Estimation of Surface Tension of Pure Fluids Using the Gradient Theory

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The modified van der Waals theory of interfaces (gradient theory) is used with the equations of state of Peng-Robinson and Mohanty-Davis to predict surface tensions of various nonpolar, quadrupolar, slightly polar and polar substances as a function of temperature. The influence parameter of the gradient theory is estimated as $0.785ab^{2/3}$ *in terms of the attractive and repulsive van der Waals parameters using the Lennard-Jones potential. The predictions made with the Mohanty-Davis equation of state agree better with experimental data than those made with Peng-Robinson, even for nonpolar fluids.*

Introduction

Surface tension of pure fluids and their mixtures is important for many processes and phenomena (Davis and Scriven, 1981). However, experimental data, particularly for mixtures, are scarce (Jasper, 1972). The need for simple and accurate models for predicting interfacial properties is clear. Several theories have been forwarded in recent years which allow the calculation of the surface tension of simple fluids composed of classical, monoatomic, pair interacting particles (Toxvaerd, 1971; Davis, 1975; Bongiorno and Davis, 1975; Bongiorno et al., 1976; Yang et al., 1976; Davis and Scriven, 1981).

The gradient theory of interfaces has been successfully used for estimating interfacial properties of pure fluids and their mixtures because it yields a single parameter, the influence parameter, which carries the information on the molecular structure of the interface and essentially determines the density gradient response to the local deviation of the chemical potential from its bulk phase value (Bongiorno et al., 1976; Lee et al., 1974). This parameter together with a homogeneous fluid equation of state characterizes inhomogeneous fluids such as liquid-vapor interfaces (Bongiorno et al., 1976). Using the Peng-Robinson equation of state and an influence parameter determined from bulk phases properties, Carey et al. (1978, 1980) predicted surface tensions of hydrocarbons, alcohols and of binary mixtures rather well. Guerrero and Davis (1980) calculated the surface tension of water with the equation of Fuller (1976). More recently, Pérez-López et al. (1991) investigated the effects of molecular shape and multipolarity on interfacial density profiles and dimensionless surface tensions of simple fluids using an equation of state developed by Mohanty and Davis (1979). This equation of state contains, in addition to the attractive and repulsive van der Waals parameters, two other parameters to account for molecular shape and polarity. The gradient theory of inhomogeneous fluids has also been extended to take into account orientational ordering at interfaces (Sweeney, 1987). For simple fluids, however, orientational ordering at interfaces appears to have a weak effect (Chapela et al., 1977; Gubbins and Thompson, 1982; Sweeney, 1987).

In this paper we calculate the surface tension of several nonpolar, quadrupolar and polar fluids as a function of temperature using the gradient theory and the Peng-Robinson (PR) or the Mohanty-Davis (MD) equation of state. Our predictions are compared with experimental data. Surface tensions predicted with MD agree better with experimental data than those calculated with PR, even for nonpolar fluids.

General Features of the Model

According to the gradient theory of inhomogeneous fluids detailed elsewhere (Bongiorno and Davis, 1975; Bongiorno et al., 1976), the differential equation that governs the density profile, $n(x)$, across a planar interface was derived assuming that the influence parameter c is a negligible weak function of the density profile. Quintana (1990) demonstrated using the mean spherical approximation that c is practically independent of density in the two-phase region. The differential equation is:

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$$c\frac{d^2n}{dx^2}=\frac{\partial\Omega}{\partial n} \tag{1}$$

$$n\rightarrow n_l \ @ \ x\rightarrow\infty$$

$$n\rightarrow n_g \ @ \ x\rightarrow-\infty$$

where $\Omega(=f_o-n\mu)$ is the thermodynamic potential, f_o the Helmholtz free energy density of the homogeneous fluid, and μ the chemical potential. For a given temperature, n_g and n_l, the bulk vapor and liquid densities, respectively, are determined from the equilibrium conditions, $\mu_o(n_g)=\mu_o(n_l)$ and $P_o(n_g)=P_o(n_l)$, where P_o is the pressure of the homogeneous fluid at density n.

The surface tension predicted by Eq. 1 is

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

or, equivalently

$$\gamma=\sqrt{2}\int_{n_g}^{n_l}\sqrt{c[\Omega(n)-\Omega_B]}dn \tag{3}$$

where $\Omega_B=\Omega(n_g)=\Omega(n_l)$ due to hydrostatic equilibrium (Bongiorno and Davis, 1976).

Let us define the following reduced variables:

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

$$T^*=\frac{bkT}{a},\ P^*=\frac{Pb^2}{a},\ \Theta=\frac{s\overline{R}}{b} \tag{4}$$

Here a and b (see below) are the molecular interaction and the excluded volume parameters of the equation of state, respectively.

