Surface Tension Prediction for Pure Fluids

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For the surface tension of organic compounds, $\sigma = [\mathcal{P}\cdot(\rho_l - \rho_v)]^4$ is proposed where $\mathcal{P} = \mathcal{P}_0\cdot(1 - T_r)^{0.37}\cdot T_r\cdot \exp(0.30066/T_r + 0.86442\cdot T_r^9)$. ρ_l and ρ_v are molar densities of liquid and vapor, respectively, $T_r = T/T_c$, and $\mathcal{P}_0$ is a temperature-independent, compound-dependent constant similar to Sugden's parachor. This new expression, derived from statistical-mechanics, represents the experimental surface tension data of 94 different organic compounds within 1.05 AAD%. We also propose $\mathcal{P}_0 = 39.6431\cdot [0.22217 - 2.91042 \times 10^{-3}\cdot(\mathfrak{R}^*/T_{br}^2)\cdot T_c^{13/12}/P_c^{5/6}$ as a corresponding-states expression to correlate the temperature-independent parameter $\mathcal{P}_0$ for various compounds. Here, $\mathfrak{R}^* = \mathfrak{R}_m/\mathfrak{R}_{m,ref}$, $\mathfrak{R}_m$ is the molar refraction, $\mathfrak{R}_{m,ref}$ is the molar refraction of the reference fluid (methane), and T_{br} is the reduced normal boiling point. When this generalized expression is used, surface tensions for all 94 compounds can be predicted within 2.57 AAD% at all temperatures investigated.

Introduction

One of the most striking demonstrations of the effect of intermolecular forces is the tension at the surface of a liquid. From a qualitative point of view, a plausible explanation for this phenomenon would be that at the interface there are asymmetric forces acting upon a molecule the net effect of which is zero at equilibrium. At low densities, the molecules experience a sidewise attraction and an asymmetric force normal to the surface which tends to pull the surface towards the bulk liquid phase. Therefore, the surface layer is in tension and, at equilibrium, it tends to minimize its area which should be compatible with the total mass of fluid, constraints posed by the container, and external forces.

The surface tension (σ), which is a quantitative index of this tension, is defined as the force exerted in the plane of the surface per unit length (such as dyne/cm). Numerous methods have been proposed to estimate the surface tension of pure liquids and liquid mixtures. An extensive review of these methods is given by Hirschfelder et al. (1964). One of the simplest is the empirical formula proposed by Macleod (1923). It expresses the surface tension of a liquid in equilibrium with its own vapor as a function of the liquid- and vapor-phase densities as

$$\sigma = K(\rho_l - \rho_v)^4 \tag{1}$$

where K is a constant that is independent of temperature but is characteristic of the liquid under consideration. Sugden (1924) modified this expression as follows

$$\sigma = [P\cdot(\rho_l - \rho_v)]^4 \tag{2}$$

where $P = K^{1/4}$. Sugden called this temperature-independent parameter (P) the parachor, and described a way to estimate it based on molecular structure. Quayle (1953) used experimental surface tension and density data for numerous compounds to calculate the parachors for organic compounds. He was able to suggest an additive procedure to correlate P with hydrocarbon group contribution.

The righthand side of Eq. 2 implies that surface tension is very sensitive to the value of the parachor and of the liquid density. It has been shown that the parachor is a weak function of temperature for a variety of fluids over wide ranges of temperature (Macleod, 1923; Sugden, 1924; Quayle, 1953), and thus it is generally assumed to be a constant. Thus, Eq. 2 has been shown to represent the surface tension of numerous compounds rather accurately over wide ranges of temperatures, so long as experimental equilibrium densities are employed. Thus, it may be considered as an equation of state for the interface (Boudh-Hir and Mansoori, 1990).

The good performance and extreme simplicity of Eq. 2 have made it a very popular method for surface tension calculation (Weinaug and Katz, 1943; Lee and Chien, 1984; Hugill and van Welsenes, 1986; Gasem et al., 1989; Fanchi, 1985, 1990; Ali, 1994). Nevertheless, there are various shortcomings associated with the use of this equation: (1) the parachor P is actually a temperature-dependent parameter whose functional form with temperature is not known; (2) the empirical nature of the parachor poses difficulty in deriving a more accurate expression for it; and (3) the absolute average percent deviation (AAD%) in surface tension prediction increases as the complexity of the molecular structure of the fluid under consideration increases. Therefore, the statistical-mechanical basis of Eq. 1 may allow for modifications to this expression for the purpose of improving its accuracy and/or extending its use to the calculation of interfacial tension.

Development

Macleod's empirical expression for surface tension calculation, as mentioned above, has proven to work very well for many substances and over a wide range of temperature. Nonetheless, deviations with respect to temperature are generally observed. Thus, efforts have been made to derive the functionality of surface tension with respect to temperature (van der Waals, 1894; Lovett et al., 1973; Guggenheim, 1945). van der Waals proposed in 1894 a power law (classical) expression for the temperature dependence of surface tension in the critical region. This theory was further revised by Cahn and Hilliard (1958) and the same power law was derived. More recently, Rowlinson and Widom presented an extensive treatment of interfaces near critical points (see Chapter 9 of Rowlinson and Widom, 1989) and nonclassical critical exponents are presented. The surface tension of argon, nitrogen, and xenon has been measured over a very wide range of temperature. It was found that the surface tension of these simple fluids was well represented by the power law with nonclassical exponents (Croxton, 1974). It should be pointed out, however, that a simple power law is not guaranteed to hold for all temperatures down to the triple point. In fact, its applicability is confined to the critical region (Levelt Sengers and Sengers, 1981) and for molecules of high symmetry (Croxton, 1974). Based on the principle of corresponding states, Brock and Bird (1955) developed an expression for nonpolar liquids that is applicable to temperatures away from the critical point by utilizing the power law concept. The accuracy of their expression is similar to that of Eq. 1. Hakim et al. (1971) modified Brock and Bird's expression to include polar liquids. However, the general reliability of their expression is not known since the values of the constants appearing in the equation are known only for a few substances. Sivaraman et al. (1984) developed a correlation for predicting the surface tensions of organic compounds over the temperature range $0.45 < T_r < 0.97$. This correlation, however, is very sensitive to the values of the acentric factor, critical temperature, and critical pressure. Somayajulu (1988) has proposed a three-parameter generalized equation for surface tension for temperatures ranging from the triple point to the critical point. Although this empirical expression is very accurate, it involves three different compound-specific parameters which are known only for the compounds analyzed. Perez-Lopez et al. (1992) used the gradient theory to predict the surface tensions of nonpolar, quadrupolar, polar, and nonpolar. Their predictions are good; however, the absolute average percent deviations observed are rather large for all the compounds that they investigated.

In spite of the various efforts made to describe the functionality of surface tension with respect to temperature, there is still a need for an analytic expression which would be applicable over a larger range of temperature and valid for a variety of compounds.

