Interfacial Energy and the Law of Corresponding States

Aly J. Castellanos,*,†,‡,§ **German Urbina-Villalba,**§ **and Máximo García-Sucre**§

Facultad de Ciencias y Tecnología, Escuela de Química, Universidad de Carabobo,
Edo. Carabobo, Venezuela, Facultad de Ciencias, Escuela de Química, Postgrado,
Universidad Central de Venezuela, Caracas, Venezuela, and Centro de Física,
Instituto Venezolano de Investigaciones Científicas (IVIC), Km. 11,
Carretera Panamericana, Apartado 21827, Caracas 1020-A, Venezuela

An extension of the mesoscopic model previously developed for fluid/liquid interfaces [*J. Phys. Chem. A* **2003**, *107*, 875; **2003**, *107*, 883] is presented. The formalism is applied here to the vapor/liquid interface of nonpolar compounds. The treatment takes into consideration the nonuniform nature of the interfacial region and the mechanisms through which its excess energy is reversibly stored. Arguments are given in favor of using the interfacial energy (instead of the interfacial tension) in the scheme of corresponding states. To calculate the free energy accumulated at the interface, an expression for the interfacial area of the molecules becomes necessary. A temperature-dependent expression for this variable based on the projection of the molecular area on the interface is implemented. The resulting correlation has an average absolute deviation for the interfacial tension of only 0.5% for 62 representative organic compounds.

Introduction

One of the first scaled-expressions of the surface tension (γ) was the one proposed by Eötvös back in 1886:[1−24]

$$\gamma \, V^{2/3} = a(T_c - T) \tag{1}$$

Here, V is the molar volume, T is the temperature, a is a constant, and c is a subscript that identifies the critical point. In this equation, the 2/3 power of V is meant to transform the molar volume into an effective surface area. The fact that *variable V* is not substituted by its *constant* value at the critical point (V_c) implicitly recognizes the dependence of the interfacial area with the temperature.

Since the formulation of eq 1, several empirical relations have become available for the evaluation of the surface tension. Sastri and Rao[3] for example, proposed an expression based on the behavior of the tension at the boiling point (b):

$$\gamma = K \, T_b^x \, P_c^y \, T_{br}^z \, [(T_c - T)/(T_c - T_b)]^m \tag{2}$$

where $T_{br} = T_b/T_c$, P_c stands for the critical pressure, and x, y, z, and m are parameters that depend on the chemical nature of the fluid. The maximum absolute deviation of the tension provided by eq 2 is 3.9% for 40 liquids, including acids and alcohols. However, despite its intrinsic value as empirical relation, eq 2 cannot be harmonized with the formalism of corresponding states due to its analytical form.

Different theoretical developments aimed to a broader generalization of the theory of corresponding states are also available.[4−11] The fundamental problem of scaled expressions

of the surface tension is that the tension vanishes at the critical point ($\gamma_c = 0$). As a consequence, the tension does not have a reduced analogue like T_r, V_r, and P_r since $\gamma_r = \gamma/\gamma_c$ is not defined. On the other hand, the use of nondimensional quotients such as $\gamma V_c^{2/3}/RT_c$ implicitly defines a critical surface tension of reference equal to $RT_c/V_c^{2/3}$ with no direct physical meaning.

Despite the above considerations, use of the ratio $\gamma V_c^{2/3}/T_c$ allowed Rice and Teja[12] to successfully predict the surface tension of several alkane isomers, alcohols, and even six binary mixtures under the principle of corresponding states. For this purpose, the acentric factor (ω) of Pitzer[13] was used along with a first-order expansion of the compressibility Z ($=PV/RT$)

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{3}$$

In eq 3, $Z^{(0)}$ stands for the compressibility of a simple fluid with zero acentric factor. Deviation function $Z^{(1)}$ is difficult to evaluate but can be suitably estimated using reference fluids. As a result an analytic expression for the reduced surface tension of the liquids can be obtained in terms of the data of two reference-fluids.[12] Extensions of this methodology were equally successful for reproducing the behavior of more than 86 compounds and 30 binary and multicomponent mixtures.[14]

Lee and Kesler[15] used eq 3 with argon and octane as reference fluids in order to evaluate the residual properties of a series of organic compounds. For this purpose, a generalized thermodynamic correlation based on a three-parameter formulation of the law of corresponding states was employed. This results from the fact that the second virial coefficient (B) can be expressed in terms of the acentric factor

$$\frac{BP_c}{RT_c} = B^{(0)} + \omega B^{(1)} \tag{4}$$

where $B^{(0)}$ and $B^{(1)}$ are functions of T_r only. Since the *residual* thermodynamic functions $(\Delta TF)^R$ (where $(\Delta TF)^R = \Delta U^R$, ΔH^R,

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* To whom correspondence should be addressed. E-mail: ajcastel@uc.edu.ve.
† Universidad de Carabobo.
‡ Universidad Central de Venezuela.
§ Instituto Venezolano de Investigaciones Científicas.

etc) can be expressed in terms of the second virial coefficient, generalized correlations for the quotients $\Delta(TP)^R/RT_c$ can also be obtained as a function of the acentric factor.[16] Furthermore, scaled free energies terms such as $[\Delta(PV)]^R/RT_c$ also fulfill this extended principle.[17] Using eq 4, it was shown in ref 16 that a residual energy like PV can be expressed in the form of two contributions: $[\Delta(PV)]^R/RT_c = (\Delta H^R - \Delta U^R)^{(0)}/RT_c + \omega (\Delta H^R - \Delta U^R)^{(1)}/RT_c$. As will be shown here, this alternative application of Pitzer's formalism[13] can be extended for the evaluation of the interfacial energy if this energy can be conveniently expressed in terms of residual functions.

