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Semiempirical Theory of Surface Tensions of Pure Normal Alkanes and Alcohols

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A comparison of experimental and theoretical surface tensions leads to a correlation between homogeneous fluid parameters and the inhomogeneous influence parameter *c*. From this correlation, it is possible to predict, to within excellent agreement with experiment, the surface tensions of normal alkanes and alcohols from bulk data only.

SCOPE

The Peng-Robinson equation of state is combined with the mean field theory of inhomogeneous systems to describe both interfacial density profiles and dimensionless surface tensions for normal alkane and alcohol systems. The influence parameter *c* of inhomogeneous fluids is determined from a comparison of experimental and theoretical surface tensions. The parameter is then correlated with homogeneous fluid parameters through a simple relationship having some theoretical meaning and is used to predict the surface tensions of the compounds studied.

CONCLUSIONS AND SIGNIFICANCE

An accurate method of calculating the surface tension of normal alkanes and alcohols has been developed. The calculation is based on the mean field theory for which an equation of state of a homogeneous fluid and values of the influence parameter are required. For the Peng-Robinson equation of state, surface tensions may be computed from the generalized curve for γ^* with the aid of

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the correlations relating the influence parameter c to the parameters a and b of homogeneous fluid. The major finding here is that it is possible to determine the strictly interfacial parameter c from bulk phase properties. We believe that the semiempirical approach herein developed will be fruitful for much broader classes of compounds than those considered.

Recent advances (Toxvaerd, 1971; Salter and Davis, 1973; Bongiorno and Davis, 1975; Bongiorno et al., 1976) in the molecular theory of fluids have made it possible to qualitatively describe the surface tension of simple fluids composed of classical, monatomic, pair interacting particles. As described by Bongiorno et al. (1976), the inputs of the theory are the interaction potential and the fluid structure function (pair correlation function or direct correlation function). In general, such inputs are not available for polyatomic fluids, even for computing the thermodynamic properties of homogeneous phases. However, for practical modeling of such properties, the semiempirical approach has been especially potent. The spirit of this approach is to use expressions for the thermodynamic functions that have some theoretical basis and that contain parameters to be fit to data for given compounds or classes of compounds. Recent examples of this approach are the UNIQUAC model of Abrams and Prausnitz (1975), the group assignment model of Wilson (1977), the much modified Redlich-Kwong equation of state (Horvath, 1974), and the equation of state developed by Peng and Robinson (1976).

The purpose of this present article is to combine the results of the mean field theory of fluid interfaces with the semiempirical approach to thermodynamic modeling in order to generate useful algorithms for computing surface tensions of polyatomic fluids. In a companion paper to follow the present one, the approach is extended to two-component liquid-vapor and liquid-liquid interfaces, with the aim of developing mixing rules for the interfacial parameters used in computing the interfacial properties of multicomponent, polyatomic systems. Our overall program is to bring the state of the art of predicting interfacial properties up to the level currently achieved for the thermodynamic properties of homogeneous fluids.

GENERAL FEATURES OF THE MODEL

Although the interfacial theory can be exploited with any equation of state, we shall concentrate on the Peng-Robinson equation. This equation, which has been quite successful for a wide variety of fluids, is given by

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

where $a(T)$ and b are molecular interaction and excluded volume parameters that are determined from critical data and the acentric factor. The prescription for determining $a(T)$ and b is detailed below.

Using thermodynamic relations, we can determine the Helmholtz free energy density f_o and the chemical potential μ_o corresponding to Equation (1). These are

$$f_o = f^+(T) - nkT \ln\left(\frac{1}{n} - b\right) - \frac{na}{2\sqrt{2}b} \ln\left\{\frac{1+nb(1+\sqrt{2})}{1+nb(1-\sqrt{2})}\right\} \tag{2}$$

$$\mu_o = \mu^+(T) - kT \ln\left(\frac{1}{n} - b\right) + \frac{nkTb}{1-nb} - \frac{a}{2\sqrt{2}b} \ln\left\{\frac{1+nb(1+\sqrt{2})}{1+nb(1-\sqrt{2})} - \frac{na}{1+2nb} - (nb)^2\right\} \tag{3}$$

where $f^+(T)$ and $\mu^+(T)$ are ideal gas contributions that are functions only of temperature. These quantities cancel out of all of the computations reported herein. The subscripts of f_o and μ_o are to emphasize that these quantities refer to the homogeneous fluid.