Because Macleod's formula has been found to be based on statistical mechanics, it seems feasible to modify this expression in order to increase its accuracy as well as the temperature range of its applicability. There have been a number of efforts made to justify the success of Macleod's formula from theoretical basis (Fowler, 1937; Green, 1969; Henderson, 1980; Rowlinson and Widom, 1989; Boudh-Hir and Mansoori, 1990). Two methods have been used: the first starts with the classical thermodynamic expression which relates the surface tension and the surface internal energy $[u_s = S\{\gamma - T(\partial\gamma/\partial T)]$. The second (Boudh-Hir and Mansoori, 1990) begins with the statistical-mechanical definition of the surface tension. Using the first method (Fowler, 1937; Green, 1969), it has been shown that the surface tension is proportional to the power four of the difference in densities $(\rho_l - \rho_v)$. However, the use of certain simplifying statistical-mechanical approximations (Green, 1969; Henderson, 1980) in these approaches leads to results different from Macleod's equation. Thus, the temperature-dependence of the surface tension is not easily observed.

Starting with the statistical-mechanical definition of the surface tension, Boudh-Hir and Mansoori (1990) have shown that, as a first approximation, the surface tension is given by the Macleod formula. As a result, the power four of the difference in densities $(\rho_l - \rho_v)$ is obtained (see Eq. 1). However, they have shown that the constant K which depends on the nature of the fluid under consideration, is not entirely independent of temperature. The only simplification they made was to consider the particles to interact via a generalized additive pairwise potential which depends on the positions and orientations of the molecules (i.e., the particles are not spherical and the potential is not necessarily a radial function).

The statistical-mechanical expression for the surface tension derived by Boudh-Hir and Mansoori (1990) is

$$\sigma = \{(kT/4)\tau^{4-2g}(z/z_c)\zeta(\tau,\rho_l,\rho_v)\}(\rho_l - \rho_v)^4 \quad \text{(3a)}$$

$$\zeta(\tau,\rho_l,\rho_v) = \int \partial_{z_1}\chi(1;\xi)e^{\rho_c\tau\chi(1;\xi)}\partial_{z_2}\chi(2;\xi) \times e^{\rho_c\tau\chi(2;\xi)}c(1,2)(r_{12}^2 - z_{12}^2)dz_1 d\Omega_1 dr_2 d\Omega_2 \quad \text{(3b)}$$

In these equations, k is the Boltzmann constant; T is the temperature of the system under consideration; $\tau = (1 - T/T_c)$; g is an exponent; $z = (2\pi mkT/\mathrm{h}^2)^{1/2}e^{\mu/kT}$ is the activity; the subscript c denotes the value of the activity at the critical temperature (i.e., $z_c = (2\pi mkT_c/\mathrm{h}^2)^{1/2}e^{\mu/kT_c}$); μ is the chemical potential; h is the Planck's constant; $\rho_c\tau\chi(i;\xi) = \Delta c(i)$; ρ_c is the critical density; $\Delta c(i) = [c(i) - c_c(i)]$ (i.e., the value of the one-particle direct correlation function at the temperature of interest minus the value of the one-particle direct correlation at the critical temperature). $\chi(i;\xi)$ is given by the expression

$$\chi(i;\xi) = \int c(i,j;\xi)\{-g_c v(i,j)e^{-g_c w(i,j)} + g_c\mu - 3/2\}e^{\Delta c(j;\xi)} \quad \text{(3c)}$$

$c(i,\ j;\ \xi)$ is the two-particle direct correlation function; $w(i,\ j)$ is a pairwise potential; $v(i,\ j)$ is the mean force potential; ξ is an order parameter which depends on τ ($\xi = 0$ corresponds to the system at its critical temperature, while $\xi = 1$ is associated with the system at the temperature of interest); g_c is the value of the exponent g at the critical temperature. Complete details of the derivation of Eq. 3 are given elsewhere (Boudh-Hir and Mansoori, 1990). Nevertheless, it is to be mentioned that Eq. 3 is general and, so, it may be applied whatever the nature of the fluid is, if the condition of additive pairwise potential is satisfied; although the form of the first term of the surface tension expansion remains the same near the critical temperature, the constant in Macleod's formula becomes very sensitive to this parameter when it increases and tends to its critical value (T_c). Because of these reasons, we have decided that Eq. 3 is a suitable expression to be approximated for the prediction of the surface tension. Thus, comparing Eqs. 2 and 3 it can be shown that the parachor is given by

$$\mathcal{P} = \mathcal{P}_0 \cdot (1 - T_r)^{1 - g/2} \cdot T_r \cdot \exp[\kappa \cdot \mu_r / (T_r)] \cdot [\zeta(\tau, \rho_l, \rho_v)]^{1/4} \quad (4)$$

where $\mathcal{P}_0$ is a temperature-independent compound-specific constant; the exponent g will be treated as an adjustable parameter; the constant κ is given by $\kappa = 2\mu_c/(4kT_c)$; μ_c is the critical chemical potential; k is the Boltzmann constant; μ_r is the reduced chemical potential; and ζ is given by Eq. 3a.

Considering the fact that for most organic substances we know little about the one- and two-particle direct correlation functions as well as the intermolecular potential, it is almost impossible to calculate ζ. Considering the success of the theory of parachors (Sugden, 1924) in correlating surface tension data, it can be safely assumed that ζ is a very weak function of densities. However, its temperature-dependence is not known. As a result, we write the expression for $\mathcal{P}$ in the following form

$$\mathcal{P} = \mathcal{P}_0 \cdot (1 - T_r)^{1 - g/2} \cdot T_r \cdot \exp(\theta_r / T_r);$$
$$\text{where} \quad \theta_r = \kappa\mu_r + [T_r \cdot 1/4 \cdot \ln \zeta(\tau, \rho_l, \rho_v)] \quad (5)$$

Note that Eqs. 4 and 5 are equivalent. Now, by combining Eqs. 2 and 5 the following expression for the surface tension is obtained

$$\sigma = \left[\mathcal{P}_0 \cdot (1 - T_r)^{1 - g/2} \cdot T_r \cdot \exp(\theta_r / T_r) \cdot (\rho_l - \rho_v) \right]^4 \quad (6)$$

where ρ_l and ρ_v are the equilibrium molar densities of liquid and vapor phases, respectively. The temperature-dependent property θ_r may be assumed to have the following simple form

$$\theta_r = a_0 + a_1 \cdot T_r^n \quad (7)$$

where a_0, a_1, and n may be regarded as universal constants.

The temperature correction term in Eq. 6 thus derived should be valid for all temperatures and for all compounds.

In order to evaluate the constants in Eqs. 6 and 7 reliable experimental data over a wide range of temperature are needed. Recently, Grigoryev et al. (1992) reported experimental surface tension data for n-pentane, n-hexane, and n-hepane, n-octane which cover the entire temperature range from the triple point to the critical point. Thus, these data were considered to be appropriate. After analysis of these data it was concluded that the most complete sets of data were those for n-hexane and n-heptane, because they cover the entire temperature range more completely. From Eq. 6, it is noticed that data for the equilibrium densities are also needed for the analysis to be completed. Considering the fact that for most substances experimental data on equilibrium densities may not be readily available, we decided to use an accurate equation of state for the purpose of evaluating the constants a_0, a_1, n, and g appearing in Eqs. 6 and 7. This is important, since in this way we eliminate the need for experimental equilibrium density data.