In a recent communication,[18] the concept of an elastic field was introduced in order to describe the mechanism through which energy can be reversibly stored as a consequence of the contact between partially miscible or completely immiscible phases. That formalism, identified in the following as model "M", allows the theoretical description of the interfacial tension in single and multicomponent systems. As shown in ref 19 for the case of a one-component system in vapor−liquid equilibrium, the interfacial energy is basically accumulated within the liquid sub-phase. This idea is not clearly visualized in the widely accepted continuous interface (CI) van der Waals model,[20] due to the continuous (yet nonuniform) description of the interface. However, the spatial dependence of the mean field potential calculated for this theory confirms the existence of two subphases for a vapor−liquid system and also evidences the mayor accumulation of energy in the liquid region (see Appendix A).

In this work, an expression for the interfacial energy, compatible with model M,[18,19] is obtained using an ideal gas as a reference state. Second, a convenient expression for the surface molar area, required for the evaluation of the interfacial energy in the context of the law of corresponding states, is proposed. Finally, a particular extension of the two-reference-fluids methodology proposed by Lee and Kesler[15] for residual energies is implemented. This formalism allows the successful application of the theory of corresponding states to the vapor/liquid equilibrium of at least 62 nonpolar liquids.

Interfacial Energy as a Residual Quantity

The model described in refs 18 and 19 starts with the common assumption that the free energy accumulated in a liquid phase (α) results from a distortion of the bulk phase structure near the interface. In the case of a vapor/liquid interface,[19] the bulk properties of the gas phase are not significantly affected by a sizable change in the mean intermolecular distance, which makes this phase ineffective to store (elastic) potential energy. Due to these considerations, the surface tension arises mainly from the contribution of the liquid sub-phase (σ_A) adjacent to an imaginary superficial plane located at $z = 0$, which delimits the sharp change in the density of the phases occurring at the interface. According to model M, the tension of the gas/liquid interface is determined by the following expression:

$$\Delta\gamma_A^\sigma = \sum_i g_\alpha^2(-\epsilon)h_i(-\epsilon)N_i y_i \delta_{\sigma A} \quad (5)$$

where $g_\alpha^2(-\epsilon)$ is an average elastic field that diminishes in the liquid phase α as the depth in the direction of $-z$ increases, ϵ is a macroscopic differential near to zero, and $h_i(-\epsilon)$ is the intrinsic contribution of the molecule i to the free energy of the plane located in the sub-phase σ_A. ($h_i(-\epsilon)$ multiplied by the field yields the potential energy stored in the considered plane). When the component i refers to a pure compound A,
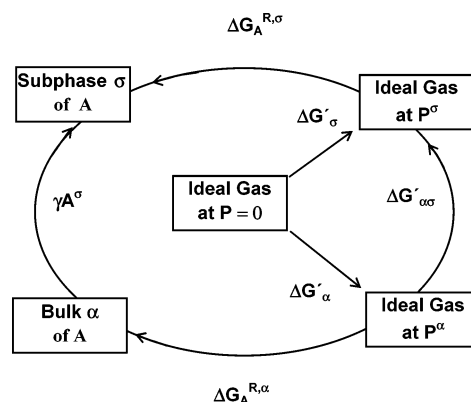

Figure 1. Free energy of formation of one mole of interface taking as a reference state that of an ideal gas at $P = 0$ (see text). Values of $\Delta G'$ stand for isothermal changes of the system with the intermolecular interaction field "turned off".

$N_A y_A \delta_{\sigma_A} = n_A^{\sigma_A}/A^{\sigma_A}$, and eq 5 reduces to the form[19]

$$\gamma^{\sigma_A} A^{\sigma_A} = g_\alpha^2(-\epsilon)h_A(-\epsilon)n_A^{\sigma_A} \quad (6)$$

In this case h_A is function of z only since the chemical environment is not perturbed by other components. It is only affected by the space configuration of the molecules of A.

The rupture of the uniformity of the liquid at the interface may be interpreted as a response to the elastic field defined in the ref 18, whose propagation goes from the plane $z = 0$ to the "bulk" of the liquid. Thermodynamically speaking, this effect is included in the absolute interfacial activity λ_A^σ, better known as the fugacity. As shown in ref 19

$$RT \ln \frac{\lambda_A^{\sigma_A}}{\lambda_A^\alpha} = g_\alpha^2(-\epsilon)h_A(-\epsilon) \quad (7)$$

where $\lambda_A^{\sigma_A}$ is the fugacity of the matrix component A at the subphase σ_A, and λ_A^α is the corresponding fugacity of A in bulk phase α.

