplify the behavior at the interface. Since component 2 is a polar organic material, it is strongly adsorbed at the interface in such a manner that the free energy of the system is reduced. The polar parts of the molecules are strongly attracted to and associated with the highly polar solvent, water. The hydrocarbon end of the solute extends into the nonpolar organic solvent. This is analogous to the situation found for alcohols or organic acids at a water-air interface. The interface is more nearly ideal than the bulk phases and is therefore amenable to calculations based on a simplified model.

For a molecule of the type under consideration the energy contributing to the activity coefficient is the sum of two terms. First, a term reflecting interactions of the water molecules and the polar end of the solute. This interaction is taken as ideal (zero excess free energy). The other contribution is due to the interaction of the nonpolar end of the solute with the nonpolar solvent. If this is expressed in terms of the regular solution equations of Hildebrand *(20)*

$$RT \ln \gamma_3^\circ = \bar{V}_3^{NP}(\delta_2 - \delta_3^{NP})^2 \tag{45}$$

$$\text{for } x_3', x_3'', \text{ and } x_3^s \to 0$$

where $\bar{V}_3^{NP}$ is a molar volume characteristic of the nonpolar part of the solute, δ_2 is the solubility parameter of the nonpolar organic solvent, and δ_3^{NP} is a solubility parameter characteristic of the nonpolar part of the solute.

FINAL RESULT

The derived Equations (36), (44), and (45) may be combined to yield a final expression for the gradient of interfacial tension with respect to concentration:

TABLE 1. ACTIVITY COEFFICIENTS FOR THE SYSTEMS WATER-ALCOHOL-SOLVENT AT 25°C.

	Alcohol (infinitely dilute in water)		
	Methyl	Ethyl	n-Propyl
$\gamma_3'^*$	1.52	3.32	11.4
Values of γ_3^* from Equation (45):			
Solvent:			
n-Hexane	1.00	1.00	1.00
Carbon tetrachloride	1.05	1.10	1.16
Benzene	1.11	1.23	1.36

[*] References *8, 27.*

$$\frac{d\sigma}{dx_3'} = -\frac{RT\,(\bar{\Omega}_1 + \bar{\Omega}_2)\,\gamma_3'\exp\dfrac{\sigma_o\bar{\Omega}_3}{RT}}{2\bar{\Omega}_1\bar{\Omega}_2\exp\{\bar{V}_3{}^{NP}\,(\delta_2 - \delta_3{}^{NP})^2/RT\}} \quad \text{as } x_3' \rightarrow 0 \tag{46}$$

EXPERIMENTAL

The interfacial tension in ternary systems was determined by a modification of the capillary rise technique due to Speakman (*36*). The apparatus consists of the three parts indicated schematically in Figure 3. These are the capillary tube apparatus, the two-fluid manometer, and a means for adjusting the pressure difference across the capillary tube apparatus. The difference in head is measured by adjusting the pressure in the capillary tube apparatus to bring the meniscus in one capillary tube to the same level previously occupied by the other meniscus. This pressure difference is determined by the difference in readings made with the two-fluid manometer. Both the capillary tube apparatus and the manometer were maintained at 25.00° ± 0.02°C.

The principal restriction on the applicability of the method is the requirement for an accurately known contact angle. In practice this limits consideration to systems where the contact angle is zero. The systems studied here, in the absence of the third component, are known to have a zero contact angle. It is assumed that the presence of the third component in dilute solution does not appreciably alter the preferential wetting of the glass by the aqueous phase and therefore maintains a zero contact angle.

The accuracy of the physical and geometric variables was checked by determination of the surface and interfacial tensions for systems with well-known values. For example the benzene-air interface at 25°C. gave for two different samples an average value of 28.17 ± 0.07 erg/sq.cm. which may be compared with the literature value of 28.18 (*21*). The corresponding value for the water-normal hexane interface, 51.0 ± 0.1 erg/sq.cm., is to be compared with the literature value of 50.97 ± 0.2 erg/sq.cm. (*21*).