Calculation of Equilibrium Densities

Recently, Riazi and Mansoori (1993) proposed a simple equation of state (R-M EOS) that accurately predicts fluid densities. This equation is a modification of that originally proposed by Redlich and Kwong (1949) such that

$$P = \rho RT/(1 - b\rho) - a\rho^2/[T^{1/2} \cdot (1 + b\rho)];$$
$$b = (0.08664\ RT_c/P_c) \cdot \delta(\mathcal{R}^*, T/T_c) \quad (8a)$$

These authors consider the fact that for liquid systems in which the free space between the molecules decreases the role of the parameter b becomes more important than that of parameter a. For this reason, a is considered to be constant and given by $a = 0.42748RT_c/P_c$. The parameter b, however, was modified using the molecular theories of perturbations and refractive index such that $b = (0.08664\ RT_c/P_c) \cdot \delta(\mathcal{R}^*, T_r)$; R is the universal gas constant; T_c and P_c are the critical temperature and pressure respectively; δ is a temperature-dependent parameter given by

$$\delta^{-1} = 1 + \{0.02[1 - 0.92.\exp(-1{,}000|T_r - 1|)]$$
$$-0.035(T_r - 1)\}(\mathcal{R}^* - 1);\ \mathcal{R}^* = \mathcal{R}_m / \mathcal{R}_m, \text{ref} \quad (8b)$$

$\mathcal{R}^*$ is a dimensionless molar refraction; $\mathcal{R}m$ is the molar refraction and $R_{m,\text{ref}}$ is the molar refraction of a reference fluid which in this case is methane with a value of 6.987. $\mathcal{R}_m$ may be calculated using the Lorentz-Lorenz function

$$\mathcal{R}_m = (4\tau NA/3)[\alpha + \mu^2 f(T)] = (1/\rho)(n^2 - 1)/(n^2 + 2)$$

NA is the Avogadro's number; α is the polarizability; μ is the dipole moment; ρ is the molar density; and n is the sodium-D light refractive index of a liquid at 20°C and 1 atm. In this derivation, the fact that the molar refraction is, as a first approximation, independent of temperature is considered. Furthermore, $\mathcal{R}^*$ is even less sensitive to temperature.

Density predictions by the R-M EOS were compared against the available experimental data (Hall, 1986) for the compounds of interest. These results are reported in Table 1 along with the properties of 94 organic compounds. According to this table, density predictions using this equation of state are good for most compounds except for those whose molecular structure are highly asymmetric and/or are polar.

Table 1. Properties of Organic Compounds and Experimental Data for Density, Surface Tension, and Saturation Pressure at Normal Boiling Point*