Let us set the reference state of the system as that of a mole of pure compound A behaving as an ideal gas at zero pressure (Figure 1). The residual energy of the "bulk" of the liquid A (α) at saturation pressure (P^α) can be calculated from eq 8

$$\frac{\Delta G^{R,\alpha}}{RT} = \int_0^{P^\alpha} (Z^\alpha - 1)\frac{dP}{P} \quad (8)$$

In the case of liquid−vapor equilibrium, P^α is equal to the saturation pressure (P^{sat}). As for the pressure P^σ in the sub-phase σ_A, it is supposed that the global effect of the tensor component P_{xy} on any molecule A located in the interfacial region, will be different to the pressure that similar molecules feel in the "bulk" of the liquid. Thus, pressure P^σ can be estimated as the average of $P(z)$ $(= \mathbf{P}_z - \mathbf{P}_{xy})$ on the profile of the interfacial zone

$$P^\sigma = \frac{\int_{-\delta_\sigma}^0 P(z)\,dz}{\delta_\sigma} \quad (9)$$

Then, the residual energy in the interfacial region may be written as

$$\frac{\Delta G^{R\sigma}}{RT} = \int_0^{P^\sigma} (Z^\sigma - 1)\frac{dP}{P} \quad (10)$$

Since the calculation of the distribution function in the interfacial region (using the grand canonical ensemble) includes the presence of an external field (elastic field in model M[18]), the factor of compressibility Z^σ differs from Z^α. This is a consequence of the existence of the neighbor phase β, which breaks the uniformity of the interfacial region σ_A.

Equations 8 and 10 can be written in a more convenient way in terms of the fugacity λ_i (or the fugacity coefficient $\phi_i = \lambda_i/P_i)^{21}$

$$\frac{\Delta G_A^{R,\alpha}}{RT} = Ln \frac{\lambda_A^\alpha}{P_A^\alpha} \quad \text{or} \quad \frac{\Delta G_A^{R,\alpha}}{RT} = Ln\,\phi_A^\alpha \qquad (11a)$$

and

$$\frac{\Delta G_A^{R,\sigma}}{RT} = Ln \frac{\lambda_A^\sigma}{P_A^\sigma} \quad \text{or} \quad \frac{\Delta G_A^{R,\sigma}}{RT} = Ln\,\phi_A^\sigma \qquad (11b)$$

Since the Gibbs free energy change corresponding to a change of pressure of an ideal gas from P^α to P^σ in an isothermal process is equal to

$$\frac{\Delta G'_{\alpha\sigma}}{RT} = Ln\frac{P_A^\sigma}{P_A^\alpha} \qquad (12)$$

the residual energy accumulated at the interface will be given by (see Figure 1)

$$\frac{\gamma_A^\sigma A_A^\sigma}{RT} = \left(\frac{\Delta G_A^{R\sigma}}{RT} - \frac{\Delta G_A^{R\alpha}}{RT}\right) + \frac{\Delta G'_{\alpha\sigma}}{RT} \qquad (13)$$

This last equation is equivalent to the expression of the interfacial energy in terms of the standard fugacities of the bulk liquid and the interface previously deduced for model M (eq 4 in ref 19). Yet, eq 13 is more convenient in this case for reasons that will be clear below.

Interfacial Energy and the Principle of Corresponding States

Pitzer[13] established a number of requirements for the application of the law of corresponding states. First, classical statistical mechanics is supposed to be valid. Second, the molecules have to have spherical symmetry or being free of quick rotation. Third, the vibrations along the intermolecular distance should be similar in the gas and liquid phases. Fourth, the potential energy should be expressed as a function of the variation of the intermolecular distance. Finally, the potential energy associated to the interaction of a couple of molecules should be a universal function (Ψ) depending on reduced characteristic parameters

$$\Psi = f\left(\frac{kT}{\varepsilon}, \frac{r}{\sigma_c}\right) \qquad (14)$$

where σ_c stands for the cross section of the molecule.

Years ago, Guggenheim[7] carried out an extensive revision on the relevancy, limitations, and applications of this principle. In that work, the author examined the case of the surface tension, accepting the existence of a universal intermolecular surface potential similar to the potential given in eq 14. According to this argument, it was concluded that $\{\gamma V_c^{2/3}\}/\{kT_c\}$ is a universal function of T/T_c. However, it is interesting to note that this procedure only reduces one intensive term (tension), while

its conjugated variable (the surface molar area) is substituted by a constant value ($V_c^{2/3}$).

In the model M,[18] it is necessary to balance the forces plane by the plane in the axial direction (z). Furthermore, a balance of forces should be guaranteed within each plane. Such balance depends on the surface molar area of the compounds in each plane. Suppression of this variable using the corresponding-states scheme implies generalization of the mechanisms of energy storage by purposely omitting the structural information characteristic of each compound, information that should be taken into account in the mechanical balance of the interface. On the other hand, one of the consequences of reducing the surface tension can only be observed when the correlations of linear hydrocarbon molecules are extrapolated to ramified molecules or to aromatic ones (see Appendix B). Faizullin[22] reported an interesting relationship between the surface tension and $\{\Delta H_{vap}\}/\{v_L\}$ (where ΔH_{vap} is the enthalpy of vaporization and v_L the molar volume of the liquid). This parameter is an equivalent measure of the internal pressure of the liquid, yet this pressure depends strongly on the density of intermolecular bonds, and in turn on the structure and spatial configuration of the compound in the liquid state. In our view, the most significant result of that work is the independence of the referred correlation with the molecular structure.