In terms of these variables, Eq. 3 becomes

$$\gamma^*=\int_{n_g^*}^{n_l^*}[2(\Omega^*-\Omega_B^*)]^{1/2}dn^* \tag{5}$$

Hence calculations of the dimensionless surface tension, γ^*, require of experimental data on the thermodynamic potential or an equation of state of homogeneous fluid. One successfully used equation of state is that of PR (1976), which has the following form

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

where n is the fluid number density, k is the Boltzmann's constant, T is the absolute temperature and $a(T)$ and b are the molecular interaction and the excluded volume parameters that are determined from critical data and acentric factor, ω, as follows:

$$a(T)=a(T_C)\alpha(T_R,\ \omega),\ b=0.0778\frac{RT_C}{P_C} \tag{7}$$

where

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

$$K=0.37464+1.54226\omega-0.26992\omega^2$$

$$T_R=T/T_C$$

With the reduced variables defined above (Eq. 4), the PR equation of state can be cast into the following dimensionless form:

$$P^*=\frac{n^*T^*}{1-n^*}-\frac{n^{*2}}{1+n^*[2-n^*]} \tag{8}$$

The MD equation of state is given by (Mohanty and Davis, 1979):

$$\frac{P}{nkT}=\frac{1}{1-nb}+\frac{s\overline{R}n}{(1-nb)^2}+\frac{(s\overline{R}n)^2}{3(1-nb)^3}-\frac{na}{kT}\left[1+\frac{\lambda a}{bkT}\right] \tag{9}$$

where λ is a parameter that accounts for multipolar force contributions and for the temperature dependence of the traditional van der Waals a (which arises from the temperature dependence of the pair correlation function). The parameters $\overline{R}$ and s are the average radius of curvature and the surface area of a convex particle and b is the volume of a convex particle and the volume parameter in the equation of state. With the reduced variables defined in Eq. 4, the MD equation of state can be also cast into dimensionless form:

$$P^*=\frac{n^*T^*}{1-n^*}+\frac{n^{*2}T^*\Theta}{(1-n^*)^2}+\frac{n^{*3}T^*\Theta^2}{3(1-n^*)^3}-n^{*2}\left[1+\frac{\lambda}{T^*}\right] \tag{10}$$

The shape parameter Θ can be calculated using the following formulas (Mohanty and Davis, 1979):

(i) Spherocylinder:

$$\Theta=\frac{[4\pi(R/L)^2+2\pi(R/L)]\left[(R/L)+\frac{1}{4}\right]}{\frac{4}{3}\pi(R/L)^3+\pi(R/L)^2}$$

(ii) Regular tetrahedron:

$$\Theta=\frac{[4\pi(R/L)^2+12(\tan^{-1}\sqrt{2})(R/L)+\sqrt{3}][(R/L)+(6/4\pi)\tan^{-1}\sqrt{2}]}{(4\pi/3)(R/L)^3+6(\tan^{-1}\sqrt{2})(R/L)^2+\sqrt{3}(R/L)+(1/6\sqrt{2})}$$

(iii) Regular hexagon:

$$\Theta=\frac{[4\pi(R/L)^2+6\pi(R/L)+3\sqrt{3}][(R/L)+(3/4)]}{(4\pi/3)(R/L)^3+3\pi(R/L)^2+3\sqrt{3}(R/L)}$$

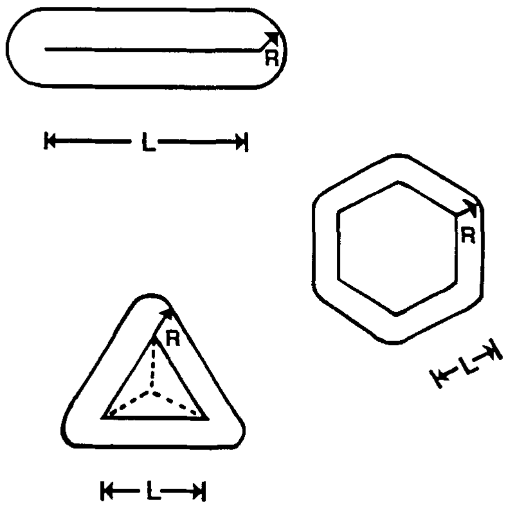

Figure 1. Convex parallel bodies obtained from spherocylindrical, tetrahedral and hexagonal cores.