According to the mean field theory detailed elsewhere (Bongiorno et al., 1976), the density of inhomogeneous fluid at equilibrium is determined by

$$c\nabla^2 n + \frac{\partial c}{\partial n} \nabla n \cdot \nabla n = \frac{\partial \omega}{\partial n} \tag{4}$$

where

$$c \equiv \frac{kT}{6} \int s^2 G(s;n)\, d^3s \tag{5}$$

and

$$\omega = f_o(n) - n\mu \tag{6}$$

The importance of the influence parameter $c(n)$ cannot be understated, for it essentially determines the density gradient response to the local deviation in chemical potential from its bulk phase value. Unfortunately, since its calculation requires the direct correlation function, it can be exactly determined for only a few simple systems. In a structureless system, it is clear that the parameter will become a constant. If it is assumed that c is a negligibly weak function of density, and if attention is focused on planar interfaces only, then the following differential equation governs the density profile $n(x)$ across an interface:

$$c \frac{d^2 n}{dx^2} = \frac{\partial \omega}{\partial n} \tag{7}$$

$$\begin{aligned} n &\to n_l \quad x \to \infty \\ n &\to n_g \quad x \to -\infty \end{aligned} \tag{8}$$

For a given temperature, n_g and n_l, the bulk vapor and liquid densities, respectively, are determined from the equilibrium conditions $\mu_o(n_l) = \mu_o(n_g) = \mu$ and $P_o(n_l) = P_o(n_g)$. These conditions are equivalent to the specified boundary conditions.

The surface tension predicted by Equation (4) is

$$\gamma = \int_{-\infty}^{\infty} c \left(\frac{dn}{dx}\right)^2 dx \tag{9}$$

or, equivalently

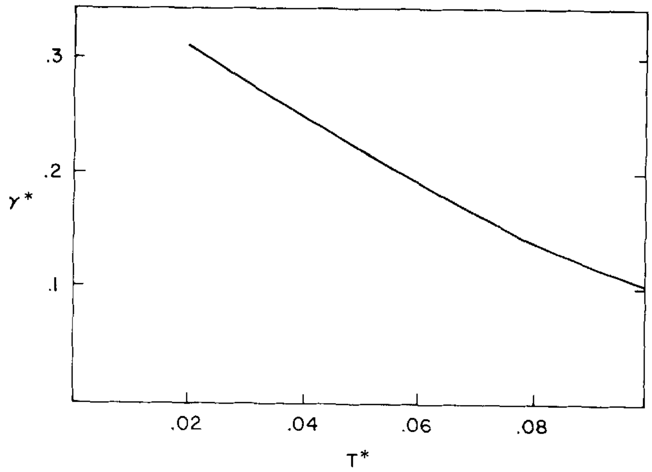

Fig. 1. Dimensionless surface tension versus dimensionless temperature.

$$\gamma = \sqrt{2}\int_{n_g}^{n_l} \sqrt{c[\omega(n) - \omega_B]}\, dn \qquad (10)$$

where $\omega_B = \omega(n_l) = \omega(n_g)$.

A LAW OF CORRESPONDING STATES

Let us define the following reduced variables:

$$n^* = nb, \quad T^* = \frac{bkT}{a}, \quad \gamma^* = \frac{\gamma b^2}{\sqrt{ac}},$$

$$\omega^* = \frac{b^2\omega}{a}, \quad x^* = \left(\frac{a}{c}\right)^{1/2} x \qquad (11)$$

In terms of those variables, Equation (7) becomes

$$\frac{d^2n^*}{dx^*} = \frac{\partial\omega^*}{\partial n^*} \qquad (12)$$

where $n^* \to n_g^*, n_l^*$ as $x^* \to \pm\infty$. Multiplying this expression by dn^*/dx and integrating twice, we find

$$x^* - x_o^* = -\frac{1}{\sqrt{2}}\int_{n_o^*}^{n^*(x^*)} \frac{dn^*}{\sqrt{\omega^*(n^*) - \omega^*(n_l^*)}} \qquad (13)$$