If γA^σ is supposed to arise from a residual Gibbs free energy the most appropriate form for reducing this function should be $\gamma A^\sigma/RT_c$, as in all other residual energies (ΔG^R, ΔH^R, ΔU^R, etc.). For a mol of molecules at the interface, eq 13 can be extended to the corresponding states scheme, in the following way:

$$\frac{\gamma_A^\sigma A_A^\sigma}{RT_c} = \left(\frac{\Delta G_A^{R\sigma}}{RT_c} - \frac{\Delta G_A^{R\alpha}}{RT_c}\right) + \frac{\Delta G'_{\alpha\sigma}}{RT_c} \qquad (15)$$

Using eqs 11 and 12 the above expression transforms into

$$\frac{\gamma_A^\sigma A_A^\sigma}{RT_c} = T_r \ln \frac{\phi_A^\sigma}{\phi_A^\alpha} - T_r \ln \frac{P_A^\sigma}{P_A^\alpha} \qquad (16)$$

It is a well-known fact that $\ln \phi_A^{sat\,16}$ and $\ln(P_A^{sat}/P_c)^{23}$ are functions that follow very well the corresponding states principle. In the case of a vapor−liquid equilibrium, ϕ_A^{sat} and P_A^{sat} correspond to ϕ_A^α and P_A^α, respectively.

Application of the Law of Corresponding States using the acentric factor of Pitzer

The usefulness of the acentric factor of Pitzer as a measure of the deviation of the spherical symmetry of a molecule is well-known. It has been successfully employed in the calculation of the extensive properties of nonpolar fluids,[24−25] as well as in the evaluation of the surface tension of pure compounds[10,11] and their mixtures.[26] In this work, we follow the suggestion of Lee and Kesler,[15] and consider argon ($\omega^{(0)} = 0.0000$) and n-octane ($\omega^{(2)} = 0.3978$) as simple fluids of reference.

To evaluate the term $\gamma A^\sigma/RT_c$, the value of the molar area of surface (A^σ) must be forwarded. However, this variable is not susceptible of direct measurement. In a previous work,[19] we have successfully used its relation with the surface density. According to Suárez et al.,[27] the use of the surface molar area of van der Waals (A_W) as a parameter to estimate the surface tension of binary systems, gives amazingly good results.[28] A_W was already considered as a parameter in several models of solutions such as UNIQUAC, UNIFAC, etc.[29] On the other hand, the volume of van der Waals (V_w) was determined by

Bondi[30] using X-rays diffraction data for non metallic compounds, along with a method for calculating group contributions to V_w and A_W. In that reference a constant relationship was established between the ratio of V_w and $N_{Av}(\pi/6)\sigma_{LJ}^3$ (where σ_{LJ} is the effective diameter of the Lennard-Jones potential), whereas no direct relationship was found between V_w and V_c. This means that the group contributions are not the same for V_w and V_c. Jalenti, López, and Azzi[31] studied the behavior of V_w as a function of the temperature taking into consideration that there is a linear dependence between the enthalpy of vaporization $\Delta H_v(T)$ at a given temperature T, and V_w/V_e

$$\Delta H_v(T) = K[V_w(T)/V_e(T)] \tag{17}$$

Here V_e is the empty volume or free molecular volume. Let us define variable ϵ_e as the fraction of empty volume at the boiling point, previously estimated by Jalenti et al.[31] to be equal to 0.5 for all fluids. This value is very similar to the maximum volume fraction occupied by spheres of equal size in a cubic arrangement (0.52). The fact that $\epsilon_e \sim 0.5$ could be an indication that despite their preferred conformations in the condensed state, the majority of substances undertake a simple cubic configuration at the boiling point. In the absence of further information, the reason for this behavior is only subject to speculation. However, it is possible that the molecules of fluid exhibit an effective spherical potential at the boiling temperature due the quick rotations that may precede the evaporation process. As a consequence, a cubic arrangement with a volume fraction around 0.5 may occur. This explanation is compatible with the findings of Faizullin[22] and the requirements of Pitzer[13] for the application of the principle of corresponding states.

Taking the boiling temperature (T_b) as a reference point, an expression for V_w at any temperature T, similar to the one proposed by Jalenti et al.[31] can be obtained

$$V_w(T) = \frac{V_L(T)}{1 + \left[\dfrac{\epsilon_e}{1 - \epsilon_e}\right]\dfrac{\Delta H_v(T_b)}{\Delta H_v(T)}} \tag{18}$$

To evaluate $V_w(T)$, the quotient of the enthalpies of vaporization appearing in eq 18 can be substituted by the relation of Watson[32]

$$\frac{\Delta H_v(T)}{\Delta H_v(T_b)} = \left(\frac{1 - T_r}{1 - T_{br}}\right)^n \tag{19}$$

where T_{br} is the reduce temperature at the boiling point, and n is a superscript that be can calculated as a function of the reduced boiling temperature ($n = 0.74T_{br} - 0.116$).[33]

In this work, it is considered that the surface molar area $A^\sigma(T)$ is a function of T that conveys information about the structure (space configuration and molecular conformation) of a compound at the interface. The structure corresponding to a minimum conformational energy within the interface may be different to that occurring in the "bulk" of the fluid, where a larger symmetry exists. This different conformation at the interface may correspond to a different value of the empty fraction ϵ_e due to the generation or extinction of interstitial spaces. On the other hand, the space configuration (or packaging factor) in the interface could also be different to the one that the compound has in the bulk liquid, since the rupture of the uniformity liquid structure at the interfacial boundary should promote changes in the effective coordination of the molecules. Accordingly, we propose to express $A^\sigma(T)$ as a product of two factors

$$A^\sigma(T) = \Theta A_W(T) \tag{20}$$

Variable $A_W(T)$ depends on the molecular structure, whereas the factor Θ is a "projection" function that transforms the surface area of a molecule to the effective area occupied by the molecule at the interfacial plane. Function Θ contains information about the possible changes of configuration that the molecules may suffer when approaching the interface. It might also be expected that Θ will be affected by the thermal energy of the system. In the case of pure nonpolar fluids, function Θ could be a universal function of the thermal energy relative to the critical point, i.e., the same one for all fluids at the same value T/T_c.