where the convex bodies obtained from spherocylindrical, tetrahedral and hexagonal cores and the characteristics dimensions, R and L, are shown in Figure 1. For spheres, $\Theta=3$. The values of R and L can be obtained from molecular structure information (Kihara, 1953) or from second virial coefficient and critical point data (Danon and Pitzer, 1962; Mohanty and Davis, 1979). Using the later approach, and starting with Kihara's general expression for the second virial coefficient of convex molecules (Kihara, 1953), given by

$$B=\left(\frac{2\pi}{3}\right)\rho_o^3F_3(Z)+M_o\rho_o^2F_2(Z)+\left[S_o+\left(\frac{M_o^2}{4\pi}\right)\right]\rho_oF_1(Z)+\left[V_o+\left(\frac{M_oS_o}{4\pi}\right)\right]$$

Danon and Pitzer (1962), considering only first-order deviations, obtained the following equation for nonpolar molecules

$$B=\left(\frac{2\pi}{3}\right)\rho_o^3[F_3(Z)+xF_2(Z)]$$

In the equations above, M_o, S_o, V_o are the surface integral of the mean curvature, the surface area and the volume of the core, respectively, and the values of the functions $F_3(Z)$, $F_2(Z)$ and $F_1(Z)$ are tabulated by Kihara (1953). By inspection it is evident that $x=3M_o/2\pi\rho_o$.

Previously Pitzer (1955) proposed the following reduced equation for the second virial coefficient of nonpolar molecules, using the Boyle point as the reducing parameter,

$$\frac{B(T)}{V_B}=\left[\frac{B}{V_B}\right]_o+x\left[\frac{\partial}{\partial x}\left(\frac{B}{V_B}\right)\right]_{x=0}$$

where T_B and V_B are the Boyle temperature and the Boyle volume, respectively. Moreover, the two terms on the righthand side of the above equation are functions of the ratio T/T_B (Pitzer, 1955). The comparison of the empirical equations with those from Kihara's theory yields the relationship for nonpolar molecules

$$x=\frac{3M_o}{2\pi\rho_o}=7.0\omega+0.24$$

In a similar fashion, but using the results of Pople (1954) for second virial coefficients of molecules with simple directional fields, Danon and Pitzer (1962, Eq. 16a) arrived at the following approximate expression for molecules interacting by a Lennard-Jones potential with permanent dipole or quadrupole moment:

$$B(T)=\left(\frac{2\pi}{3}\right)\rho_o^3[F_3(Z)+xF_2(Z)-K_1s^2H_\zeta(Z)] \tag{11}$$

where $Z=U_o/kT$, U_o being the depth of the Lennard-Jones potential, ρ_o $(=2R)$ the minimum distance of approach of two convex molecules, and K_1 is equal to 1/24 for dipolar molecules and 7/320 for quadrupolar molecules. The values of $H_\zeta(Z)$ are reported by Pople (1954) with $\zeta=6$ for dipolar and $\zeta=10$ for quadrupolar molecules. In reduced form the above equation, referred to the Boyle point, can be written (Pitzer, 1962, Eq. 16b):

$$\frac{B(T)}{V_B}=\left[\frac{B}{V_B}\right]_o+x\left[\frac{\partial}{\partial x}\left(\frac{B}{V_B}\right)\right]_{x=0}+s^2\left[\frac{\partial}{\partial s}\left(\frac{B}{V_B}\right)\right]_o$$

In the above equation, all terms of the righthand side are functions of T/T_B. Again, by comparing Eq. 11 with experimental data on $B(T)$ and the Eq. given above, Danon and Pitzer (1962) were able to calculate U_o/k and ρ_o and to relate these quantities to the acentric factor and to molecular shape and interactions as follows:

$$x=\frac{3M_o}{2\pi\rho_o}=7.0\omega+0.24-3.2s^2 \tag{12}$$

where $s=(\theta/U_o\rho_o^5)$ for molecules with permanent quadrupoles, $s=\mu^2/\sqrt{8}\;U_o\rho_o^3$ for molecules with permanent dipole, and $s=0$ for nonpolar molecules.

Evidently, x is proportional to a linear dimension of the core. From geometry and the definition of x, we have obtained the following equations to estimate R/L for different molecular shapes in terms of x:

- *Spherocylinder*

$$\frac{R}{L}=\frac{3}{4(x-0.6\pi)} \tag{13}$$

- *Regular tetrahedron*

$$\frac{R}{L}=\frac{2.737\sin(\alpha/2)}{x} \tag{14}$$

- *Regular hexagon*

$$\frac{R}{L}=\frac{9}{4x} \tag{15}$$

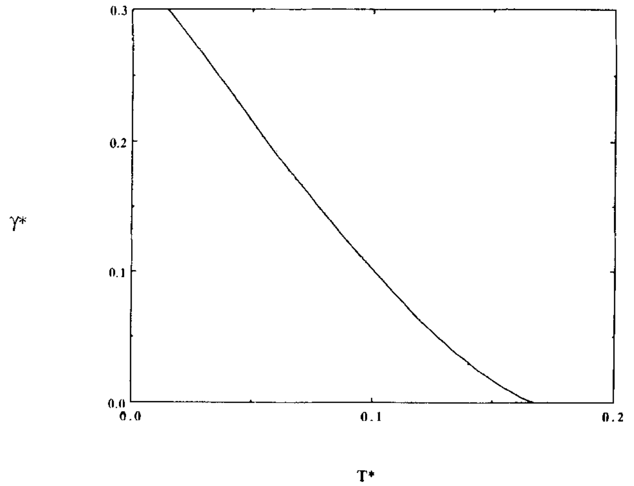

Figure 2. Dimensionless surface tension vs. dimensionless temperature as predicted by the Peng-Robinson equation of state.