											AAD%, Surface Tension Prediction			
Compound	T_c K	P_c bar	$\mathcal{R}^*$	ω	T_b K	P	$\mathcal{P}_0$	Temp. K	Density AAD%	$P^{sat}(T_b)$ AAD%	$\mathcal{P}_0$ Eq. 10	P Eq. 2	Calc. $\mathcal{P}_0$ Eqs. 10, 14	Calc. P Eqs. 2, 15
Methane	190.4	46.0	1.0	0.011	111.6	72.6	102.31	90–170	0.90	1.74	3.39	5.52	3.96	7.57
Ethane	305.4	48.8	1.620	0.099	184.6	110.5	158.50	113–280	1.10	0.87	3.18	11.54	4.00	8.16
Propane	369.6	42.5	2.259	0.153	231.1	150.8	215.23	143–330.7	1.40	1.06	4.38	10.05	4.52	8.21
n-Butane	425.2	38.0	2.929	0.199	272.7	190.3	270.21	173–385	1.10	0.50	1.86	6.72	6.72	6.23
Ethylene	282.4	50.4	1.504	0.089	169.3	100.2	143.20	113–173	1.30	0.09	1.64	4.05	1.88	1.87
Isobutane	408.2	36.5	2.955	0.183	261.4	**	266.81	173–283	1.40	0.05	0.60	‡	1.90	7.41
n-Pentane	469.7	33.7	3.616	0.251	309.2	231.5	327.75	156–440	1.22	0.11	2.30	4.53	2.33	5.68
Isopentane	460.4	33.9	3.620	0.227	301.0	230.0	318.29	273–313	1.50	0.35	0.67	5.98	0.93	5.62
n-Hexane	507.4	30.1	4.281	0.299	341.9	270.4	387.60	172.12–450	1.46	0.16	1.55	7.30	2.84	4.26
2-Methylpentane	497.5	30.1	4.286	0.278	333.4	270.0	376.96	273–343	0.57	0.11	0.84	2.60	0.82	4.61
3-Methylpentane	504.5	31.2	4.265	0.272	336.4	267.7	370.33	273–343	1.64	0.19	0.26	6.57	0.83	6.84
2,2-Dimethylbutane	488.8	30.8	4.289	0.232	322.8	266.4	358.62	273–303	4.83	0.26	0.62	18.79	2.95	16.60
2,3-Dimethylbutane	500.0	31.3	4.267	0.247	331.1	266.2	363.54	273–333	2.93	0.12	0.51	12.24	2.52	13.25
n-Heptane	540.3	27.4	4.945	0.349	371.6	310.8	441.60	183.21–508	0.49	0.03	3.87	4.99	3.74	4.84
2-Methylhexane	530.4	27.3	4.951	0.329	363.2	309.2	431.63	273–333	0.83	0.11	0.42	3.18	0.40	4.32
3-Methylhexane	535.3	28.1	4.932	0.323	365.0	307.4	424.71	283–313	2.10	0.31	0.31	7.64	0.57	6.14
n-Octane	568.8	24.9	5.608	0.398	398.8	351.2	500.25	218.15–520	0.49	0.06	2.86	6.11	3.81	3.84
2-Methylheptane	559.6	24.8	5.614	0.378	390.8	348.8	487.74	273–333	0.84	0.11	0.27	3.16	0.45	4.58
3-Methylheptane	563.7	25.5	5.596	0.370	392.1	347.7	480.19	273–333	1.99	0.17	0.18	8.53	0.27	5.99
4-Methylheptane	561.7	25.4	5.599	0.371	390.9	347.4	479.88	273–333	2.01	0.08	0.17	8.38	0.27	5.82
n-Nonane	594.6	22.9	6.274	0.445	424.0	391.1	551.20	273–343	0.14	0.30	0.59	0.86	0.95	0.50
Cyclopentane	511.7	45.1	3.310	0.196	322.4	205.0	284.50	273–470	1.81	0.04	3.66	8.82	4.70	8.96
Methylcyclopentane	532.7	37.8	3.984	0.231	345.0	242.8	336.09	273–343	2.14	0.12	0.31	6.76	0.29	11.54
Cyclohexane	553.5	40.7	3.966	0.212	353.8	241.7	330.37	273–343	3.81	0.33	0.30	12.82	2.40	13.56
1,1-Dimethylcyclopentane	547.0	34.4	4.648	0.273	361.0	281.2	364.11	273–343	†	1.70	0.21	39.90	3.82	17.96
Methylcyclohexane	572.2	34.7	4.652	0.236	374.1	281.3	379.74	273–343	4.55	0.01	1.27	19.14	2.36	24.45
Ethylcyclopentane	569.4	34.0	4.637	0.271	376.6	283.3	387.56	273–343	3.06	0.00	0.23	12.90	0.54	14.64
1,1-Dimethylcyclohexane	591.0	29.6	5.302	0.238	392.7	318.8	446.73	273–333	†	0.40	0.43	3.36	2.52	27.56
1,2-Dimethylcyclohexane cis	606.0	29.6	5.273	0.236	402.9	317.4	462.23	273–333	†	1.57	0.90	11.04	4.73	24.87
1,2-Dimethylcyclohexane trans	596.0	29.6	5.314	0.242	396.6	320.3	448.75	273–333	†	0.78	0.33	3.58	0.66	29.43
1,3-Dimethylcyclohexane cis	591.0	29.6	5.338	0.224	393.3	321.3	441.06	273–333	†	6.08	0.62	12.24	2.31	36.76
1,3-Dimethylcyclohexane trans	598.0	29.7	5.297	0.189	397.6	318.7	451.19	273–333	†	16.38	0.68	0.60	2.35	36.32
1,4-Dimethylcyclohexane cis	598.0	29.7	5.224	0.234	397.5	318.8	451.56	273–333	†	2.28	0.42	0.83	1.73	28.07
1,4-Dimethylcyclohexane trans	587.7	29.7	5.339	0.242	392.5	322.7	437.27	273–333	†	4.99	0.75	18.11	2.72	33.28
Ethylcyclohexane	609.0	30.0	5.297	0.243	404.9	320.6	456.63	273–343	0.85	0.95	1.12	2.94	2.60	26.69
Benzene	562.2	48.9	3.748	0.212	353.2	206.14	289.59	283–343	0.20	0.43	0.55	1.42	2.77	11.87
Toluene	591.8	41.0	4.450	0.263	383.8	245.9	348.29	273–550	†	0.17	2.20	6.13	3.34	11.59
o-Xylene	630.3	37.3	5.124	0.310	417.6	283.3	394.89	273–343	1.26	0.02	0.62	6.39	0.65	16.90
m-Xylene	617.1	35.4	5.147	0.325	412.3	284.3	404.15	273–343	0.56	0.11	0.87	1.98	0.94	13.00
p-Xylene	616.2	35.1	5.153	0.320	411.5	283.8	405.92	293–343	0.75	0.12	0.70	4.37	0.71	14.27
Ethylbenzene	617.2	36.0	5.118	0.302	409.3	284.3	398.69	273–593	0.70	0.26	1.18	6.83	1.43	12.46
1,2,3-Trimethylbenzene	664.5	34.5	5.790	0.366	449.3	317.8	437.30	273–373	2.81	0.32	0.88	12.09	1.63	17.46
1,2,4-Trimethylbenzene	649.2	32.3	5.824	0.376	442.5	320.4	452.94	273–343	0.27	0.36	0.58	1.02	0.58	13.78
1,3,5-Trimethylbenzene	627.3	31.3	5.842	0.399	437.9	**	457.05	273–343	0.23	0.11	0.74	‡	0.74	8.63
n-Decane	617.7	21.2	6.915	0.489	447.3	431.15	602.86	273–393	0.74	1.06	1.28	3.65	1.28	0.55
n-Undecane	638.8	19.7	7.962	0.535	469.1	470.5	646.66	273–393	2.76	1.11	1.31	11.77	1.37	4.30
n-Tridecane	676.0	17.2	8.935	0.619	508.6	550.55	757.61	283–393	2.80	0.40	1.32	11.62	1.31	1.34
2,2-Dimethylhexane	549.9	25.3	5.618	0.338	380.0	346.05	467.32	273–323	4.50	0.01	0.83	17.83	1.88	13.02
2,4-Dimethylhexane	553.5	25.6	5.600	0.343	382.6	345.2	466.63	273–323	4.47	0.19	0.71	17.85	1.57	11.75
2,5-Dimethylhexane	550.1	24.9	5.620	0.356	382.3	346.3	475.67	273–373	27.4	0.13	0.82	10.10	1.19	8.49
3,3-Dimethylhexane	562.0	26.5	5.583	0.320	385.1	343.05	458.96	273–323	5.57	0.10	0.69	22.61	2.31	17.52
3,4-Dimethylhexane	568.9	26.9	5.561	0.338	390.9	342.5	461.68	273–333	4.82	0.12	0.54	19.15	0.99	12.48
2-Methyl-3-ethylpentane	567.1	27.0	5.559	0.330	388.8	338.3	458.16	273–323	5.47	0.16	0.40	16.90	1.08	14.18
3-Methyl-3-ethylpentane	576.0	28.1	5.542	0.303	391.4	340.1	448.01	273–323	7.28	0.02	0.46	30.86	2.77	22.13
2,2,4-Trimethylpentane	544.0	25.7	5.620	0.303	372.4	344.3	451.63	273–363	7.00	0.07	0.62	32.36	4.30	23.08
2,2-Dimethylheptane	576.8	23.5	6.286	0.390	405.9	373.1	513.69	283–323	5.34	0.17	0.67	10.48	3.48	14.79
2,2,4-Trimethylhexane	573.7	23.7	6.304	0.321	399.7	381.6	505.73	283–333	5.91	6.31	0.21	28.53	2.80	27.53
2,2,5-Trimethylhexane	568.0	23.3	6.288	0.357	397.2	383.9	507.84	283–333	5.84	0.02	0.19	29.34	3.26	20.81
3,3-Diethylpentane	610.0	26.7	6.172	0.338	419.3	**	488.40	273–333	8.28	0.50	0.48	‡	3.25	26.84
2,2,4,4-Tetramethylpentane	592.7	26.0	6.279	0.313	406.1	378.65	481.35	283–323	10.9	25.41	0.24	52.68	0.24	33.55
n-Propylcyclopentane	603.0	30.0	5.307	0.335	404.1	**	450.04	273–373	1.21	14.81	0.60	‡	0.59	12.74
Isopropylcyclopentane	601.0	30.0	5.297	0.240	399.6	**	446.28	273–373	†	1.85	0.89	‡	1.09	30.55
n-Propylcyclohexane	639.0	28.0	5.965	0.258	429.9	360.4	499.48	273–343	2.49	2.20	0.40	9.10	2.08	35.50
Isobutylcyclohexane	659.0	31.2	6.635	0.319	444.5	397.7	422.55	273–373	†	0.60	2.08	161.78	15.91	60.92
Secbutylcyclohexane	669.0	26.7	6.593	0.264	452.5	397.5	533.01	273–373	†	1.37	1.37	24.42	1.38	48.08
Tertbutylcyclohexane	659.0	26.6	6.599	0.252	444.7	394.65	524.52	273–373	†	1.79	1.62	28.64	1.63	51.89
1-Hexene	504.0	31.7	4.181	0.285	336.6	**	437.18	273–333	1.54	0.52	0.71	‡	0.68	2.59
1-Octene	566.7	26.2	5.550	0.386	394.4	**	472.71	273–373	0.76	0.30	0.25	‡	0.45	2.77
1-Decene	615.0	22.0	6.880	0.491	486.5	**	581.81	273–373	1.70	0.10	0.79	‡	0.80	0.72
1-Dodecene	657.0	18.5	8.206	0.558	486.5	**	704.61	273–373	0.29	0.60	0.94	‡	1.97	0.54
n-Propylbenzene	638.2	32.0	5.790	0.344	432.4	323.35	448.29	273–373	2.01	0.25	1.04	8.14	1.05	17.58
Isopropylbenzene (Cumene)	631.1	32.1	5.786	0.326	425.6	321.1	440.06	273–373	3.19	0.16	1.22	13.07	1.22	22.16
2-Ethyltoluene	651.0	30.4	5.790	0.294	438.3	320.0	483.96	273–373	6.50	1.51	1.10	23.41	6.11	20.17
3-Ethyltoluene	637.0	28.4	5.816	0.360	434.5	322.15	503.41	273–373	9.58	7.98	1.73	32.43	6.93	6.76
4-Ethyltoluene	640.0	29.4	5.833	0.322	435.2	323.3	486.78	273–373	6.15	1.52	1.57	22.29	3.93	16.98
n-Butylbenzene	660.5	28.9	6.455	0.393	456.5	362.9	497.21	273–373	3.08	0.04	1.74	13.95	1.89	18.91
Isobutylbenzene	650.0	31.4	6.471	0.380	445.9	360.3	445.77	273–373	†	3.13	1.01	70.96	9.33	32.28

