Semiempirical Theory of Surface Tension of Binary Systems

Surface tensions of several binary mixtures are computed using the gradient theory of inhomogeneous fluids. The interfacial influence parameters are determined from mixing rules and pure fluid experimental tensions. A comparison of the compositional dependence of the predicted and experimental tensions indicates that the best results for nonpolar hydrocarbons are obtained from a geometric mixing rule for the influence parameter. Predicted tensions vs. composition for nonpolar systems are in excellent agreement with experiment, generally lying within 2% of observed data. Predictions are poor for alcohol solutions.

B. S. CAREY
L. E. SCRIVEN
and
H. T. DAVIS
University of Minnesota
Minneapolis, Minnesota 55455

SCOPE

The Peng-Robinson equation of state is used with the gradient theory of inhomogeneous fluids to investigate surface tension and density profiles of binary solutions. Mixing rules are sought for the influence parameters c_{ij} of inhomogeneous fluid. Such mixing rules allow one to compute interfacial properties from pure fluid data when similar mixing rules are available with empirical or theoretical equations of state. The focus is on polyatomic fluids such as nonpolar hydrocarbons and alcohols.

CONCLUSIONS AND SIGNIFICANCE

A method for predicting the compositional dependence of surface tension of binary mixtures has been developed. The only input parameters required are the pure component critical data and influence parameters c. The geometric mixing rule

$$c_{ij} = \sqrt{c_{ii}c_{jj}}$$

yields the best results for nonpolar mixtures and leads to the numerical simplification of having to solve algebraic rather than differential equations, even for mixtures containing more than two chemical species. The model predicts the presence of surface activity in several systems. The predictions for alcohol mixtures are poor. As the equation of state used is known not to be accurate for alcohol, one cannot tell at this point whether the poor performance for alcohols arises from using gradient theory with constant influence parameters or from inadequacies of the Peng-Robinson equation of state.

THEORY

Given an inhomogeneous system at temperature T, volume V and with N_i particles of species $i = 1,2$, it can be shown (Bongiorno et al., 1977) that the differential equations which govern the density variations through a planar interface are of the form

$$\sum_{j=1}^{2} \nabla_{\underset{\sim}{r}} \cdot (c_{ij}\nabla_{\underset{\sim}{r}} n_j) - \frac{1}{2} \sum_{j,k=1}^{2} \left(\frac{\partial c_{ij}}{\partial n_{ai}}\right) \nabla_{\underset{\sim}{r}} n_k \cdot \nabla_{\underset{\sim}{r}} n_j = \mu_i^0(\underset{\sim}{n}) - \mu_i \quad (1)$$

where

$$c_{ij} \equiv \frac{kT}{6} \int_V s^2 C_0^{ij}(s,\underset{\sim}{n}) d^3s \quad (2)$$

C_0^{ij} denotes the direct correlation function between a pair of particles of types i and j, $\mu_i^0(\underset{\sim}{n})$ the local chemical potential of species i in a homogeneous state at composition n and μ_i the chemical potential of species i.

Although Equation (2) is the rigorous expression for the influence parameters, a more convenient approximate formula is (Vargas, 1976)

$$c_{ij} = \frac{1}{2} w_2^{ij} + \frac{1}{8} \sum_{k=1}^{2} n_k \left[\frac{\partial w_2^{ik}}{\partial n_j} - \frac{\partial w_2^{jk}}{\partial n_i}\right] \quad (3)$$

$$w_2^{ij} \equiv -\frac{1}{3} \int s^2 u_{ij}(s)\, g_{ij}(s;\underset{\sim}{n}) d^3s \quad (4)$$

where $g_{ij}(s,\underset{\sim}{n})$ represents the pair correlation function between particles of species i and j, with u_{ij} denoting the pair potential function between the corresponding molecules. Equations (2) and (4) have been shown to agree quite well for a simple fluid model (McCoy and Davis, 1979).

It is now assumed that the pair correlation is a weak enough function of density that c_{ij} can be considered to be independent of composition. This assumption is supported by the works of Carey et al. (1978*a*) and McCoy and Davis (1979) in which surface tensions and density profiles of simple one-component fluids were shown to be relatively insensitive (say 10% variation) to the density dependence of the influence factor. Given this assumption, the governing Equations (1) for a planar interface reduce to

$$\sum_{j=1}^{2} c_{ij} \frac{d^2 n_j}{dx^2} = \mu_i^0(\underset{\sim}{n}) - \mu_i, \; i = 1,2 \quad (5)$$

The boundary conditions associated with Equation (5) state that $\underset{\sim}{n} \to \underset{\sim}{n}^I$ as $x \to \infty$ and $\underset{\sim}{n} \to \underset{\sim}{n}^{II}$ as $x \to -\infty$. Correspondingly, the density gradients, curvatures and all higher-order derivatives will vanish in the bulk phases. The bulk densities $\underset{\sim}{n}^I$ and $\underset{\sim}{n}^{II}$ are computed via equalities of bulk pressures and chemical potentials for each species [which are equivalent to the boundary conditions on Equation (5)].

Correspondence concerning this paper should be sent to H. T. Davis.

0001-1541-80-3827-0705-$00.95.