TABLE 2. INTERFACIAL TENSION DERIVATIVES FOR THE SYSTEMS WATER-ALCOHOL-SOLVENT AT 25°C. AND AT INFINITE DILUTION*

		$-d\sigma/dx_3'$ (erg/sq. cm.) Alcohol		
Solvent		Methyl	Ethyl	n-Propyl
n-Hexane	exptl.†	650 ± 100	1,610 ± 160	5,200 ± 260
	calc.**	790	1,730	5,940
Carbon tetra-chloride	calc.**	270 ± 80	1,880 ± 160	3,680 ± 170
		550	1,140	3,710
Benzene	calc.**	250 ± 50	880 ± 80	2,540 ± 130
		300	590	1,830

[*] Recent data of Valentine and Heideger (*39*) for the systems water-methanol-carbon tetrachloride and water-methanol-benzene at 20°C. provide a comparison for the two corresponding values of this table. The slopes from the interfacial tension-concentration curves (Figure 3 of the above reference) are estimated to be in the range −410 ± 95 and −195 ± 35 for the two systems, respectively. These values overlap those of this work (−270 ± 80 and −250 ± 50 at 25°C.).

† This work.

** In accordance with Equation (46).

TABLE 3. ACTIVITY COEFFICIENTS FOR THE SYSTEMS WATER-ORGANIC ACID-SOLVENT AT 20°C.

	Acid (infinitely dilute in water)		
	Acetic	Propionic	Butyric
$\gamma_3'^*$	3.22	11.1	38.2
Values of γ_3^* from Equation (45):			
Solvent:			
n-Heptane	1.00	1.00	1.00
Benzene	1.23	1.36	1.51

[*] Reference *40.*

The predominating factor influencing the uncertainty in the calculated interfacial tension derivative is the uncertainty in the values for the interfacial tension. The overall percent uncertainty in the interfacial tension ranges from 2 to 20% depending on the particular system. This corresponds to individual error ranges for the interfacial tension derivative of from ± 50 to ± 260 erg/sq.cm.

COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

Results calculated from Equation (46) following the sample calculation of the Appendix, are summarized in Tables 1 to 4. Table 1 is a presentation of the bulk and surface activity coefficients, γ_3' and γ_3^*, for the systems water phase-alcohol-organic phase where the alcohol is methanol, ethanol, or normal propanol, and the principal component of the organic phase is normal hexane, carbon tetrachloride, or benzene. Table 2 compares calculated and experimental results.

The indicated variation of the surface concentration, Equation (35), used as an intermediate variable in these calculations, is substantiated by the trends observed in the recent work of Shinoda and Kinoshita (*35*). The relative adsorption of long-chain molecules at a liquid-vapor interface is observed to increase by a factor of 3 for each addition of a methyl group to the chain. The activity coefficients of such molecules in aqueous solution increase by approximately this same factor for each additional methyl group.

A similar summary of calculations and comparison is made in Tables 3 and 4 for data selected from the work of Vignes (*40*) for the systems water phase-organic acid-nonpolar organic phase where the organic acid is acetic

TABLE 4. INTERFACIAL TENSION DERIVATIVES FOR THE SYSTEMS WATER-ACID-SOLVENT AT 20°C. AND AT INFINITE DILUTION

		$-d\sigma/dx_3'$ (erg/sq. cm.) Acid		
Solvent		Acetic	Propionic	Butyric
Heptane	exptl.*	2,040	5,650	17,400
	calc.†	1,670	5,760	19,800
	calc.**	2,390	7,550	23,900
Benzene	exptl.*	780	2,200	6,600
	calc.†	590	1,840	5,710
	calc.**	930	2,950	9,330

[*] Data of Vignes (*40*).

† In accordance with Equation (46).

** Equation (36) of Vignes.

acid, butyric acid, or propionic acid, and the organic phase is heptane or benzene.