(Continued)

Table 1. Properties of Organic Compounds and Experimental Data for Density, Surface Tension, and Saturation Pressure at Normal Boiling Point* (Continued)

											AAD%, Surface Tension Prediction			
Compound	T_c K	P_c bar	$\mathcal{R}^*$	ω	T_b K	P	$\mathcal{P}_0$	Temp. K	Density AAD%	$P^{sat}(T_b)$ AAD%	$\mathcal{P}_0$ Eq. 10	P Eq. 2	Calc. $\mathcal{P}_0$ Eqs. 10, 14	Calc. P Eqs. 2, 15
Secbutylbenzene	664.0	29.4	6.445	0.274	442.3	359.95	488.71	273–373	†	2.25	1.22	18.24	1.21	45.00
Tertbutylbenzene	660.0	29.6	6.440	0.265	442.3	356.8	481.45	273–373	†	1.78	1.31	21.10	1.39	48.27
1,4-Diethylbenzene	657.9	28.0	6.518	0.404	456.9	361.45	509.95	273–373	†	0.31	1.44	1.28	1.45	15.53
1-Methylnaphthalene	772.0	36.0	6.980	0.310	517.9	353.8	483.33	273–303	3.81	0.11	0.60	17.63	5.39	44.00
1-Tetradecene	689.0	15.6	9.471	0.644	524.3	**	839.84	293–373	2.12	8.15	0.94	‡	3.31	4.94
Carbon tetrachloride	556.4	49.6	3.784	0.193	349.9	219.68	279.37	288–525	†	8.95	2.62	42.64	2.73	15.50
Chloroform	536.4	53.7	3.071	0.218	334.3	183.4	260.02	288–348	†	1.88	0.76	3.29	1.98	1.49
1,1,2-Trichloroethane	606.0	51.4	3.709	0.2598	386.7	223.8	304.39	288–378	†	5.76	0.65	15.34	4.57	0.84
1-Chlorobutane	542.0	36.8	3.641	0.218	351.6	230.3	359.96	283–343	†	3.23	0.41	34.34	5.96	1.68
Fluorobenzene	560.1	45.5	3.742	0.244	357.9	214.15	306.62	283–353	†	0.07	0.21	5.92	1.40	6.24
Chlorobenzene	632.4	45.2	4.458	0.249	404.9	244.4	344.11	283–403	†	0.05	0.69	0.84	2.85	15.98
Bromobenzene	670.0	45.2	4.858	0.251	429.2	258.32	359.26	283–423	†	0.11	1.20	6.25	1.34	25.58
Iodobenzene	721.0	45.2	5.602	0.249	461.6	279.19	378.58	283–433	†	0.11	1.26	18.48	1.66	41.41
Acetone	508.1	47.0	2.316	0.304	329.2	161.22	297.03	293–333	†	0.27	2.71	66.20	18.89	35.07
Benzonitrile	699.4	42.2	4.500	0.362	464.3	**	414.43	293–363	†	0.21	0.53	‡	6.70	6.072
Dibutylether	580.0	25.3	5.866	0.502	413.4	**	493.37	283–393	†	2.37	0.11	‡	0.22	12.64
Cyclooctane	647.2	35.6	5.255	0.236	422.0	315.15	417.11	283–393	†	0.26	1.82	29.38	1.87	34.57
OVERALL AAD%									**2.80**	**1.76**	**1.05**	**16.81**	**2.57**	**16.75**

*Experimental densities were taken from Hall (1986); experimental surface tensions from Jasper (1972), Hall (1986), Grigoryev et al. (1992), and Beaton and Hewitt (1989); the physical properties T_c, P_c, ω, and T_b from Reid et al. (1988). $\mathcal{R}^* = \mathcal{R}_m/\mathcal{R}_{m,\mathrm{ref}}$, $\mathcal{R}_m$ data were taken from Hall (1986) or calculated using the Lorentz-Lorenz function, $\mathcal{R}_{m,\mathrm{ref}} = 6.987$ for the reference fluid (methane). Parachors were taken from Quayle (1953).

**The Quayle's fitted parachors for these substances were not available.

†Experimental densities for these compounds are not readily available.

‡These values could not be calculated since there are no parachor data available.

The necessary vapor pressures are calculated using a recently proposed (Edalat et al., 1993) generalized vapor pressure equation for various fluids. This new expression is as follows

$$\ln(P^s/P_c) = [a(\omega)\cdot\tau + b(\omega)\cdot\tau^{1.5} + c(\omega)\cdot\tau^3 + d(\omega)\cdot\tau^6]\cdot(1-\tau)^{-1} \quad (9)$$

In this equation

$$a(\omega) = -6.1559 - 4.0855\cdot\omega;$$

$$b(\omega) = 1.5737 - 1.0540\cdot\omega - 4.4365\times 10^{3}\cdot d(\omega);$$

$$c(\omega) = 0.8747 - 7.8874\cdot\omega;$$

$$d(\omega) = (-0.4893 - 0.9912\cdot\omega + 3.1551\cdot\omega^2)^{-1}; \quad \tau = 1 - T_r$$

P^s is the saturation pressure, and ω is the acentric factor. Table 1 shows the absolute average percent deviation (AAD%) in the calculation of the saturation pressure at the normal boiling for all 94 compounds. It is observed that the saturation pressure at the normal boiling point is represented within an overall AAD% of 1.76.