Similarly, Equation (10) becomes

$$\gamma^* = \sqrt{2}\int_{n_g^*}^{n_l^*} \sqrt{\omega^*(n^*) - \omega^*(n_l^*)}\, dn^* \qquad (14)$$

For the Peng-Robinson model, n_l^* and n_g^* are functions only of T^*, and ω^* is a function only of n^* and T^*. Therefore, γ^* is a function only of T^*. The predicted γ^* vs. T^* curve predicted by the Peng-Robinson model is shown in Figure 1. Unfortunately, this relationship cannot be used directly in computation of surface tensions. This is because the reduction of γ to γ^* involves the quantity c, which is not determined by the equation of state. In the next sections, we shall discuss empirical methods of obtaining c.

Before going to the next section, let us outline the Peng-Robinson procedure for determining the parameters $a(T)$ and b. As with any two-parameter equation of state, the two constants $a(T_c)$ and b can be located by setting $(\partial P/\partial V)_T = 0$ and $(\partial^2P/\partial V^2)_T = 0$ along the critical isotherm. The temperature dependence of $a(T)$ is then determined by curve fitting data for several compounds at several reduced temperatures ($T_R = T/T_c$). The specific equations given by Peng and Robinson (1976) are as follows:

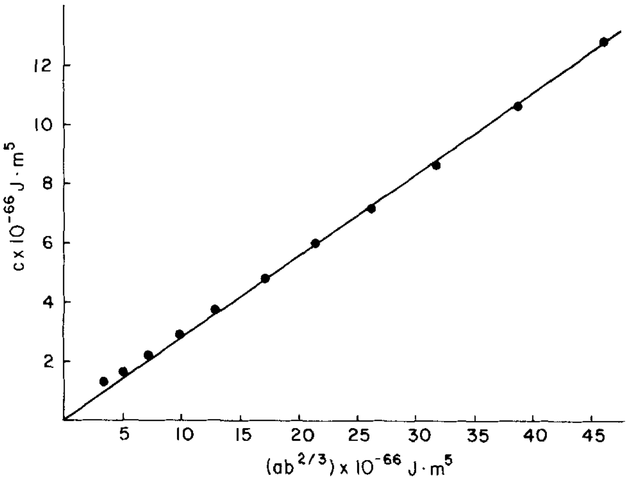

Fig. 2. Correlation between the influence parameter c and the dimensional group (ab$^{2/3}$) for several alkanes (c-6 through c-16) at 293°K.

$$b = 0.07780\,\frac{RT_c}{P_c} \quad a(T) = a(T_c)\cdot\alpha(T_R, \omega) \qquad (15)$$

where

$$a(T_c) = 0.45724\,\frac{R^2T_c^2}{P_c}, \; \alpha^{1/2}(T_R, \omega) = 1 + K(1 - T_R^{1/2})$$

$$K = 0.37464 + 1.54226\,\omega_a - 0.26992\,\omega_a^2 \qquad (16)$$

ALKANES

Consider the oversimplified case that the potential of interaction between the molecules of a fluid is pairwise additive and of the form $\epsilon\phi(s/\sigma)$. For such a fluid, the ratio $c/ab^{2/3}$ is a function only of kT/ϵ and $n\sigma^3$. Thus, for all such fluids, the value of $c/ab^{2/3}$ will be the same function of these dimensionless groups. For the original Van der Waals model (Bongiorno and Davis, 1975), for which the form of c differs (Bongiorno et al., 1976)