The agreement of theoretical and experimental results for these systems is comparable to those of Table 2. Vignes (*40*) presents a theoretical equation similar in form to Equation (46). He uses the partial molal area of water instead of an average area and takes the interface to be ideal with respect to the third component, that is $\gamma_3^* = 1$. Values of the interfacial tension derivative calculated from Equation (36) of Vignes are included in Table 4 and are substantially higher than those calculated from Equation (46) of this work. Because Vignes compares experimental and calculated results on the basis of logarithms of the values of the derivatives, the discrepancies reported in his paper are not as apparent as they are in Table 4.

The regular solution equations discussed in this work may be used for the calculation of interfacial tension for mixtures of finite concentrations. A suggestion toward this end is contained in reference 34.

RELATION TO INTERFACIAL INSTABILITY

The work presented here has been aimed at elucidating the relation between the interfacial tension and the properties of the individual components in a ternary system. However since the motivation for this work has its basis in the problem of interfacial instability, it is appropriate to comment on the implications of the results in affecting the instability of interfaces.

The analysis presented by Sternling and Scriven (37) indicates that large (negative) values of the interfacial tension are conducive to pronounced Marangoni effects. Equation (46) indicates that the following list of factors will contribute to such large interfacial tension gradients. The list is arranged in order of probable decreasing importance of influence.

1. A large interfacial tension in the binary system.
2. A large hydrocarbon chain attached to the polar organic molecule. This factor leads to a large adsorption of the molecule at the interface and subsequent large influence on the interfacial tension.
3. A large effective size for the polar organic molecule in the interface, that is a branched hydrocarbon chain attached to the polar group, would be expected to have a larger influence than the normal chain molecules studied.
4. A small size for the nonpolar solvent molecule.
5. A hydrocarbon chain attached to the polar organic molecule which resembles the nonpolar solvent molecule.

LIMITATION TO THE APPLICABILITY OF RESULTS

An important limitation to the applicability of Equation (46) is indicated by a discrepancy between the indicated influence of the length of the hydrocarbon chain on the polar molecule on the interfacial tension gradient (which is verified by the experimental results) and the effect of very long chain surface-active molecules on systems in which interfacial turbulence is occurring. Molecules of the type in question have a very striking terminating effect on the turbulent flows at the interface. The situation however is a dynamic one and does not correspond to the equilibrium situation assumed in the derivation of Equation (46).

For the situation in which such large surface active molecules are present in the surface, a local expansion in the surface results in a local depletion of these molecules. The rate of diffusion of additional molecules of large size to the interface is slow. The local interfacial tension rises and imposes a restoring force on the stretched interface. The interfacial tension becomes controlled by the local rate of expansion of the interface rather than being the value which would exist in an equilibrium situation. The effect may be taken into account in a stability analysis through the use of a surface viscosity effect; that is the surface appears to resist deformations of the nature of expansions. A similar argument applies to a local contraction of the interface.

Equation (46) can be considered adequate for situations involving small molecules. The implications based on the equation are limited in application and should be applied with caution in situations requiring analysis of dynamic values of the interfacial tension.

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NOTATION

A_{ij} = pair interaction parameters, cal./mole
a = activity
G = Gibbs free energy, cal.
K = partition coefficient
N = moles
N_o = Avogadro's number, equal to 6.023×10^{23} molecules/g.-mole
n = carbon number
P = pressure, lb./sq. in. abs.
S = entropy, cal./°K.
s = specific entropy, cal./(°K.) (sq. cm.)
T = temperature, °K.
U = total energy, cal.
V = volume, cc.
v = specific volume, cm.
x = concentration, mole fraction

Greek Symbols

Γ = specific interfacial concentration, g.-moles/sq. cm.
γ = activity coefficient
Δ = difference
δ = solubility parameter, cal.$^{1/2}$/cm.$^{3/2}$
ϵ_{ij} = pair interaction energy parameter, erg
μ = chemical potential
σ = surface tension, erg/sq. cm.
Ω = area, sq. cm.
ω = area per molecule, Å.^{2}

Subscripts

i = component i, where $i = 1, 2, 3, \ldots$
ref = reference system
mix = property of mixing

Superscripts

E = excess function
NP = nonpolar
o = pure component
s = interfacial region
$'$ = aqueous phase
$''$ = organic phase
$*$ = defined quantity
$\overline{}$ = partial molal quantity, /mole
$\sim$ = molar quantity, /mole

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APPENDIX

Sample Calculation

The system selected for the sample calculation is water-ethanol-normal hexane. The physical properties and thermodynamic variables used are from the tabulation which follows.