Equations 13 to 15 and the formulas of Mohanty and Davis (1979) written above, allow the calculation of Θ for any nonpolar, quadrupolar or polar molecule with the shapes given. The polar parameter, λ, which is a function of the acentric factor (ω) and Θ, can be estimated as described elsewhere (see Figure 3 of Mohanty and Davis, 1979).

Results

In the PR equation of state, n_g^* and n_l^* are functions of T^* only (see Eq. 8) and Ω^* is a function of n^* and T^* only. Therefore γ^* is a unique function of T^* (Figure 2). However, in the MD equation of state, γ^* depends not only on T^*, but also on the molecular shape (Θ) and multipolar (λ) parameters. Figure 3 shows curves of γ^* vs. T^* for molecules with $\lambda = 0$ as a function of Θ where it can be seen that γ^* increases with Θ at constant temperature. Figure 4 reports curves of γ^* vs. T^* for spherical molecules ($\Theta = 3$) for different values of λ.

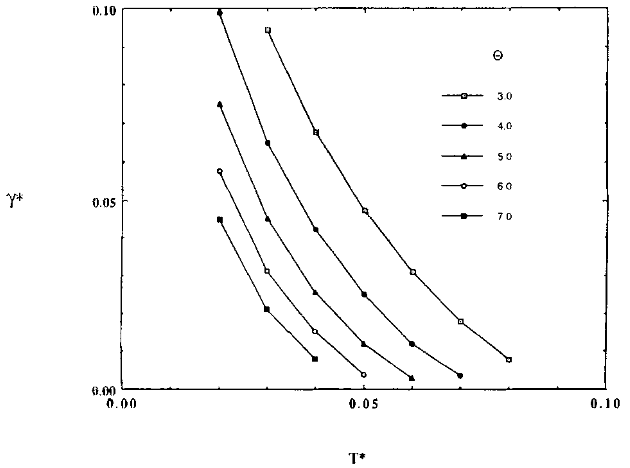

Figure 3. Dimensionless surface tension of nonpolar substances (λ = 0) vs. dimensionless temperature for different molecular shape parameter, Θ.

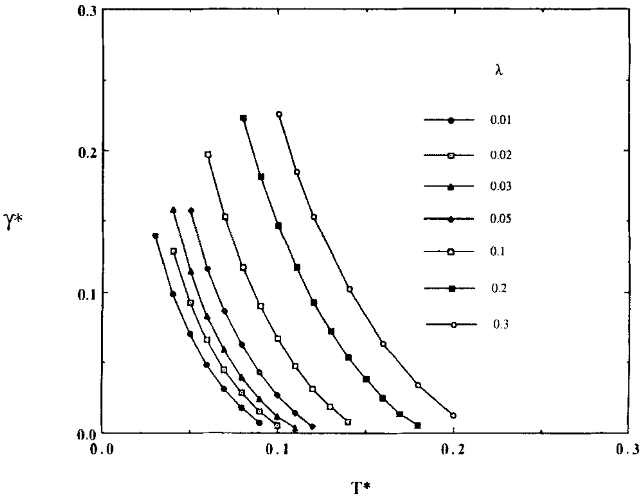

Figure 4. Dimensionless surface tension of spherical molecules (Θ = 3) vs. dimensionless temperature for different polar parameters, λ.

The dimensionless surface tension increases rapidly as λ increases, reflecting the importance of multipolar interactions on interfacial properties.