Assuming that A_W is a simple function of the van der Waals volume (V_w)

$$A_W(T) = k_R V_w^{2/3}(T) \tag{21}$$

The value of the constant k_R in eq 21 can be obtained from the value of A_w of n-octane at $T = 298$ K and the respective group contributions, using the parameter (Q_k) proposed by Gmehling et al.[34] in a previous modification of the UNIFAC method

$$A_{W,i} = 2.5 \times 10^9 \sum_k v_{k,i} Q_k \tag{22}$$

Here Q_k is the contribution of the functional group k to the van der Waals area, and $v_{k,i}$ is the number of times that this group occurs in molecule i. The value obtained for k_R in eq 21 is equal to 6164.0213 if V_w is introduced in cm^3/mole and the resulting area is expressed in m^2/mol. The surface molar area of van der Waals corresponding to argon and n-octane (reference fluids) are assigned arbitrarily in order to reproduce a constant value $\epsilon_e = 0.5000$. For all other fluids ϵ_e is taken as an adjustable parameter.

It is clear that k_R depends strongly on the method of estimation of A_w for the reference compound (eq 21). However, it will be shown below (eq 23–27) that k_R, or more generally $\Theta(T_r)$, does not appear in the final equations of the interfacial energy (eq 26). This means that the exact magnitude of A_w is not important as long as it changes consistently with the molecular structure. Thus, the value of k_R calculated for water using the data of $V_w^{2/3}$ and A_w reported in refs 31 and 27 is 1631.9931, considerably lower than the one calculated for octane using eq 22.

Based on the assumptions expressed in eq 20, a convenient reduced variable for simple fluids will be

$$\left(\frac{\gamma A^\sigma}{RT_c}\right)^{(0)} = \Theta(T_r)\left(\frac{\gamma A_W}{RT_c}\right)^{(0)} \tag{23}$$

The corresponding correction function is then given by

$$\left(\frac{\gamma A^\sigma}{RT_c}\right)^{(1)} = \frac{\Theta(T_r)}{\omega^{(2)}}\left[\left(\frac{\gamma A_W}{RT_c}\right)^{(2)} - \left(\frac{\gamma A_W}{RT_c}\right)^{(0)}\right] \tag{24}$$

Index 2 in the above equation refers to the reference compound n-octane. Assuming that the residual properties of the compound A (eq 16) fulfills the principle of corresponding states suggested by Pitzer,[13] the following first-order Taylor expansion in the acentric factor ω_A can be proposed:

$$\left(\frac{\gamma_A^\sigma A_A^\sigma}{RT_c}\right) = \left(\frac{\gamma A^\sigma}{RT_c}\right)^{(0)} + \omega_A\left(\frac{\gamma A^\sigma}{RT_c}\right)^{(1)} \tag{25}$$

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If $\Theta(T_r)$ is a universal function, the reduced surface free energy of compound A given by $(\gamma_A^\sigma A_A^\sigma/RT_c)$ can be substituted by $\Theta(Tr)(\gamma_A^\sigma A_W/RT_c)$. From eqs 23−25, we have

$$\left(\frac{\gamma_A^\sigma A_W}{RT_c}\right) = \left(\frac{\gamma A_W}{RT_c}\right)^{(0)} + \omega_A\left(\frac{\gamma A_W}{RT_c}\right)^{(1)} \quad (26)$$

where

$$\left(\frac{\gamma A_W}{RT_c}\right)^{(1)} = \frac{1}{\omega^{(2)}}\left[\left(\frac{\gamma A_W}{RT_c}\right)^{(2)} - \left(\frac{\gamma A_W}{RT_c}\right)^{(0)}\right] \quad (27)$$

is the correction function. Thus, the interfacial energy can be calculated employing two reference substances, an analogous procedure to that employed by Rice and Teja[12] for the calculation of the reduced surface tension of pure systems and binary mixtures.

Results

The van der Waals area of argon was calculated using eq 21 along with the data of Stewart and Jacobsen.[35] As can be observed in Figure 2a, this area presents a maximum as a function of the reduced temperature. In the case of *n*-octane, we used the data published by Perry.[36] As one observes in Figure 2b, the behavior is similar to that of the argon. The area presents a sizable continuous variation with the temperature. In both cases we have fixed the value of ϵ_e to 0.5000.

To calculate the reduced surface free energy for argon, the data of parameters of Sugden published by Gielen and Verbeke[37] were used. In the case of *n*-octane, the data of surface tension published by Grigoryev et al.[38] was employed. In both cases, the reduced surface free energy can be well adjusted to the following equation:

$$\left(\frac{\gamma A_W}{RT_c}\right)^{(i)} = (G_1^i + G_2^i T_r) + \sum_{x=1}^{7} G_{x+2}^i(1 - T_r)^{(x-1)/4} \quad (28)$$

Table 1 shows the parameters of eq 28 corresponding to Argon ($i = 0$) and to the correction term ($i = 2$) for a range of reduced temperatures going from 0.380 to 0.980. Outside this range, good results are only obtained in a few cases.