Results and Discussion

Equilibrium densities for n-hexane and n-heptane were calculated by first predicting the saturation pressure from Eq. 9 and then using Eq. 8 to predict the vapor- and liquid-phase densities. These were used along with the experimental surface tension data of Grigoryev et al. (1992) for n-hexane and n-heptane to evaluate the universal constants appearing in Eq. 7. The values for the constants thus obtained are: $a_0 = 0.30066$; $a_1 = 0.86442$; and $n = 10$. By substituting Eq. 7 into Eq. 6, using the constants just found, the following new expression for the surface tension of a fluid is obtained

$$\sigma = \Big[\mathcal{P}_0\cdot(1-T_r)^{0.37}\cdot T_r\cdot\exp(0.30066/T_r + 0.86442\cdot T_r^9)\cdot(\rho_l - \rho_v)\Big]^4 \quad (10)$$

In this expression $\mathcal{P}_0$ is a temperature-independent compound-specific constant characteristic of the fluid under consideration similar to Sugden's parachor. It should be pointed out that, because of the approximations introduced, Eq. 10 is not expected to hold valid for the critical region.

Experimental surface tension data (Jasper, 1972; Hall, 1986; Beaton and Hewitt, 1989) for 94 compounds and equilibrium densities calculated as previously explained were used to evaluate the constant $\mathcal{P}_0$ for these substances. The results obtained are reported in Table 1 along with the surface tension predictions using this new parameter $\mathcal{P}_0$. The temperature range used in the analysis is also reported. For comparison purposes, Table 1 also shows the surface tension predictions obtained by using the Quayle's fitted parachors (Quayle, 1953) and the equilibrium densities calculated using the R-M EOS. According to Table 1, the surface tension, for all 94 compounds is represented within an overall average absolute percent deviation (AAD%) of 1.05 when the new parameter $\mathcal{P}_0$ is used along with Eq. 10. This proves this equation to be valid for a large variety of organic compounds. When the Quayle parachor is used along with Eq. 2, the surface tension for all 94 compounds is represented within an overall average absolute deviation of 16.81%.

In order to show the predicting capabilities of Eq. 10, the results obtained for 12 different compounds are plotted in Figures 1–3. Figure 1 shows the results obtained for methane, ethane, propane and n-butane over a wide range of tempera-

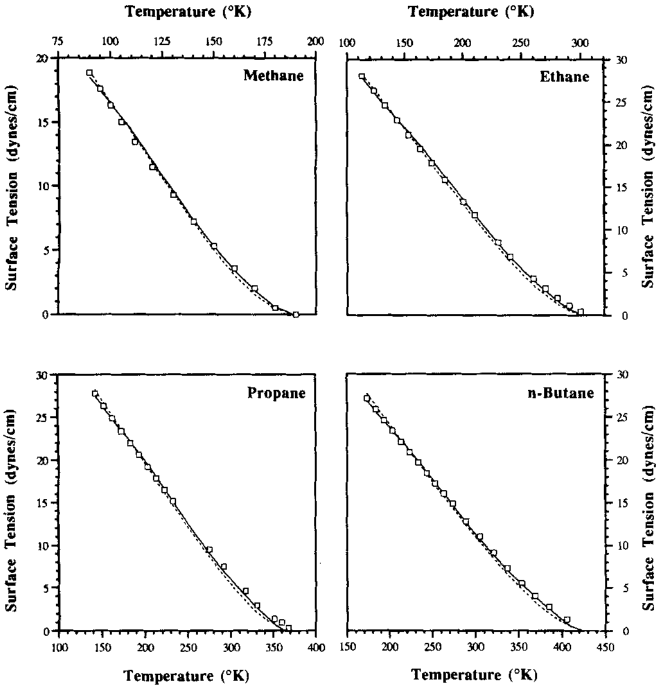

Figure 1. Surface tension σ as a function of temperature for low-boiling-point compounds.

□, experimental data of Jasper (1972), Hall (1986), and Beaton and Hewitt (1989); ——, values calculated with Eq. 10; ----, calculated by fitting Eq. 2 to the experimental surface tension data.

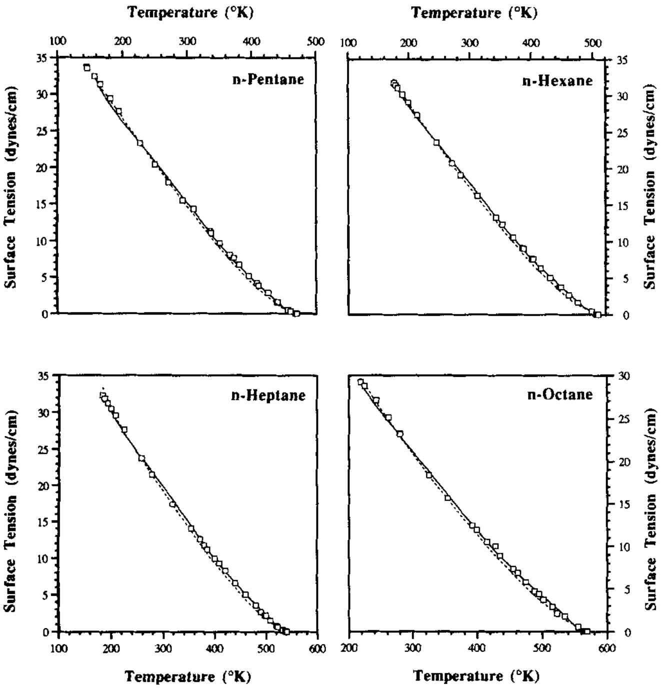

Figure 2. Surface tension σ of normal paraffins as a function of temperature from the triple point to the critical point.

□, experimental data of Grigoryev et al. (1992), Hall (1986), and Beaton and Hewitt (1989); ——, values calculated with Eq. 10, ----, values calculated by fitting Eq. 2 to the experimental surface tension data.

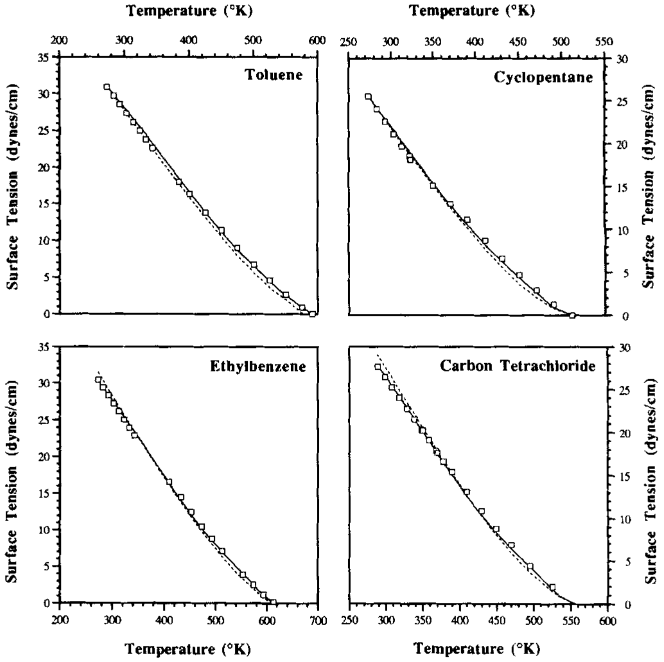

Figure 3. Surface tension σ as a function of temperature for various compounds.