To compare experimental with predicted surface tensions, it is necessary to compute first the influence parameter. This is because the transformation of γ^* to γ involves the quantity c. The calculation of c is difficult because it requires the direct correlation function which is not readily available for polyatomic fluids. However, for the oversimplified case of molecules interacting via a pairwise additive potential of the form $U_o\phi(s/\rho_o)$, such as Lennard-Jones potential, the ratio $c/ab^{2/3}$ should be the same function of U_o/kT and $n\rho_o^3$. Taking the pair correlation function to be a step function, $u(s)$ as the Lennard-Jones potential, and if the volume parameter b is estimated as $(2/3)\pi\rho_o^3$ (Reif, 1965), then c can be approximated as (Carey et al., 1978):

$$\frac{c}{ab^{2/3}} = \frac{\int_{s>\rho_o} u(s)\, s^2 d^3s}{3\left(\frac{2\pi}{3}\rho_o\right)^{2/3}\int_{s>\rho_o} u(s)\, d^3s} = 0.785$$

Figure 5 reports predicted and experimental surface tensions as a function of temperature for several n-alkanes. The parameters U_o/k and ρ_o as well as the values of the shape and polar parameters for the different substances reported here are shown in Table 1. These parameters were estimated by comparing the theoretical expression of $B(T)$ as a function of log (kT/U_o) and comparing with experimental data of $B(T)$ for different values of ρ_o. The values reported in Table 1 are those that gave the best fit between experimental and theoretical values. In all cases the equation of Mohanty-Davis predicts experimental data better than Peng-Robinson at all temperatures. In general, the predictions of MD are quite good at all temperatures except for the lower molecular weight alkanes.

Experimental and predicted surface tensions as a function of temperature for nonpolar substances with different shapes (benzene and carbon tetrachloride) are presented in Figure 6.

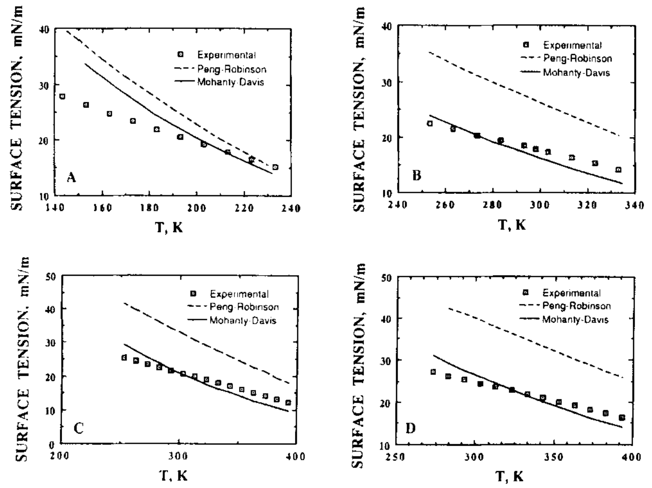

Figure 5. Surface tension as a function of temperature for nonpolar substance.

(A) n-propane, (B) n-hexane, (C) n-octane, and (D) n-dodecane.

Again, the values estimated with the MD equation of state match the experimental data more closely than the PR equation of state. In fact, the agreement is remarkably good for such a simple theory over the whole temperature range of liquid-vapor coexistence.

Experimental data and predictions made with PR and MD equations of state for CO_2 and N_2 are shown in Figure 7. These two molecules possess a quadrupole. Again, for N_2 the values estimated with MD agree better than the ones made with PR. However, for CO_2 the predictions with both equations of state depart significantly, although PR agrees better with experimental surface tensions at higher temperatures.

Experimental and predicted data for several polar molecules are shown in Figures 8 and 9. Cyclohexane and propylene are slightly polar whereas ammonia, fluorobenzene and methylacetylene have large dipole moments. In all cases, MD predicts better experimental data than PR at all temperatures.

Discussion and Conclusions

Although the gradient theory of interfaces can be exploited with any equation of state, here we use the well-known equation of state of Peng-Robinson (1976) and an equation developed by Mohanty and Davis (1979). The former equation was chosen because it predicts vapor-liquid equilibria (VLE) of nonpolar substances well. In addition the PR equation of state has been successfully used in combination with the gradient theory to calculate surface tensions of alkanes and alcohols (Carey et al., 1978) and of binary mixtures (Carey et al., 1980). The MD