Table 2 presents the results of applying eq 26 to 62 compounds corresponding to different hydrocarbons families. Apart from a few exceptions, the absolute deviation (AD) of the surface tensions is below 0.60%. The larger deviations were observed in those cases where most of the data corresponds to a value of T_r larger than 0.80. The average value of the absolute deviation (AAD) for compound is 0.50%. To calculate the van der Waals area of the compounds listed in Table 2, the values of the density of the liquids were used (except for the case of methane and propane) along with the method of Hankinson and Thomson.[44] In the case of some paraffins of eight and nine carbon atoms (C8 and C9), the method of Cambell et al.[45] was employed. In this case, "α" and "β" were calculated using eq 17 from the same reference, and the data of critical volumes and densities at 20 °C, published by Wakeham et al.[39]

It is clear that the fraction of empty volume ϵ_e at the boiling point is a characteristic parameter for each compound (see Table 2). Minor deviations of this parameter from the value of 0.5 can generate substantial differences in the interfacial energy (see Appendix B). Variable ϵ_e allows fitting of possible relative differences between A^σ and A_w calculated by using eq 22. This is equivalent to assume that this parameter contains information
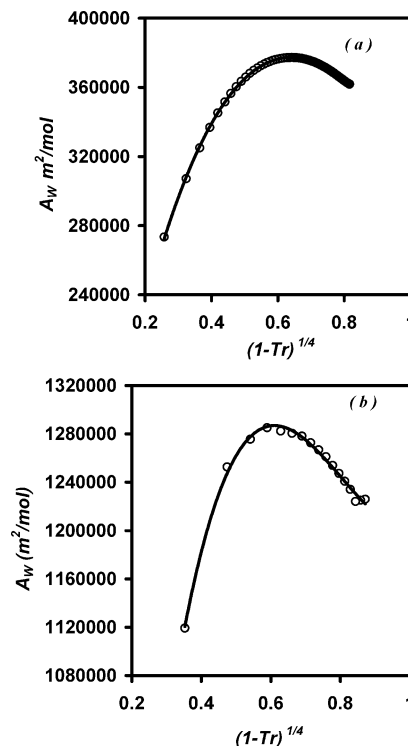

Figure 2. Temperature behavior of the van der Waals area for argon (a) and *n*-octane (b), calculated by mean of eq 21.

TABLE 1: Constants of Equation 28

$G_1^\circ = 8.5452$	$G_1^1 = 10.541$
$G_2^\circ = -8.9321$	$G_2^1 = -11.971$
$G_3^\circ = 0.6381$	$G_3^1 = 14.264$
$G_4^\circ = -3.0958$	$G_4^1 = -111.58$
$G_5^\circ = 15.344$	$G_5^1 = 372.62$
$G_6^\circ = -38.071$	$G_6^1 = -596.33$
$G_7^\circ = 33.974$	$G_7^1 = 443.95$
$G_8^\circ = -0.4083$	$G_8^1 = -122.01$
$G_9^\circ = -8.6391$	$G_9^1 = 0$

on the molecular structure at the interface. In some cases, it is observed for a group of isomers (for example C_8H_{18}) that the molar free volume at the boiling point increases as the ramifications of the molecule grow. Except for some exceptions, it is possible to observe that the free volume in linear chains (n-paraffins) diminishes when increasing the number of $-CH_2-$ groups. This might be due to an increase of the correlation at short range that has also been observed in some mixing processes.[20] However, the uncertainty in our estimates of the density of the liquid prevents us to reach a more precise conclusion.

Figure 3 also shows the agreement of the model with the data of surface tension of methane and propane, including values very near the critical point. The good fitting of eq 26 to the experimental data allows us to conclude that the function $\Theta(T_r)$ defined in eq 20, does tend to be an universal function of the reduced temperature (T_r) for nonpolar fluids.

Conclusions

Use of a formerly developed theory based on the accumulation of elastic energy at the interface[18,19] allows the formulation of a convenient expression of the interfacial energy that follows the law of corresponding states. Evaluation of this expression requires an appropriate expression for the interfacial area, which was calculated as a projection of the molecular area over the interface. Predictions of the surface tension using the present

TABLE 2: Results from Equation 26[a]