□, experimental data of Jasper (1972), Hall (1986), and Beaton and Hewitt (1989); ——, values calculated with Eq. 10; ----, values calculated by fitting Eq. 2 to the experimental surface tension data.

tures. These are compared against experimental surface tension data (Jasper, 1972; Hall, 1986; Beaton and Hewitt, 1989) and against the best fit of Eq. 2 (equilibrium densities were calculated as explained above) to the experimental surface tension data. From this figure, it can be seen that predictions by Eq. 10 are quite good. Figure 2 presents the results obtained for *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane over temperatures ranging from the triple point to near the critical point. These results are compared with the experimental data of Grigoryev et al. (1992) and with the best fit of Eq. 2 (equilibrium densities were calculated as explained above) to the experimental surface tension data. Notice from this figure that the experimental data for all four compounds are quite well represented by Eq. 10 except in the region close to the critical point. This is because Eq. 10 and the R-M EOS, as most other equations of state, do not hold in the critical region. Figure 3 depicts the results for toluene, cyclopentane, ethylbenzene, and carbon tetrachloride over a wide temperature range. The experimental data for these compounds were obtained from Jasper (1972), Hall (1986), and Beaton and Hewitt (1989). It can also be seen from this figure that the experimental data are well represented by Eq. 10. Judging from Figures 1–3 we may say that overall performance of our method for surface tension prediction is good. Knowing that parameter $\mathcal{P}_0$ provides such a good surface tension prediction for all the compounds and for all temperatures investigated, it is only logical to attempt to find a way to correlate this parameter using the principle of corresponding states.

Following the principle of corresponding states (Hirschfelder, 1964), a reduced surface tension may be defined and expected to be a universal function of the reduced temperature ($T_r = T/T_c$), as follows

$$\sigma_r = \sigma / \left[P_c^{2/3} \cdot (kT_c)^{1/3} \right] \qquad (11)$$

where P_c and T_c are the critical pressure and critical temperature, respectively. From Eqs. 10 and 11 it can be shown that a reduced parameter $\mathcal{P}_r$ can be expressed as follows

$$\mathcal{P}_r = \mathcal{P}_0 \cdot P_c^{5/6} / (39.6439 \cdot T_c^{13/12}) \qquad (12)$$

According to the principle of corresponding states, it is expected that a reduced parameter thus defined would be a universal function of the acentric factor. The calculated values of $\mathcal{P}_r$ for all 94 compounds listed in Table 1 were plotted against the acentric factor in Figure 4. From this figure, one may notice a trend as a function of acentric factor. However, the scattering in the data is rather large. Therefore, we have concluded that attempts to correlate our reduced parameter ($\mathcal{P}_r$) to acentric factor would not be a feasible approach.

From the Lorentz-Lorenz function for molar refraction ($\mathcal{R}_m$), defined earlier in this article, we notice that this quantity ($\mathcal{R}_m$) depends on the polarizability of the molecule and the dipole moment. Furthermore, the molar refraction provides an approximate measure of the actual volume (without free space) of the molecules per unit mole (Hirschfelder, 1964). Therefore, it implicitly accounts for the asymmetry of the molecules. This fact gave the authors confidence that $\mathcal{R}_m$ would be useful in finding a good correlation for $\mathcal{P}_r$. It has also been found that substances with higher polarities have higher viscosities, normal boiling and freezing points. Therefore, $\mathcal{R}_m$ and the normal-boiling-point temperature could be useful for the purposes at hand.

In Figure 2 the reduced parachor $\mathcal{P}_r$ (value at the normal boiling point, T_b) vs. $\mathcal{R}^*/T_{br}^2$ have been plotted. $\mathcal{R}^*$ is as previously defined and T_{br} is the reduced normal boiling point temperature. Judging from Figure 5 it may be said that there is a clear relationship between $\mathcal{P}_r$ and $\mathcal{R}^*/T_{br}^2$. Thus, the following simple correlation for $\mathcal{P}_r$ was obtained

$$\mathcal{P}_r = 0.22217 - 2.91042 \times 10^{-3} \cdot (\mathcal{R}^*/T_{br}^2) \qquad (13)$$

Therefore, the new expression proposed to predict parameter $\mathcal{P}_0$ in Eq. 10 is the following

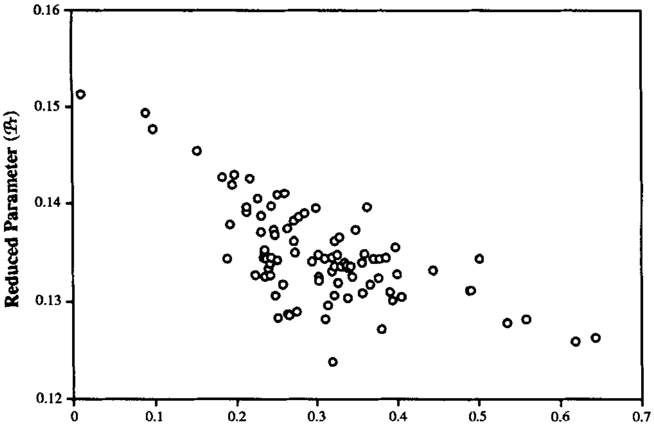

Figure 4. Reduced parameter ($\mathcal{P}_r$) vs. acentric factor (ω).

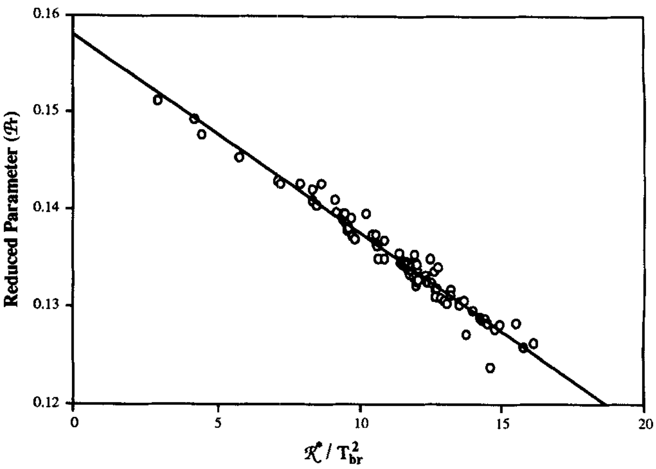

Figure 5. Reduced parameter ($\mathcal{P}_r$) vs. $\mathcal{R}^*/T_{br}^2$.