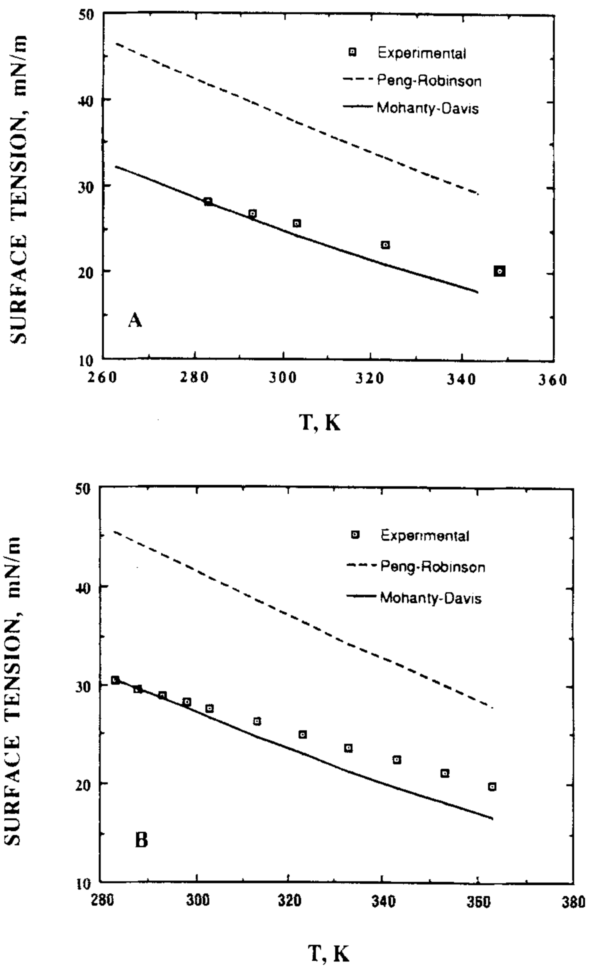

Figure 6. Surface tension as a function of temperature for nonpolar substances.

(A) carbon tetrachloride and (B) benzene.

Table 1. Values of ρ_o, U_o/k, of the Shape and Multipolar Parameters, and Energy of Vaporization Temperatures of the Substances

Substance	ρ_o, Å	U_o/k, K	R/L	Θ	λ	ΔE_{vap}, *k*cal/mol
n-Propane	4.00	411	0.6737	3.392	0.034	4,028
n-Hexane	6.43	390	0.3532	3.96	0.051	6,217
n-Octane	5.16	626	0.267	4.38	0.064	7,433
n-Dodecane	*	*	0.1882	5.12	0.092	9.457
Carbon Tetrachloride	8.33	306	1.4049	3.11	0.045	6,435
Carbon Dioxide	3.44	275	1.0424	3.201	0.052	3,713
Nitrogen	3.62	117	4.31	3.018	0.017	1,179
Benzene	3.00	490	1.3043	3.273	0.049	6,649
Propylene	4.24	356	0.6901	3.36	0.031	3,952
Ammonia	3.48	343	0.8964	3.216	0.059	5,105
Fluorobenzene	5.55	449	1.1639	3.324	0.057	
Methylacetylene	3.92	399	0.4781	3.639	0.041	4,793

* Experimental values of the second virial coefficient are not available.

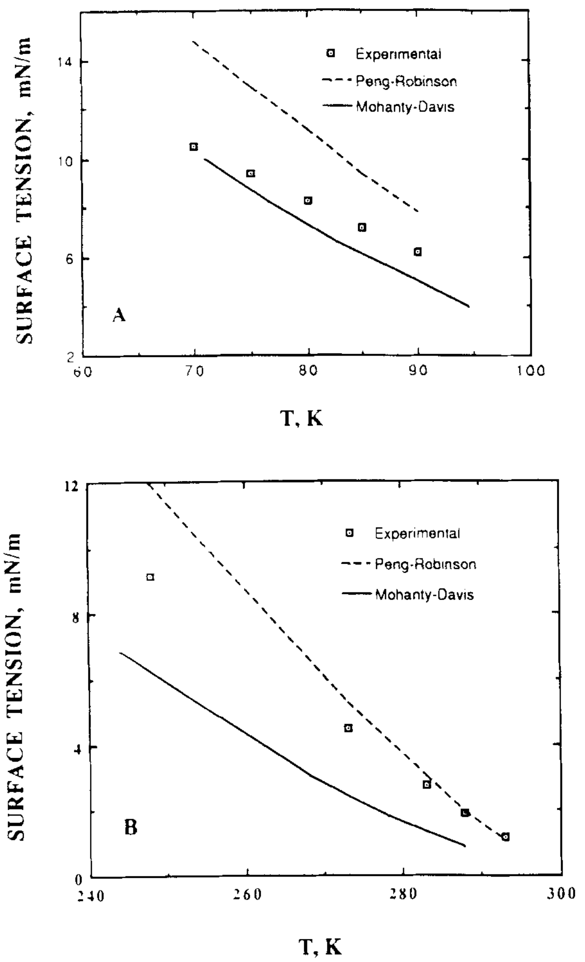

Figure 7. Surface tension as a function of temperature for quadrupolar substances.

(A) nitrogen and (B) carbon dioxide.