An equation of state for homogeneous fluids is now required to determine an expression for the chemical potential. The equation of state used for the pressure P_0 of a homogeneous fluid has been developed by Peng and Robinson (1976) and is of the form

$$P_0 = \frac{nkT}{1-nb} - \frac{n^2a(T)}{1+2nb-(nb)^2} \tag{6}$$

As with any equation of state, mixing rules for the parameters must be adopted to relate the mixture parameters to those of pure fluids. In this instance, they are of the form

$$b_m = \sum_i x_i b_i \tag{7}$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{8}$$

$$a_{ij} = (1-\delta_{ij})\sqrt{a_{ij}a_{ij}} \tag{9}$$

where x_i is the mole fraction of species i and δ_{ij} is an adjustable parameter, with a_{ii} and b_i the pure component energy and volume parameters. The chemical potential expressions corresponding to Equation (6) are obtained from the appropriate thermodynamic relations.

Although mixing rules have now been established for the bulk phase parameters, the relationship between the pure component influence parameters c_{ii} and the cross terms c_{12} has remained unspecified. Since these terms essentially represent weighted energy parameters, c_{12} will be scaled in the same manner as the bulk energy parameter a_{12}:

$$c_{12} = \beta\sqrt{c_{11}c_{22}} \tag{10}$$

β is an adjustable parameter. The determination of the c_{11} parameters from pure component surface tension data is described elsewhere (Carey et al., 1978*b*).

The surface tension corresponding to Equation (1) is (Vargas, 1976; Bongiorno et al., 1977)

$$\gamma = \int_{-\infty}^{\infty} \sum_{i,j=1}^{2} c_{ij}\left(\frac{dn_i}{dx}\right)\left(\frac{dn_j}{dx}\right)dx \tag{11}$$

or, from the profile independent equation

$$\gamma = \int_{n_i^I}^{n_i^{II}} \sqrt{2[\omega(\underset{\sim}{n})-\omega(\underset{\sim}{n}^{bulk})]}\,\sqrt{\sum_{j,k=1} c_{kj}\left(\frac{dn_k}{dn_i}\right)\left(\frac{dn_j}{dn_i}\right)}\,dn_i \tag{12}$$

where i can represent either species. $\omega(\underset{\sim}{n})$ represents a grand thermodynamic potential defined by

$$\omega(\underset{\sim}{n}) = f^0(\underset{\sim}{n}) - \sum_i n_i\mu_i \tag{13}$$

where $f^0(\underset{\sim}{n})$ is the local Helmholtz free energy density of homogeneous fluid at composition $\underset{\sim}{n}$. For the Peng-Robinson model

$$f^0(\underset{\sim}{n}) = f^+(T) + kT\sum_i n_i \ln x_i + \frac{n^2a(T)}{2\sqrt{2}\,b}\ln\left[\frac{1+nb(1-\sqrt{2})}{1+nb(1+\sqrt{2})}\right] - nkT\ln(1-nb) \tag{14}$$

NUMERICAL SOLUTIONS

Before we seek a solution, it is convenient to put all variables in dimensionless form using the following relations:

$$n_i^* = n_ib_1 \quad T^* = b_1kT/a_1 \quad \gamma = \gamma b_1{}^2/\sqrt{a_{11}c_{11}}$$
$$\omega^* = b_1^2\,\omega/a_{11} \quad x^* = x\sqrt{a_{11}/c_{11}} \quad \mu_i^* = \mu_ib_1/a_{11}$$
$$P = b_1{}^2P/a_{11} \tag{15}$$

For the bulk and interfacial parameters

$$a^* = a/a_{11} \quad b^* = b/b_1 \quad c^*_{\alpha\beta} = c_{\alpha\beta}/c_{11} \tag{16}$$

In these terms, the problem is now restated as

$$c^*_{11}\frac{d^2n^*_1}{dx^{*2}} + c^*_{12}\frac{d^2n^*_2}{dx^{*2}} = \Delta\mu^*_1 \equiv \partial\omega^*/\partial n^*_1 \tag{17}$$

$$c^*_{21}\frac{d^2n^*_1}{dx^{*2}} + c^*_{22}\frac{d^2n^*_2}{dx^{*2}} = \Delta\mu^*_2 \equiv \partial\omega^*/\partial n^*_2 \tag{18}$$

where $\Delta\mu^*_\alpha \equiv \mu_\alpha^{0*}(\underset{\sim}{n}^*) - \mu^*_\alpha$ and $c^*_{21} = c^*_{12}$. The second set of equalities can be derived from the definition of $\omega^*(\underset{\sim}{n}^*)$ and from the fact that the chemical potential expression μ_α^{0*} is the partial derivative of the Helmholtz free energy density $f^{0*}(\underset{\sim}{n}^*)$ with respect to n^*_α.

Multiplying (17) by (dn^*_1/dx^*) and (18) by (dn^*_2/dx^*), adding and integrating from a bulk phase, we get

$$\sum_{i,j} c^*_{ij}\left(\frac{dn^*_i}{dx^*}\right)\left(\frac{dn^*_j}{dx^*}\right) = 2(\omega^*(\underset{\sim}{n}^*) - \omega^*_B) \tag{19}$$

where $\omega^*_B = \omega^*[\underset{\sim}{n}^*(x^* \rightarrow \pm\infty]$.