$\mathcal{R}^*$ is the dimensionless molar refraction defined as $\mathcal{R}^* = \mathcal{R}_m/\mathcal{R}_{m,\text{ref}}$, $\mathcal{R}_m$ is the molar refraction and $\mathcal{R}_{m,\text{ref}}$ is the molar refraction of the reference substance (methane) with a value of 6.987. T_{br} is the reduced normal-boiling-point.

$$\mathcal{P}_0 = 39.6431 \cdot [0.22217 - 2.91042 \times 10^{-3} \cdot (\mathcal{R}^*/T_{br}^2)] \cdot T_c^{13/12}/P_c^{5/6} \qquad (14)$$

Equations 10 and 14 were used along with the Riazi-Mansoori equation of state to predict the surface tension for the 94 compounds of interest. These results are reported in Table 1 from which it can be seen that the predictions obtained from these new equations are quite good. The experimental surface tension data for all 94 compounds can be represented within an overall absolute average deviation (AAD%) of 2.57% for all temperatures investigated.

Hugill and van Welsenes (1986) proposed the following correlation for the prediction of the Sugden's parachor

$$P = 40.1684 \cdot (0.151 - 0.0464 \cdot \omega) \cdot T_c^{13/12}/P_c^{5/6}. \qquad (15)$$

For comparison purposes this correlation was used to predict the surface tension for the compounds of interest using Eq. 2 and calculating the equilibrium densities as explained above. These results are also reported in Table 1. From this table, it may be noticed an overall absolute average deviation of 16.75% for all temperatures investigated for this correlation.

Table 2 contains the comparisons made between the experimental surface tension data and the values predicted by the present method and by other methods (Macleod and Sugden; Brock and Bird, 1955; Sivaraman et al., 1984). This table shows that the method proposed in this article for surface tension calculation generally performs better than the other methods. It can also be noticed that it performs equally well for all representative compounds (i.e., low-boiling-point, linear and branched alkanes, cyclic and branched cyclic, aromatic and alkyl-substituted aromatic, as well as halogenated compounds). It should be pointed out that the method proposed by Sivaraman et al. (1984) was found to be very sensitive to the values of acentric factor employed and to a lesser extent to the values of the critical pressure and temperature. On the other hand, the method proposed in this work is not very sensitive to the value of these physical properties.

Table 2. Our Experimental Data and Predicted Values of Surface Tension[*] vs. Other Methods for Representative Compounds (Low Boiling Point, Linear and Branched Alkanes; Cyclic and Branched Cyclic; Aromatic and Substituted Aromatic; Halogenated Compounds): AAD% = $|(\sigma_{exp} - \sigma_{calc})/\sigma_{exp} \cdot 100|$

					This Work	
Compound	Temp. K	Macleod and Sugden[‡]	Brock and Bird (1955)	Sivaraman et al. (1984)	$\mathcal{P}_0$ and Eq. 10	Eqs. 10 and 14
Methane	93.15	—	12.11	6.37[**]	0.13	1.22
	103.15	—	12.31	8.97[**]	0.57	1.96
	113.15	—	12.81	11.09[**]	0.47	0.87
n-Butane	203.15	11.0	1.6	6.24[**]	0.18	1.53
	233.15	5.2	0.9	6.67[**]	0.86	0.86
n-Heptane	293.15	0.6	0.3	0.89[†]	0.05	0.15
	313.15	0.7	0.1	1.43[†]	0.11	0.22
	323.15	3.1	0.3	1.85[†]	0.02	0.04
n-Nonane	298.15	1.35	0.35	0.58[†]	0.31	1.18
2-Methyl-3-Ethylpentane	273.15	—	0.69	14.65[**]	0.08	0.90
	293.15	—	0.88	15.06[**]	0.32	1.30
	313.15	—	1.05	15.52[**]	0.51	1.47
	333.15	—	1.3	16.04[**]	0.22	1.23
	353.15	—	1.45	16.50[**]	0.31	0.68
	373.15	—	1.51	16.98[**]	1.12	0.15
Cyclopentane	293.15	5.6	2.0	1.46[**]	0.45	1.72
	313.15	2.4	0.1	3.93[**]	1.26	0.25
Cyclohexane	293.15	3.9	4.8	11.44[**]	0.13	2.71
	313.15	3.5	4.5	11.15[**]	0.22	2.40
	333.15	2.2	4.3	10.64[**]	0.33	2.25
Ethylcyclopentane	273.15	—	0.05	9.15[**]	0.19	0.15
	293.15	—	0.47	9.34[**]	0.07	0.44
	313.15	—	0.72	7.96[**]	0.23	0.59
	343.15	—	1.48	10.47[**]	0.69	0.32
Benzene	293.15	5.1	2.0	2.71[†]	0.49	3.5
	313.15	5.6	1.9	2.94[†]	0.19	3.2
	333.15	5.0	0.4	3.29[†]	0.13	3.16
Toluene	293.15	—	0.27	0.35[†]	0.56	1.86
	313.15	—	0.035	0.05[†]	0.26	1.07
	333.15	—	5.56	0.56[†]	1.15	0.18
n-Propyl benzene	313.15	0.8	0.7	2.77[**]	0.26	0.82
	333.15	2.1	0.1	2.88[**]	0.48	0.16
	353.15	3.9	0.7	2.84[**]	1.19	0.52
	373.15	6.6	1.9	2.90[**]	1.49	0.87
Carbon Tetrachloride	288.15	1.1	4.9	48.49[**]	0.32	2.24
	308.15	1.2	5.1	48.40[**]	0.51	2.41
	328.15	1.0	5.0	48.28[**]	0.35	2.30
	348.15	0.1	4.9	48.19[**]	0.10	1.82
	368.15	2.5	4.4	47.78[**]	0.78	1.11

[*] The experimental surface tension data for all compounds were taken from Jasper (1972).

[**] Calculated using the method outlined by Sivaraman et al. using the acentric factor, critical pressure, and temperature reported here.

[†] Calculated using the Sivaraman et al.'s method but values for the acentric factor, critical pressure, and temperature, which differ slightly from the ones reported here.

[‡] Taken from Reid et al. (1988).

[††] Not reported in this reference.

Conclusions

This article presents a new expression for surface tension which contains a temperature correction term derived from statistical mechanics. It also introduces a corresponding-states correlation to predict the parameter $\mathcal{P}_0$ in this new equation as a function of molar refraction and normal boiling point temperature. This represents an accurate and generalized expression to predict surface tensions of pure fluids of industrial interest.

Acknowledgment

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Notation

a = energy parameter in equation of state
b = volume parameter in equation of state
$c(i)$ = one-particle direct correlation function at the temperature of interest

g = an exponent related to the difference in densities
$\mathcal{P}_0$ = compound-characteristic constant similar to the Sugden's parachor
$\mathcal{P}_r$ = reduced parameter $\mathcal{P}_0$
T_b = normal-boiling-point temperature
r_{ij} = separation distance between particles i and j
$\mathbf{r}_{ij}$ = vector joining the center of masses of particles i and j

Greek letters

α = polarizability of the molecules
γ = critical exponent for surface tension
δ = temperature-dependent parameter in equation of state
ρ_c = critical density
Ω_i = orientation of particle i

Subscripts

l = liquid
r = reduced property
v = vapor

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