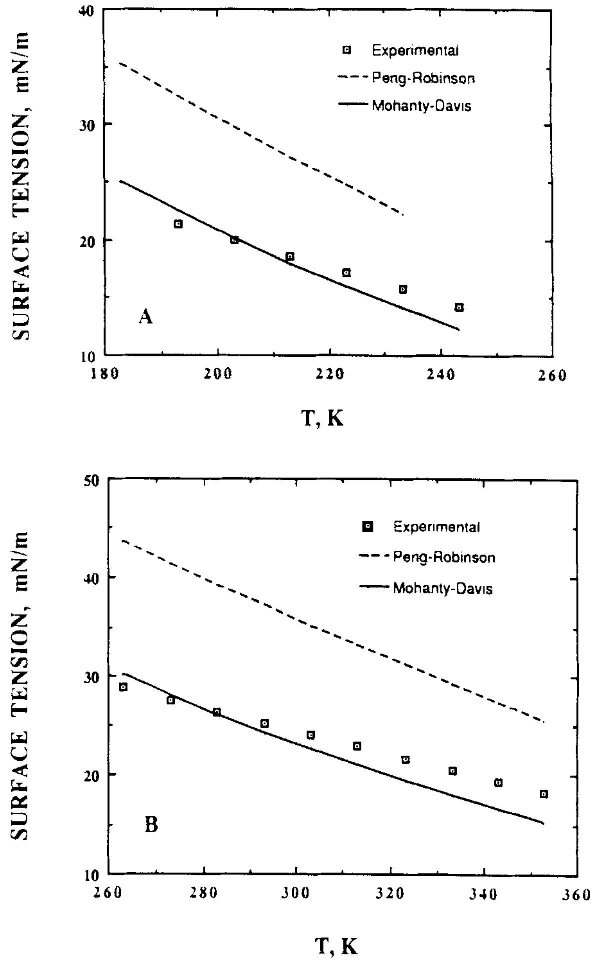

Figure 8. Surface tension as a function of temperature for slightly polar substances.

(A) propylene and (B) cyclohexane.

equation of state, on the other hand, has four parameters. Nevertheless, it has the advantage that its form and parameters have a theoretical basis and that the qualitative effects of molecular shape and polarity on thermodynamic and interfacial properties of polyatomic fluids can be investigated.

Mohanty and Davis (1979) predicted VLE of several fluids using PR, MD and Redlich-Kwong (RK) equations of state and found that MD predicts VLE as well as PR and RK. Previously, we examined the effect of molecular shape and polarity on interfacial properties of pure fluids (Pérez-López et al., 1991). We found that the dimensionless surface tension varies exponentially with Θ (Figure 3) and linearly with the multipolar parameter (Figure 4). The same trends are observed experimentally.

As detailed above, the influence parameter, needed to transform γ^* into γ, was estimated as $0.785ab^{2/3}$. Using this approximation and the PR and MD equations of state we predicted surface tension as a function of temperature of several nonpolar (Figures 5 and 6), quadrupolar (Figure 7), slightly polar (Figure 8) and strongly polar (Figure 9) fluids. With the exception of CO_2, which has a quadrupole, MD consistently predicts better surface tension than PR. Even for nonpolar

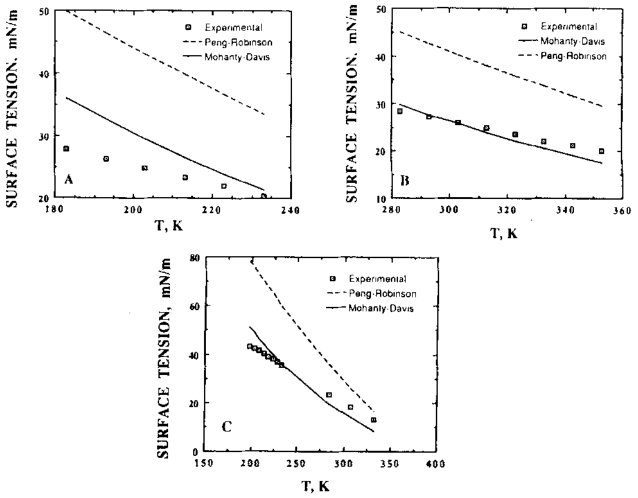

Figure 9. Surface tension as a function of temperature for polar substances.

(A) methylacetylene, (B) fluorobenzene and (C) ammonia.

fluids, PR fails to predict adequately experimental surface tensions.

Examination of Table 1 shows that the multipolar parameter, λ, for the *n*-alkanes is similar or larger than those of the polar substances reported here. This is because the λ parameter reflects not only multipolar interactions but also the temperature dependence of the pair correlation function. The parameter λ depends also on the shape parameter, Θ (Mohanty and Davis, 1979). The heat of vaporization (ΔE_{vap}) is a measure of the intermolecular forces (Castellan, 1971). Hence, it is expected that the values of ΔE_{vap} (or the normal boiling point) should correlate with λ. With the exception of NH_3 and CO_2, there is a very good correlation between these two parameters (Figure 10). In fact, *n*-dodecane has the largest value of ΔE_{vap} and of λ. For NH_3 the deviations are likely to be due to the hydrogen-bonding association exhibited by this molecule.