The problem now arises as to the method of solving a boundary value problem on the infinite domain $(-\infty,\infty)$. This problem can be avoided by eliminating the differential terms in x^* and, instead, solving one differential equation in the $n^*_2 - n^*_1$ phase plane, thereafter regenerating the x^* dependence of n^*_1 and n^*_2 from Equation (19). With the appropriate manipulation, it can be shown (Carey, 1978) that the phase plane differential equation is given by

$$\begin{aligned}&\left\{1+2c^*_{12}\frac{dn^*_2}{dn^*_1} + c^*_{22}\left(\frac{dn_2}{dn^*_1}\right)^2\right\}\\ &\qquad\left\{\left(c^*_{22}\Delta\mu^*_1 - c^*_{12}\,\Delta\mu^*_2\right)\frac{dn^*_2}{dn^*_1}\right.\\ &\qquad\left.-(c^*_{11}\Delta\mu_2 - c^*_{12}\Delta\mu^*_1)\right\} + 2[\omega^*(\underset{\sim}{n}^*)-\omega^*_B]\\ &\qquad\qquad(c^*_{11}c^*_{22}-c^*_{12}{}^2)\cdot\frac{d^2n^*_2}{dn^{*2}_1} = 0\end{aligned} \tag{20}$$

with the boundary conditions

$$\begin{aligned}n^*_2(n^{*I}_1) &= n^{*I}_2\\ n^*_2(n^{*II}_1) &= n^{*II}_2\end{aligned} \tag{21}$$

The problem has now been posed on a bounded domain and can be solved using a finite difference technique. Once $n^*_2(n^*_1)$ has been determined, the profiles $n^*_1(x^*)$ and $n^*_2(x^*)$ can be derived by a rearrangement and integration of (19) to obtain

$$x^*(n^*_i) = x^*(n_i^{*0}) + \int_{n_i^{*0}}^{n_i^*}\sqrt{\frac{\sum_{j,k=1}^{2} c^*_{kj}\left(\frac{dn^*_k}{dn^*_i}\right)\left(\frac{dn^*_j}{dn^*_i}\right)}{2[\omega^*(\underset{\sim}{n}^*)-\omega^*_B]}}\,dn^*_i \tag{22}$$

Finally, the surface tension can be computed from either (11) or (12).

For the special case in which $\beta = 1$, the cross term becomes $c^*_{12} = \sqrt{c^*_{11}c^*_{22}}$, and Equations (11) and (18) become degenerate. In this instance, for a nontrivial solution to exist, it is required that

$$\sqrt{c^*_{22}}\,\Delta\mu^*_1(\underset{\sim}{n}^*) = \sqrt{c^*_{11}}\,\Delta\mu^*_2(\underset{\sim}{n}^*) \tag{23}$$

a single, nonlinear algebraic equation. By setting a value of n^*_1, a corresponding value of n^*_2 can be calculated, and thus the $n^*_2 - n^*_1$ solution path may be determined. This algebraic solution may also be used to verify the differential solution to (20) when $\beta = 1$. For cases in which $\beta \neq 1$, a second method was used (Carey, 1978) to check the results of the finite difference algorithm in the phase plane.

For a system with ν components, the geometric mixing rule reduces the differential profile Equations (5) to the set of algebraic equations

$$\sqrt{c^*_{11}}\,\Delta\mu^*_1(\underset{\sim}{n}^*) = \sqrt{c^*_{ii}}\,\Delta\mu^*_1(\underset{\sim}{n})\ ,\ i=2,\ldots,\nu \tag{24}$$

Table 1. Effect of Molecular Sizes on Energy Parameters

b_2/b_1	σ_2/σ_1	β	$(1-\delta_{12})$
1.0	1.000000	1.000	1.000
1.5	1.144714	1.011	1.006
2.0	1.259921	1.033	1.020
2.5	1.357209	1.059	1.035
3.0	1.442250	1.086	1.051
3.5	1.518294	1.114	1.067
4.0	1.587401	1.141	1.082
4.5	1.650964	1.168	1.097
5.0	1.709976	1.194	1.112
5.5	1.765174	1.220	1.126
6.0	1.817121	1.245	1.140
6.5	1.866256	1.270	1.154
7.0	1.912931	1.294	1.167
7.5	1.957434	1.318	1.180
8.0	2.000000	1.342	1.193

MIXING RULES

Although the mixing rule parameter β must be calculated empirically, it is possible to qualitatively determine its value from a simple molecular model. Substituting a Lennard-Jones potential

$$u_{ij}(s) = 4\,\epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{s}\right)^{12} - \left(\frac{\sigma_{ij}}{s}\right)^{6}\right\} \tag{25}$$

into (4) and approximating the correlation function by a step function

$$g_{ij}(s,n) = \begin{cases} 0 & s < \sigma_{ij} \\ 1 & s \geq \sigma_{ij} \end{cases} \tag{26}$$

we find

$$c_{ij} \propto \sigma_{ij}^5 \epsilon_{ij} \tag{27}$$

σ_{ij} and ϵ_{ij} represent length and energy parameters characteristic of molecular interactions between the species.

Using the conventional mixing rules for the molecular parameters of the Lennard-Jones potential

$$\sigma_{ij} = \left(\frac{\sigma_{ii}+\sigma_{jj}}{2}\right), \quad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{28}$$

with the definition of $\beta \equiv c_{12}/\sqrt{c_{11}c_{22}}$, we find

$$\beta = \frac{1}{32}\left[\sqrt{\frac{\sigma_1}{\sigma_2}} + \sqrt{\frac{\sigma_2}{\sigma_1}}\right]^5 \tag{29}$$

This expression attains its minimum value of unity at $\sigma_2 = \sigma_1$. A molecular volume ratio (σ_2^3/σ_1^3) of 8:1 corresponds to a β value of 1.34 (see Table 1). Thus, the simple model predicts that β will be a weak function of the volume ratio and ought to be well approximated by unity.

A similar analysis can be performed for the energy parameter $a_{\alpha\beta}$ which is generally defined by

$$a_{ij} = -\frac{1}{2}\int_V u_{ij}(s)\, g_{ij}(s) d^3s \tag{30}$$

Defining $(1-\delta) \equiv a_{12}/\sqrt{a_{11}a_{22}}$, we find for this simple molecular model

$$(1-\delta) = \frac{1}{8}\left[\sqrt{\frac{\sigma_1}{\sigma_2}} + \sqrt{\frac{\sigma_2}{\sigma_1}}\right]^3 \tag{31}$$

Like β, $(1-\delta)$ is a weak function of the volume ratio (see Table 1) and attains a minimum value of unity, or $\delta = 0$. This value will be used in all calculations presented herein.