formulas	compound	N	T_r	ϵ_e	w	average deviation	ref
CH_4	methane	12	0.839−0.986	0.5017	0.011	1.43	A
C_3H_8	propane	30	0.739−0.987	0.5387	0.153	3.57	B
C_4H_{10}	*n*-butane	11	0.558−0.712	0.5145	0.199	0.62	C
	isobutane	42	0.580−0.979	0.5267	0.183	1.39	D, B
C_5H_{12}	*n*-pentane	11	0.385−0.969	0.4877	0.251	4.38	E
	isopentane	5	0.550−0.648	0.5194	0.227	0.28	C
C_6H_6	benzene	8	0.503−0.628	0.5195	0.212	0.05	C
C_6H_{12}	1-hexene	7	0.562−0.661	0.5080	0.285	0.13	C
C_6H_{14}	*n*-hexane	11	0.392−0.981	0.5067	0.296	1.81	C
	2-methyl-pentane	5	0.570−0.671	0.5215	0.278	0.35	C
	3-methyl-pentane	7	0.561−0.660	0.5146	0.272	0.15	C
	2,2-di-methyl-butane	5	0.579−0.641	0.5308	0.232	0.19	C
	2,3-di-methyl-butane	6	0.566−0.646	0.5176	0.247	0.21	C
C_7H_8	toluene	10	0.478−0.630	0.4855	0.263	0.38	C
C_7H_{14}	1-heptene	9	0.526−0.657	0.4813	0.358	0.41	C
C_7H_{16}	*n*-heptane	18	0.339−0.985	0.4891	0.349	1.61	F
	2-methyl-hexane	12	0.477−0.685	0.5097	0.329	0.55	C
	3-methyl-hexane	12	0.473−0.678	0.5006	0.323	0.61	C
	3-ethyl-pentane	11	0.468−0.653	0.5134	0.310	0.33	C
	2, 2-di-methyl-pentane	12	0.486−0.678	0.5183	0.287	0.27	C
	2, 3-di-methyl-pentane	11	0.471−0.657	0.5125	0.296	0.22	C
	2, 4-di-methyl-pentane	11	0.487−0.679	0.5150	0.264	0.30	C
	3, 3-di-methyl-pentane	11	0.472−0.658	0.5215	0.273	0.25	C
	2,2,3-tri-methyl-butane	10	0.533−0.683	0.5177	0.250	0.45	C
C_8H_{10}	ethyl-benzene	10	0.458−0.605	0.4975	0.302	0.13	C
	o-xylene	10	0.449−0.592	0.4768	0.310	0.11	C
	m-xylene	10	0.459−0.605	0.4774	0.325	0.15	C
	p-xylene	9	0.476−0.605	0.4723	0.320	0.19	C
C_8H_{16}	1-octene	11	0.500−0.658	0.4892	0.386	0.26	C
C_8H_{18}	2-methyl-heptane	11	0.506−0.667	0.5001‡	0.378	0.28	C
	3-methyl-heptane	11	0.502−0.662	0.5040‡	0.370	0.59	C
	4-methyl-heptane	11	0.504−0.664	0.5040‡	0.371	0.57	C
	3-ethyl-hexane	11	0.500−0.660	0.5072‡	0.361	0.75	C
	3-ethyl-2-methyl-pentane	11	0.499−0.658	0.5145‡	0.254	0.29	C
	3-ethyl-3-methyl-pentane	11	0.491 − 0.647	0.5163‡	0.267	0.21	C
	2, 2, 3-tri-methyl-pentane	11	0.502−0.662	0.5200‡	0.254	0.22	C
	2, 2, 4-tri-methyl-pentane	11	0.520−0.686	0.5179‡	0.266	0.17	C
	2, 3, 3-tri-methyl-pentane	11	0.494−0.651	0.5182‡	0.269	0.26	C
	2, 3, 4-tri-methyl-pentane	11	0.500−0.659	0.5153‡	0.267	0.24	C
C_9H_{18}	*n*-nonene	11	0.478−0.630	0.4916	0.430	0.20	C
C_9H_{20}	*n*-nonane	12	0.476−0.661	0.4847	0.445	0.21	C
	2-methyl-octane	7	0.482−0.568	0.4869‡	0.423	0.13	C
	2, 2, 3-tri-methyl-hexane	7	0.482−0.567	0.5233‡	0.332	0.21	C
	2, 2, 4-tri-methyl-hexane	7	0.494−0.581	0.5332‡	0.321	0.15	C
	2, 2, 5-tri-methyl-hexane	7	0.499−0.581	0.5146‡	0.357	0.12	C
	3, 3-di-ethyl-pentane	7	0.464−0.546	0.5065‡	0.338	0.41	C
	2,2,3,3-tetra methyl-pentane	7	0.466−0.548	0.5196‡	0.303	0.16	C
	2,2,3,4-tetra methyl-pentane	7	0.478−0.562	0.5185‡	0.313	0.01	C
$C_{10}H_{20}$	2,2,4,4-tetra methyl-pentane	7	0.493−0.580	0.5226‡	0.312	0.37	C
$C_{10}H_{22}$	2,3,3,4-tetra methyl-pentane	7	0.466−0.548	0.5276‡	0.313	0.27	C
$C_{11}H_{24}$	*n*-decene	11	0.460−0.606	0.4788	0.491	0.22	C
$C_{12}H_{26}$	*n*-decane	12	0.458−0.637	0.4815	0.489	0.23	C
$C_{13}H_{28}$	*n*-undecane	12	0.443−0.615	0.4743	0.535	0.31	C
$C_{14}H_{30}$	*n*-dodecane	12	0.430−0.597	0.4727	0.575	0.29	C
$C_{15}H_{32}$	*n*-tridecane	12	0.419−0.582	0.4708	0.619	0.27	C
$C_{16}H_{34}$	*n*-tetradecane	12	0.409−0.568	0.4830	0.626	0.44	C
$C_{17}H_{36}$	*n*-pentadecane	11	0.414−0.555	0.4612	0.706	0.31	C
$C_{18}H_{38}$	*n*-hexadecane	11	0.406−0.544	0.4550	0.742	0.41	C
$C_{19}H_{40}$	*n*-heptadecane	10	0.412−0.534	0.4670	0.770	0.36	C
$C_{20}H_{42}$	*n*-octadecane	10	0.405−0.525	0.4706	0.790	0.47	C
	n-nonadecane	11	0.385−0.517	0.4803	0.827	0.43	C
	eicosane	11	0.380−0.510	0.4489	0.907	0.38	C

[a] The density was calculated using data from ref 39. Tension data was taken from: A, Gielen, H. et al ref 37; B, Baidakov, V. G. et al. ref 40; C, Jasper, J. et al. ref 41; D, Coffin, C. C. et al. ref 42; E, Grigoryev, B. A. et al. ref 38; F, Volyak, L. D. et al. ref 43. The average deviation was calculated using the following formula, where N is the number of points specified in the third column: A.D. = $\{\Sigma_N |[\gamma_{cal} - \gamma_{exp}]/\gamma_{exp}| \times 100\}/N$.

expression are satisfactorily accurate for a reasonably large list of organic compounds.