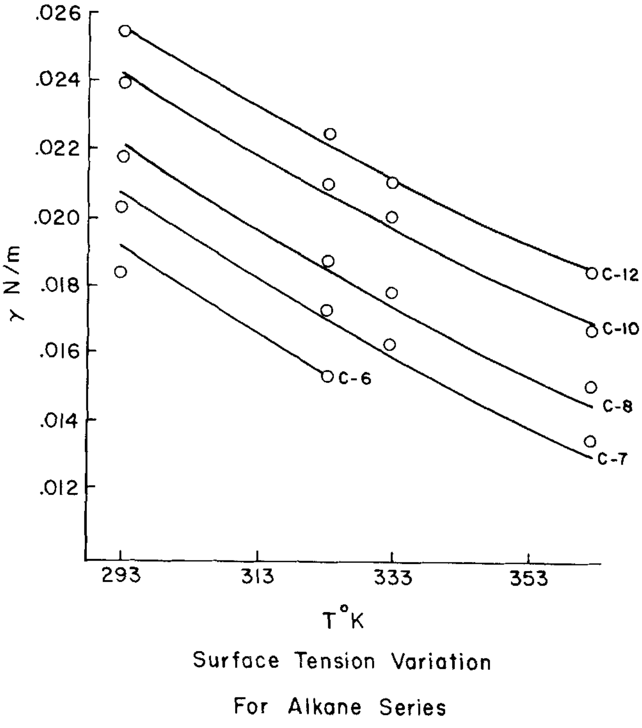

Fig. 3. Surface tension vs. temperature for several alkanes. Solid curves denote predicted values and open circles experiment.

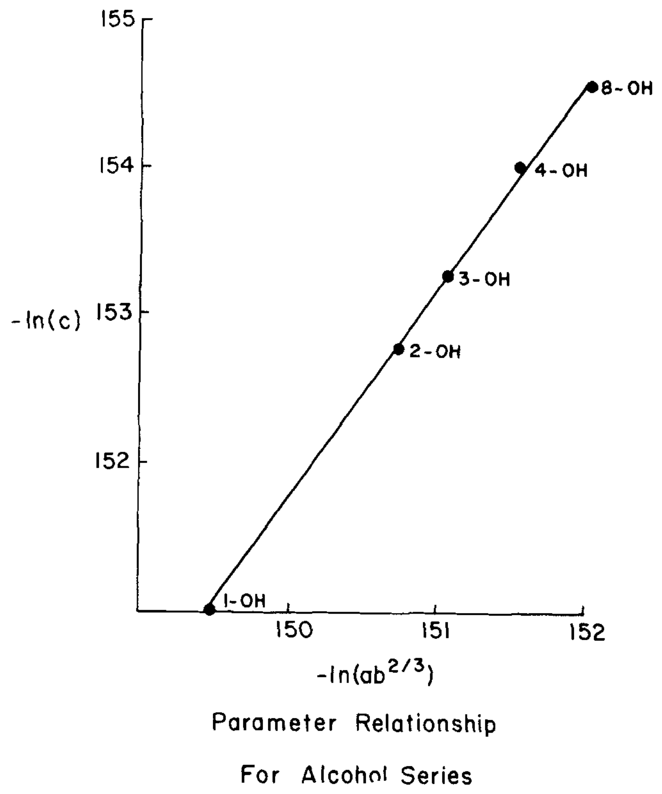

Fig. 4. Correlation between the influence parameter c and the dimensional group ($ab^{2/3}$) for several alcohols at 293°K. Both c and ($ab^{2/3}$) are in units of $J \cdot m^5$.

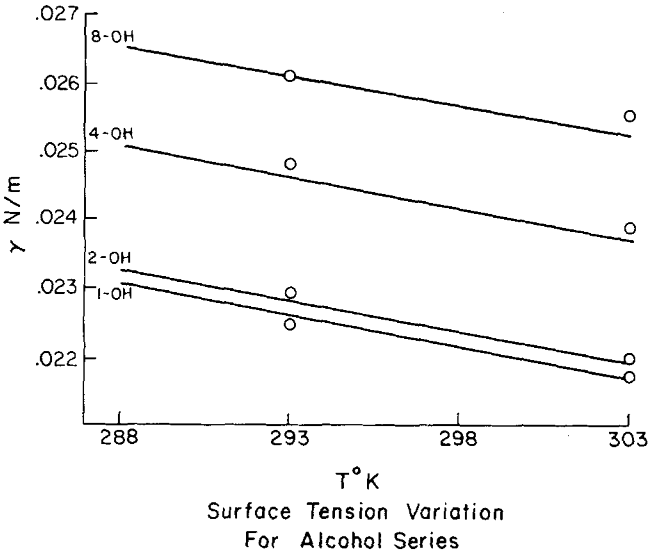

Fig. 5. Surface tension vs. temperature for several alcohols. Solid curves denote predicted values and open circles experiment.

from Equation (5), taking the pair correlation function to be a step function, we estimate

$$\frac{c}{ab^{2/3}} = \int_{s>\sigma} u(s) s^2 d^3 s / 3b^{2/3} \int_{s>\sigma} u(s) d^3 s \qquad (17)$$

If $u(s)$ is taken to be the 6-12 Lennard-Jones potential, and if the estimate (Reif, 1965) $b \approx 2/3\ \pi\sigma^3$ is used, Equation (17) yields the prediction $c/ab^{2/3} \simeq 0.78$. This result indicates that for nonpolar fluids, one may expect that $c/ab^{2/3}$ will be a slowly varying function of T^* and n^* (mainly of T^*, as c tends to be a weak function of n^* for nonpolar fluids of spherical molecules).