Empirical values for the mixing parameter were obtained by fixing a liquid phase mole fraction and parameter β, calculating the corresponding surface tension and then comparing it with experimental data for the binary system. The pure fluid c_{ii} parameters were determined by fitting theory to experiment for pure fluid tensions. By varying the mole fraction and the mixing parameter, a complete picture of the surface tension dependence on these two parameters was obtained. Results for two characteristic systems are illustrated in Figures 1 and 2. The dependence of the surface tension on the β parameter at fixed composition is illustrated in Figure 3 and is representative of the general behavior observed. In all nonpolar systems studied, the optimal β parameter was found to be equal to or slightly greater than unity. Best results were obtained for binary systems in which the molecules were similar in size (as measured by the volume parameter b) and were nonpolar in nature.

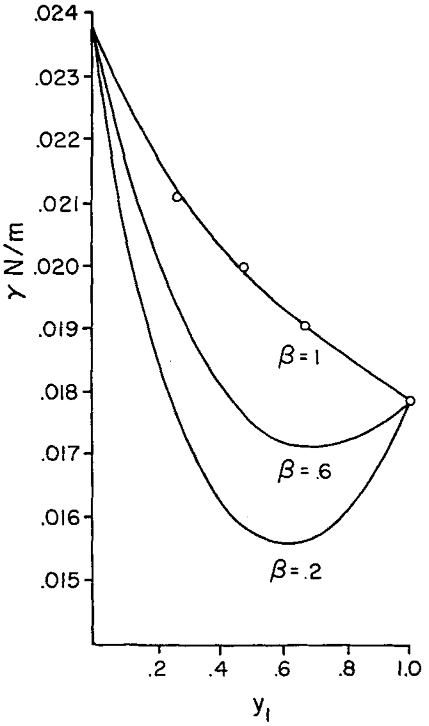

Figure 1. Surface tensions for mixtures of cyclohexane (1) and iso-octane (2) at 303°K for several values of β.

The influence of β on the phase plane solution to Equation (30) for a binary hydrocarbon system and a binary alcohol system

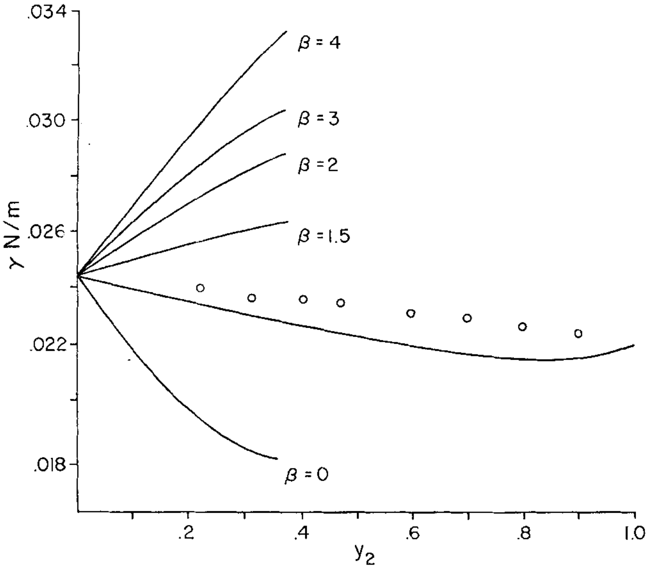

Figure 2. Surface tensions for mixtures of *n*-butanol (1) and methanol (2) at 298°K for several values of β.

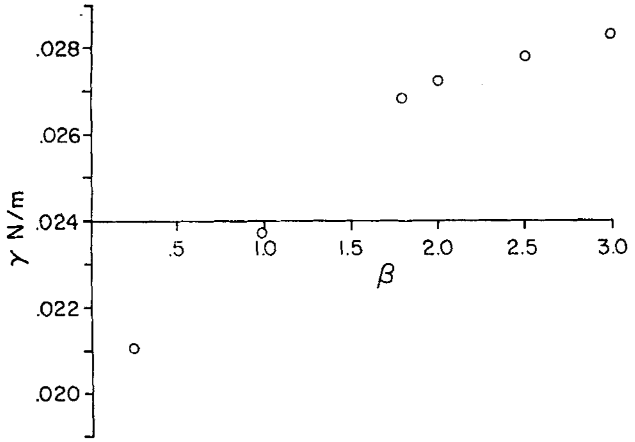

Figure 3. Surface tension variation with β for *n*-butanol and methanol $y_1=0.56$.

is shown in Figures 4 and 5. A change in this parameter has very little influence in the gas phase of the system, while at higher densities it significantly alters the character of the curves. Specifically, higher values of β tend to introduce surface activity (that is, a density maximum) in one of the species.

PREDICTED SURFACE TENSIONS OF BINARY MIXTURES

From the work discussed in the preceding section, we conclude that simplicity, accuracy and the success of the estimates suggest the mixing rule $\beta = 1$. Thus we have used $\beta = 1$ and $\delta = 0$ to analyze several binary systems. A related mixing rule has been introduced by Girifalco and Good (1957) and explored for binary liquid-vapor interfaces by Winterfeld, Scriven and Davis (1978). As illustrated in Figures 6 to 10, predicted compositional dependence of surface tension agrees well with experimental data. The predictions in Figure 10 compare favorably with experiment at two temperatures.