The activity coefficient for the alcohol in the aqueous phase γ_3' is taken directly from experimental determinations since the regular solution equations are not applicable for the bulk fluid. For this system the value is 3.32.

The surface activity coefficient for the alcohol is calculated from Equation (45). The volume of the nonpolar group is taken to be given by the volume of one methyl group (taken as the value for ethanol minus methanol) times the hydrocarbon chain length

$$\overline{V}^{NP} \cong 17.9\, n \text{ cc./mole}$$

which, since $n = 2$ for ethanol, gives a value of 35.8 cc. Since the nonpolar solvent and the nonpolar part of the alcohol are similar hydrocarbon chains, the solubility parameters for each are the same, each taken to be 7.3 cal.$^{1/2}$/cm.$^{3/2}$. This gives a value for the surface activity coefficient of 1.00, that is the surface is ideal. For the systems in which the solvents are carbon tetrachloride or benzene, the solubility parameter for hexane is taken as the value characterizing the hydrocarbon chain on the polar organic molecule. Even in these cases the interface is very nearly ideal, the largest value for the surface activity coefficient of an alcohol being 1.36 (Table 1). For this reason the estimate using Equation (45) and the above relation for $\overline{V}^{NP}$ need not be refined.

The partial molal area for water $\overline{\Omega}_1$ is 9.64 Å.^{2}/molecule, while that for hexane $\overline{\Omega}_2$ is 39.7 Å.^{2}/molecule. The average area is then given by Equation (44) to be 15.5 Å.^{2}/molecule.

The partial molal area for the alcohol molecule at the interface $\overline{\Omega}_3$ is taken as 24.0 Å.^{2}/molecule which corresponds to the area occupied by a vertically oriented normal hydrocarbon chain (*41*). This same value is applied to all of the normal alcohols or organic acids.

The above values, along with the experimental value for the interfacial tension in the absence of the alcohol of 51.0 erg/sq.cm., are combined in Equation (*36*) to give 1,660 erg/sq.cm. as the interfacial tension derivative. The corresponding results for other systems of interest are summarized in Tables 1 through 4. The calculations are most sensitive to the values of σ_o and $\overline{\Omega}_3$, since these terms appear in an exponential factor in Equation (36). In the above example each 1% change in the product$\sigma_o\overline{\Omega}_3$ would result in a 3% change in the calculated interfacial tension derivative.

Physical Properties and Thermodynamic Data

The following tables with indicated references to the literature summarize the information used in the calculations leading to the presentation of Tables 1 through 4.

PROPERTIES OF PURE COMPONENTS AT 25°C.

Component	$\rho, \frac{g}{cc.}$ *	ω, Å.^{2}	$\sigma, \left(\frac{cal.}{cc.}\right)^{1/2}$ †
Water	0.9971	9.64	—
Hexane	0.6548	39.7**	7.3
Carbon tetrachloride	1.5843	29.7	8.6
Benzene	0.8738	28.0	9.15
Methanol	0.7867	—	—
Ethanol	0.7851	—	—
n-Propanol	0.7999	—	—

* References *11, 12, 13, 38.*
† Reference *20.*
** Equation (2.90) of reference *34.*

DISTRIBUTION COEFFICIENTS AT INFINITE DILUTION FOR THE SYSTEMS WATER-ALCOHOL-SOLVENT AT 25°C.

$K = \gamma_3'/\gamma_3''$ Solvent:		Alcohol Methyl	Ethyl	*n*-Propyl
Hexane	(8, 27)	0.0172	0.0652	0.267
Carbon tetrachloride	(29, 8, 27)	0.0534	0.125	0.295
Benzene	(29, 8, 27)	0.0773	0.411	2.14