For the case of CO_2, MacCormack and Scheneider (1950) found that no unique values of U_o/k and ρ_o could fit experimental second virial coefficient data and that it was necessary to use different values to fit the high- and the low-temperature data. These authors postulated dimer formation due to the attraction between the lone-pair of electrons of an oxygen atom of one molecule and the electron-deficient carbon of another. The formation of these dimers at low temperatures can explain the large deviations of the predictions made with MD at the lower temperatures and the anomalously high value of λ since the value of Θ for dimers should be substantially different from the value used here.

It is noteworthy that MD predicts VLE of real fluids as well as, *but not better than*, PR. However, MD is far superior to PR (and Redlich-Kwong) for predicting interfacial properties of nonpolar and polar fluids without adjustable parameters. Of course, a least-squares fit to data might improve agreement between experiment and predictions. Our results evidently reflect the importance of the molecular shape and multipolar parameters on interfacial properties.

The conclusion that emerges from this work is that the gradient theory combined with an equation of state that contains parameters for molecular shape and multipolar interactions can give strong insights in the understanding of molecular interfaces and inhomogeneous fluids. More important, the MD equation of state may prove to give better predictions of thermodynamics and interfacial properties of mixtures than conventional equations since molecular shape and long-range interactions may play more important roles in mixtures than in single component systems due to the more complex dense fluid packing geometry and interactions of the former. Moreover, because orientational ordering at interfaces of multicomponent systems may prove to be more important than in one-component systems, more complex theories such as the extended gradient theory for dumbbell molecules interacting via anisotropic intermolecular potentials (Sweeney, 1987) may be needed.

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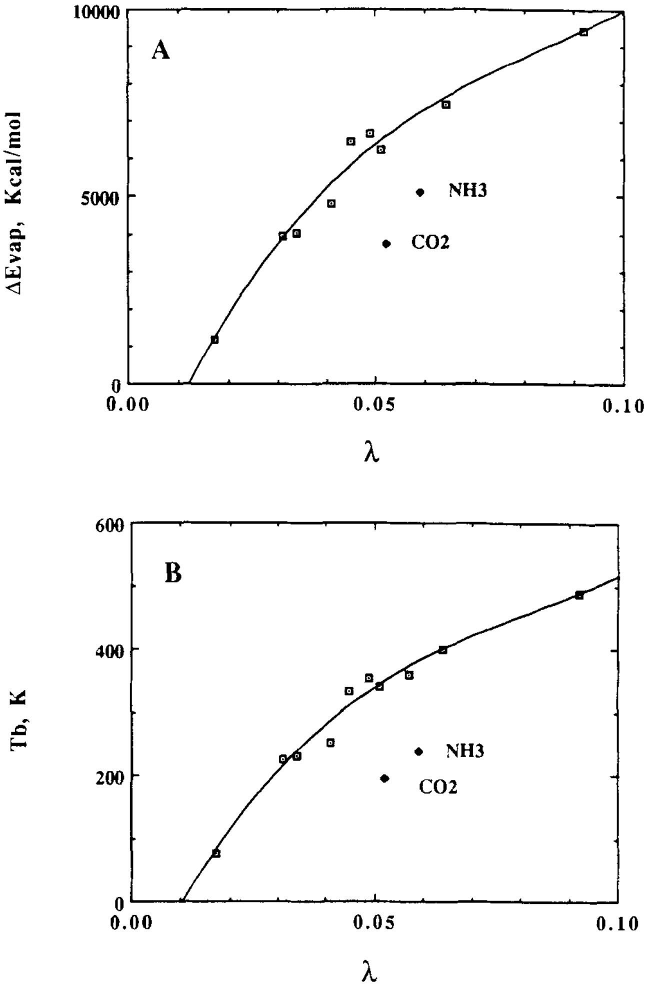

Figure 10. (A) Heat of vaporization (ΔE_{vap}) and (B) normal boiling temperature (T_b) vs. the multipolar parameter (λ).

Notation

a = energy parameter in equation of state
b = volume of a convex particle and volume parameter in equation of state
c = influence parameter
f = Helmholtz free energy density
k = Boltzmann's constant
M_o = surface integral of the mean curvature of the core
n = number density
P = pressure
R = average radius of curvature of a convex particle
S_o = surface area of the core
s = surface area of a convex particle
T = temperature
U_o = depth of Lennard-Jones potential
u = pair potential between molecules
V_o = volume of the core
x = distance across interface

Greek letters

γ = surface tension
λ = parameter which accounts for multipolar interactions
Ω = thermodynamic potential
ω = acentric factor

μ = chemical potential
Θ = shape parameter ($=sR/b$)
ρ_o = closest distance of approach between two molecules

Subscripts

o = homogeneous fluid
l = liquid
g = gas

Superscript

$*$ = reduced variable

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