Corresponding to each surface tension prediction is a solution path in the phase plane, several of which are shown in Figure 11. The presence of surface activity is indicated by a maximum in the density of one of the species. While this behavior is apparently present for all mole fractions in the example given, in certain systems it occurs only over a restricted compositional range.

As described earlier, phase plane solutions are transferred into spatial solutions by the integration of Equation (22). An example of a typical surface active system is illustrated in Figure 12. In this instance, the density profile of one component goes through an inflection point in an apparent response to the corresponding surface activity of n_1^*.

Although the geometric rule is quite successful in describing binary hydrocarbon systems, it does not yield good predictions of the behavior of binary alcohol systems. As illustrated in Figures 13 and 14, predictions of surface tensions using $\beta = 1$ are quite poor. These predictions appear even worse in view of the closeness of the pure component surface tensions. Unfortunately, certain numerical difficulties are encountered in solving systems for which $\beta > 1$. In addition, the character of the phase plane solution dramatically changes as β increases through unity. These problems require additional investigation and will not be discussed further in this publication.

A summary of the results using the geometric mixing rule is given in Table 2 for several binary mixtures. A measure of the deviation between predicted and experimental values is given by the quantities $\overline{\Delta}$ and $\Delta_{\max}$, where

$$\Delta_i = \frac{\gamma_i^{\text{expt}} - \gamma_i^{\text{prod}}}{\gamma^{\text{expt}}} \qquad i = 1, \ldots N$$

$$\overline{\Delta} = \frac{1}{N} \Sigma \Delta_i$$

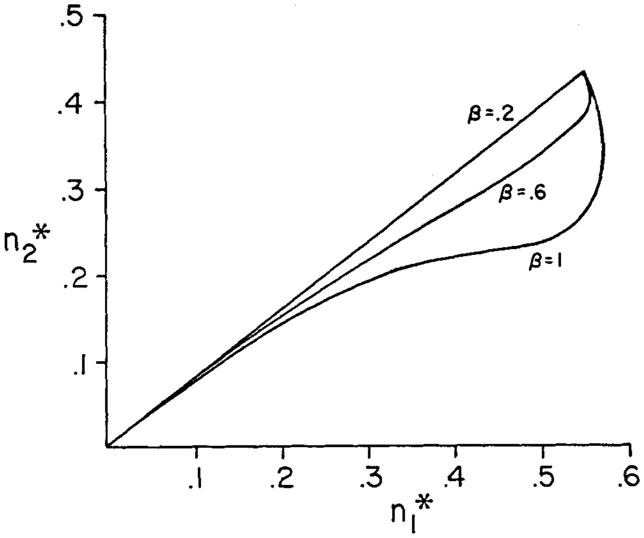

Figure 4. Phase plane solution for iso-octane (1) - cyclohexane (2) at 303°K for several values of β. $y_1=0.56$.

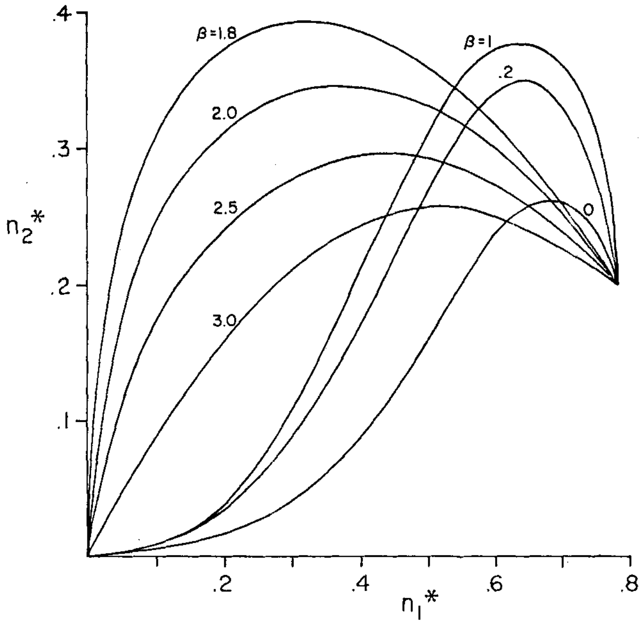

Figure 5. Phase plane solutions for *n*-butanol (1) and methanol (2) at 298°K and $y_2 = 0.202$ for several values of β.

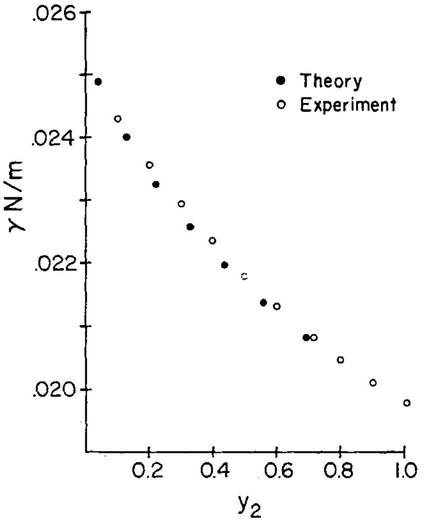

Figure 6. Surface tensions for mixtures of cyclohexane (1) and *n*-heptane (2) at 298°K for $\beta = 1$.