Surface tension data were located for eleven alkanes at 20°C and were used to determine c by the rearranged version of Equation (11):

TABLE 1

Alkane No. carbons	$c/ab^{2/3}$
6	0.34
7	0.32
8	0.31
9	0.30
10	0.29
11	0.28
12	0.28
13	0.27
14	0.27
15	0.28
16	0.28

$$c = \left(\frac{\gamma}{\gamma^*}\right)^2 \frac{b^4}{a} \qquad (18)$$

As seen in both Table 1 and Figure 2, c is not only linear with the group $ab^{2/3}$, but the ratio $c/ab^{2/3}$ is also of the same order of magnitude as that predicted by the van der Waals' estimate.

Our conclusion is that the Peng-Robinson parameters $a(T)$ and b, determined from homogeneous fluid properties, suffice for computation of the influence parameter c required for tension predictions for the normal alkanes.

Finally, the temperature variation of the surface tension was predicted from the relation

$$c = 0.27(ab^{2/3}) + 2.0 \times 10^{-67}\ J \cdot m^5$$

obtained as a best fit of the data displayed in Figure 2 for several alkanes over the temperature range 293° to 363°K. The results, compared with the experiment in Figure 3, are quite good, the worst error being about 0.7×10^{-4} N/m for n-hexane at 293°K.

ALCOHOLS

After a similar analysis was performed on a series of alcohols, it was found that the relationship between c and ($ab^{2/3}$) was nonlinear. However, as illustrated in Figure 4, c can be well represented by the relation

$$c = 2.5 \times (ab^{2/3}/J \cdot m^5)^{1.38}\ J \cdot m^5 \qquad (19)$$

The deviation from the Van der Waals theoretical curve perhaps results from the unsymmetric, polar character of the molecules. Using Equation (19), the surface tensions for several alcohols were computed, with the results shown in Figure 5. Agreement between experiment and prediction is as good as it was for the alkane systems.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation and the Computer Center of the University of Minnesota for financial support of the research reported herein.

NOTATION

a = Peng-Robinson energy parameter
b = Peng-Robinson volume parameter
c = influence parameter for inhomogeneous systems
f = local Helmholtz free energy density
$f_0(n)$ = Helmholtz free energy density of homogeneous fluid at density n
$G(s;n)$ = direct correlation function of a pair of molecules in homogeneous fluid of density n.
k = Boltzmann's constant

n = number density
P = pressure
$P_o(n)$ = pressure of homogeneous fluid at density n
R = gas constant
T = temperature
u = intermolecule potential
V = volume
x = distance

Greek Letters

α = Peng-Robinson parameter
∇ = gradient operator
γ = surface tensions
ϵ = energy parameter
ω = grand thermodynamic potential
ω_a = accentric factor
σ = length parameter
μ = chemical potential

Superscripts and Subscripts

B = bulk
C = critical
g = gas
l = liquid
R = reduced
$+$ = density independent
o = homogeneous fluid property
$*$ = dimensionless

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Time Resolution of Rapid Processes Using Numerical Calculation and Inversion of Laplace Transforms

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A method for the interpretation of data which results from a signal altered by a process of known weighting function was developed. The method is based on the numerical evaluation and inversion of the Laplace transform. For two different weighting functions, it is shown how narrow a signal can be interpreted accurately. The method is then applied to coal volatilization data.

SCOPE

In many chemical engineering problems, a rapid process can be experimentally followed by a detector, only after some (known) distortion of the signal has occurred. The effect of the distortion is to retard and broaden the time span measured, thus allowing for a finite detector response. This paper is concerned with numerical procedures that allow recovery of a signal (input) which has been distorted by a process with a known transfer function and where the

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