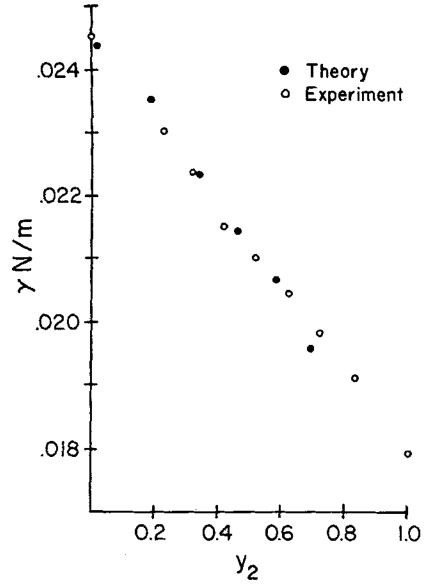

Figure 7. Surface tensions for mixtures of *n*-dodecane (1) and iso-octane (2) at 303°K for $\beta = 1$.

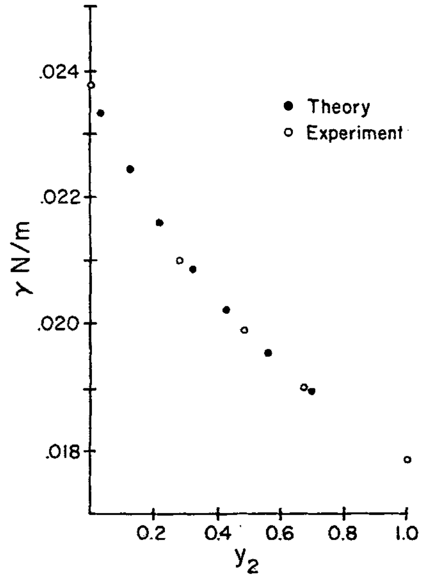

Figure 9. Surface tensions for mixtures of cyclohexane (2) and iso-octane (1) at 303°K for $\beta = 1$.

$$\Delta_{\max} = \max_i(\Delta_i) \tag{32}$$

N is the number of different mole fractions at which Δ_i is computed. In all hydrocarbon mixtures examined, the mean deviation of predicted surface tensions from experimental data is within 2%, while alcohol systems show a much greater disparity.

DISCUSSION

Given the complex nature of the molecules studied and the reliance on pure component data alone, the agreement of the surface tensions predicted by the geometric mixing rule with experimental data is excellent. A possible explanation of this rule is demonstrated herein by a Lennard-Jones model of the parameter. Although this simple model assumes a structureless system of spherical molecules, its prediction of a volume-ratio-dependent parameter does appear to be borne out. The hydrocarbon systems studied were composed of similarly sized molecules and showed the best agreement between predicted and experimental tensions; conversely, alcohol molecules showed a greater disparity in size and a corresponding decrease in the quality of predicted tensions. In all cases, the mixing parameter appeared to be greater than or equal to unity, as predicted by Equation (29).

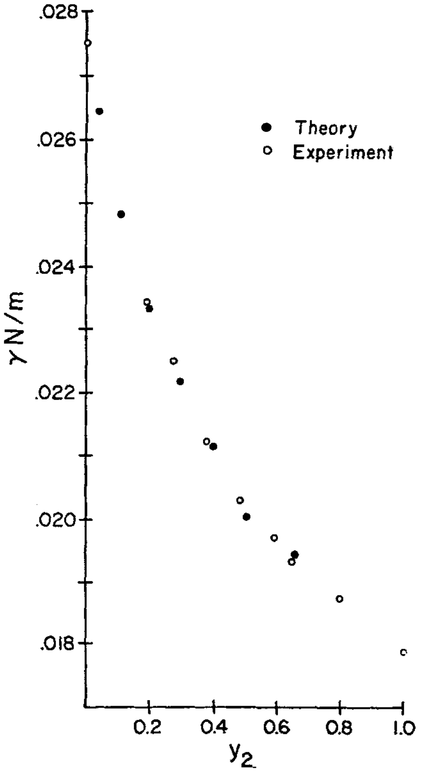

Figure 8. Surface tensions for mixtures of benzene (1) and iso-octane (2) at 303°K for $\beta = 1$.

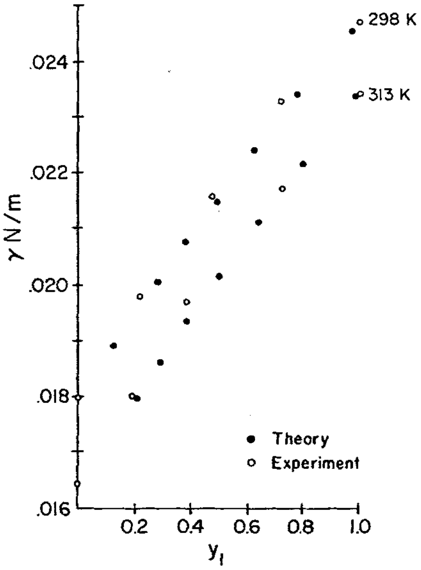

Figure 10. Surface tensions for mixtures of *n*-dodecane (1) and *n*-hexane (2) at 298°K and 313°K for $\beta = 1$.

The poor results obtained for alcohol systems could arise from a number of factors. The Peng-Robinson equation of state is perhaps the problem. Although the equation of state predicts accurately the bulk properties of the nonpolar hydrocarbons considered here and of the butyl alcohols, it does not quantitatively describe the bulk properties of methanol. An attempt was made to improve both bulk and interfacial predictions by fitting the δ_{12} parameter to experimental data for the methanol-butanol system (Chu et al., 1956). The change showed only minimal improvement in tension predictions. Because of numerical difficulty (which we are presently trying to overcome), β values only slightly greater than unity could not be used. From the

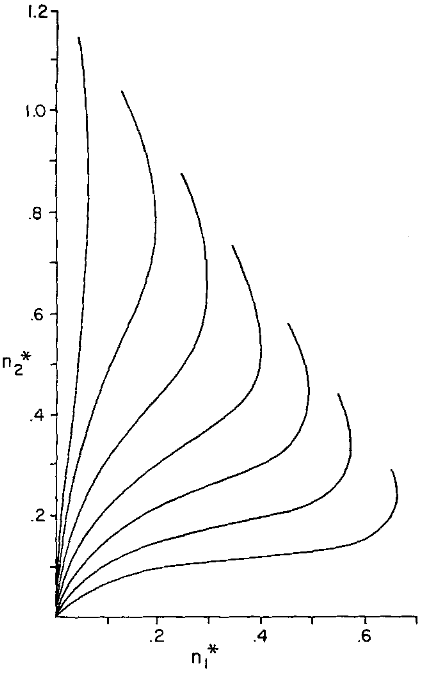

Figure 11. Phase plane solutions for iso-octane (1)- cyclohexane (2) at 303°K for several liquid compositions. $\beta = 1$.

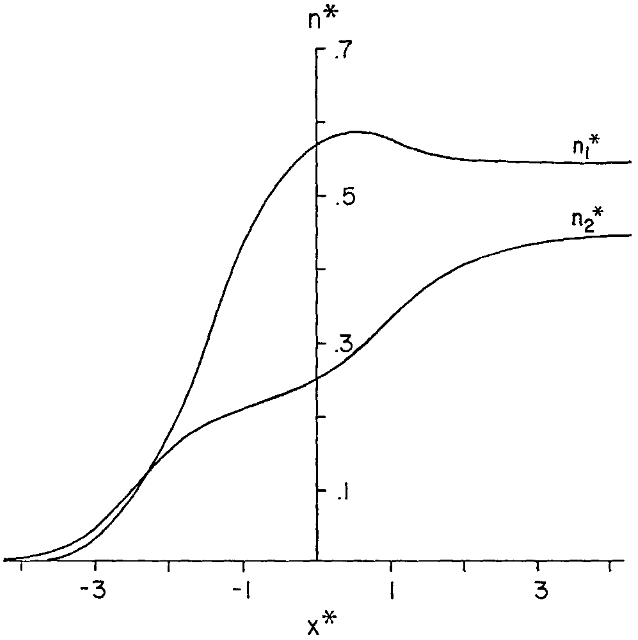

Figure 12. Density profiles for iso-octane (1)- cyclohexane (2) at 303°K for $\beta = 1$.

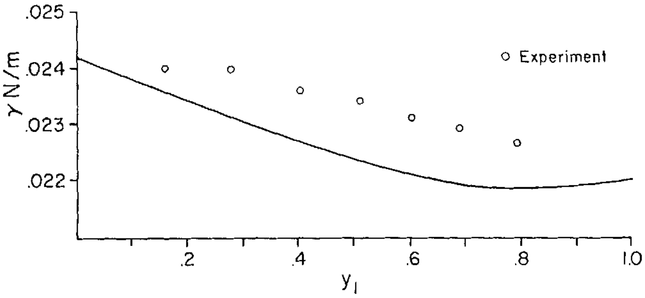

Figure 13. Surface tensions for mixtures of *n*-butanol (1) and methanol (2) at 298°K for $\beta = 1$.

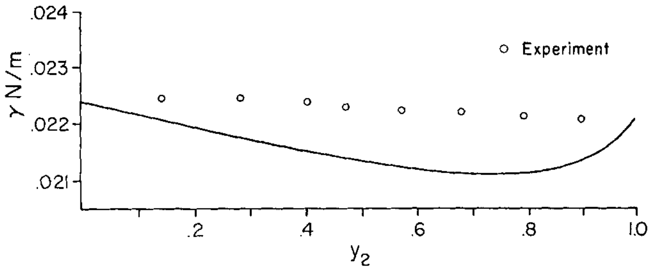

Figure 14. Surface tensions for tert-butanol (1) and methanol (2) at 298°K for $\beta = 1$.

trend shown in Figure 2, it is reasonable to expect such values of β to lead to better predictions. It is also possible that a dipole induced surface voltage occurs at polar interfaces and affects the tension. This effect can be included in the basic equations of the theory, but we have not investigated the matter at this point.

The value of the theory developed here lies only partly in its ability to predict tensions of planar interfaces. Empirical correlations may well serve this purpose. However, the detailed molecular structure of the interface zone provided by the present theory cannot be obtained from empirical correlations. Thus, the theory is important as a basis for understanding surface activity, the molecular compositions of interfacial zones, the mechanisms of low tensions, the relationship between homogeneous fluid equations of state and inhomogeneous fluid properties. Moreover, the theory is not restricted to planar interfaces. With appropriate choice of geometry and boundary conditions, it can be applied to the study of other fluid microstructures such as thin films, drops, bubbles, micelles, microemulsions and liquid crystals. Such applications will form the basis of future publications.

TABLE 2. AVERAGE AND MAXIMUM ERRORS IN PREDICTED SURFACE TENSIONS

	T(°K)	γ_1^0(N/m)	γ_2^0(N/m)	$\bar{\Delta}$	$\Delta_{\max}$
Cyclopentane-carbon tetrachloride	298	0.02185	0.02613	0.00	0.00
Cyclopentane-tetrachloroethylene	298	0.02185	0.03130	0.01	0.01
Cyclopentane-benzene	298	0.02185	0.02820	0.02	0.02
Cyclopentane-toluene	298	0.02185	0.02794	0.01	0.01
Cyclohexane-benzene	293	0.02438	0.02886	0.01	0.02
Cyclohexane-(cis)decalin	298	0.02438	0.03224	0.00	0.01
Cyclohexane-(trans)decalin	298	0.02438	0.02997	0.01	0.01
Cyclohexane-toluene	298	0.02438	0.02794	0.02	0.02
Cyclohexane-(*n*)hexadecane	298	0.02438	0.01980	0.00	0.01
Iso-octane-cyclohexane	303	0.01789	0.02377	0.00	0.00
Iso-octane-dodecane	303	0.01789	0.02447	0.01	0.07
Iso-octane-benzene	303	0.01789	0.02753	0.01	0.02
(*n*)hexane-(*n*)dodecane	298	0.01794	0.02469	0.00	0.00
(*n*)hexane-(*n*)dodecane	313	0.01638	0.02342	0.01	0.01
Methanol-(*n*)butanol	298	0.02210	0.02418	0.04	0.05
Methanol-(*t*)butanol	298	0.02210	0.02011	0.07	0.12

NOTATION

a = Peng-Robinson energy parameter
b = Peng-Robinson volume parameter
c = interfacial influence parameter
C = direct correlation function
f = Helmholtz free energy density
g = pair correlation function
k = Boltzmann's constant
n = number density
P = pressure
T = temperature
u = intermolecular potential
x = distance
y = mole fraction of species

Greek Letters

β = influence parameter scaling parameter
γ = surface tension
δ = adjustable energy parameter
∇ = gradient operator
ϵ = Lennard-Jones energy parameter
μ = chemical potential
σ = Lennard-Jones length parameter
ω = grand thermodynamic potential

Superscripts

0 = homogeneous fluid
$+$ = ideal fluid
$*$ = dimensionless
I, II = bulk phases

Subscript

m = mixture

LITERATURE CITED

Benson, G. C., and V. T. Lam, "Surface Tensions of Binary Liquid Systems II. Mixtures of Alcohols," *J. Col. Int. Sci.*, **38**, 294 (1972).
Bongiorno, V., L. E. Scriven and H. T. Davis, "Molecular Theory of Fluid Interfaces," *ibid.*, **57**, 462 (1976).
Carey, B. S., L. E. Scriven and H. T. Davis, "Semi-Empirical Surface Tensions of Pure Normal Alkanes and Alcohols," *AIChE J.*, **24**, 1076 (1978).
Carey, B. S., "Molecular Thermodynamics of Multicomponent Interfaces," Ph.D. thesis, Univ. Minn., Minneapolis (1978).
Chu, J. C., S. L. Wang, S. L. Levy and R. Paul, *Vapor-Liquid Equilibrium Data*, J. W. Edwards, Ann Arbor, Mich. (1956).
Lam, V. T., and G. C. Benson, "Surface Tensions of Binary Liquid Systems. I. Mixtures of Non-electrolytes," *Can. J. Chem.*, **48**, 3774 (1970).
McCoy, B. F., and H. T. Davis, "On the Free Energy Theory of Inhomogeneous Fluids," *Phys. Rev.*, **A20**, 1201 (1978).
Peng, D. Y., and D. B. Robinson, "A New Two Constant Equation of State," *Ind. Eng. Chem. Fundamentals*, **15**, 59 (1976).
Vargas, A., Ph.D. thesis, "On the Molecular Theory of Dense Fluids and Fluid Interfaces," Univ. Minn., Minneapolis (1976).

Manuscript received August 30, 1978; revision received January 18 and accepted January 23, 1980.

Mass Transfer and Adsorption in Liquid Full and Trickle Beds

Experimental breakthrough curves were determined for a liquid full and a trickle bed reactor in which benzene was adsorbed from water on small activated carbon particles at 298°K and 1 atm. The step function of benzene was introduced into the water feed and the response measured in the liquid effluent. Benzene transfer also occurred from the liquid feed to the gaseous feed of pure helium.

Moment analysis of data for liquid full conditions indicated that the first moment of the response curve could be used to obtain the adsorption equilibrium constant *K* for benzene on activated carbon. Comparison of results obtained by this new method with the *K* value determined from static equilibrium runs demonstrated the validity of the moment theory.

Analysis of the response curves for trickle bed operation showed that the liquid-to-gas mass transfer coefficient $(ka)_L$ could be evaluated from either the zero or first moment. Results were obtained in both the trickling flow and pulse flow regimes. Values of $(ka)_L$ in the pulse flow regime, which were not heretofore available, were sharply higher than those for trickle flow.

HASSAN A. SEIRAFI
and
J. M. SMITH
University of California
Davis, California 95616

SCOPE

Mass transfer between gas and liquid and also between liquid and catalyst particles can significantly affect the performance of trickle bed reactors (Satterfield, 1978; Goto and Smith, 1975). Steady state methods have been used to obtain transport coefficients in the trickling flow (gas continuous) and pulsing flow regimes by steady state studies. These experiments have been carried out by two methods: in the absence of reaction by dissolution of solids which were unlike porous catalyst particles, or under catalytic reaction conditions where reaction effects have to be accounted for before mass transfer effects are evaluated.

One objective of our research was to use breakthrough curve (BTC) data to evaluate the gas-liquid mass transfer coefficient $(ka)_L$. Also, we wanted to carry out the experiments under conditions of rapid physical adsorption. Then equilibrium could be assumed at an intraparticle adsorption site, avoiding the complications of finite reaction rate and possible variations in catalyst activity, etc. The procedure was to measure breakthrough curves in the liquid effluent when a step function of

---

Hassan A. Seirafi is on leave from Abadan Institute of Technology, Abadan, Iran.

0001-1541-80-3778-0711-$00.95.