In this work, the described methodology was only applied to nonpolar compounds. The reason for this limitation is that the generalized expressions of the residual energies previously

reported in the literature[13,15−16] were specifically deduced for nonpolar and nonassociated fluids. However, Rice and Teja[12] proved that the formalism of Pitzer[13] also reproduces the values of the surface tension of alcohols with a good accuracy. As discussed by these authors, such applications require the use of
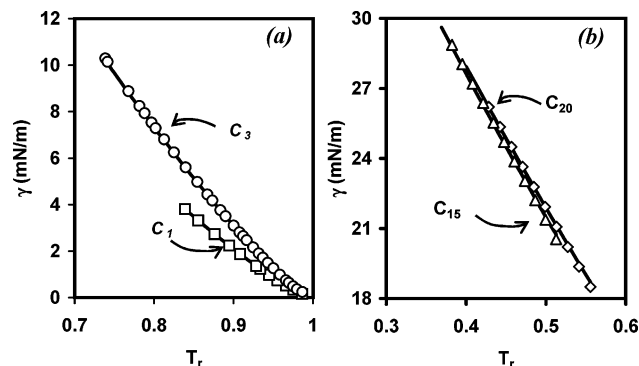
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Figure 3. Surface tension of (a) methane and propane, and (b) pentadecane and eicosane, as a function of the reduced temperature up to near the critical point. (○) Experimental values. (—) Calculated values from eq 26.

representative reference molecules. As shown in Appendix B, the present methodology makes a satisfactory evaluation of the interfacial energy of benzene, ethyl-benzene, and *p*-xylene using argon and octane as the reference parameters. These molecules cannot be generally fitted employing hydrocarbon references. However, the convenient application of the present theory to polar compounds remains to be studied.

Appendix A: Accumulation of Energy in a Vapor/Liquid Interface

Contrary to what might be expected, continuous interface models can also evidence the unequal distribution of energy among the two subphases of a vapor/liquid interface. In the classical treatment of Widom,[46,47] the interface is viewed as a nonuniform fluid whose mean field potential $\Phi(z)$ is different from that of the bulk, due to its dependence on the density ρ. Under the assumption of continuous density variation of the interface and using a Taylor series expansion about $\rho(z)$, the following expression for the mean field potential can be obtained:

$$\Phi(z) = -l\rho(z) - (1/2)m\rho''(z) + ... \qquad (A.1)$$

Here l and m are assumed to be positive constants depending on intermolecular forces only. According to Baydakov,[48] m is similar to the density of free energy postulated by the van der Waals theory.[19] For the "bulk" ($z = -\infty$) of a van der Waals fluid, only the first term of eq A.1 remains, giving a mean field potential proportional to the density $\Phi(z = -\infty) = -(1/2)a_W(z = -\infty)\rho^\alpha$, and $a_W(z = -\infty) = 2l$. The spatial variation of the mean field $\Phi(z)$ can be understood as the result of the coupling of the field of one phase with the field of the neighboring phase.

If the description of the interfacial interactions is simplified employing a pseudo-potential of molecular interaction like a Lennard-Jones or van der Waals (vdW) potential, the coupling effect among the phases can be related to the value of the effective parameters ϵ_{LJ} or a_W, respectively. In the latter case

$$\Phi(z) = -(1/2)a_W(z)\rho(z) \qquad (A.2)$$

where

$$a_W(z) = 2l + m\left(\frac{\rho''(z)}{\rho(z)}\right) + ... \qquad (A.3)$$

If the elastic field described in refs 18 and 19 is assumed to be the consequence of a distortion of a network of springs
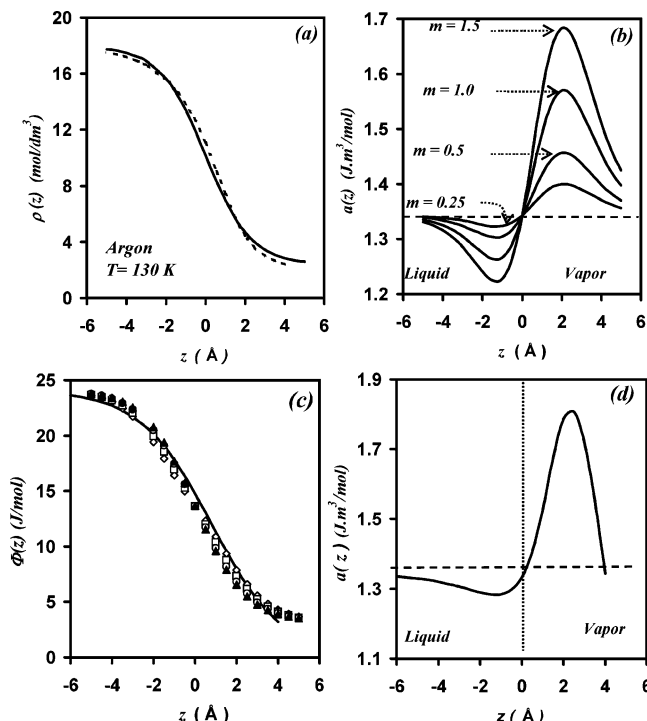

Figure 4. *z*-Axis interfacial profiles of argon at 130 K. (a) Density profiles calculated by means of eq A.4 (continuous curve) and eq A.5 (dashed curve). (b) *z* dependence of the intermolecular interaction parameter $a(z)$, for different values of *m* (eq A.3). (c) Mean field intermolecular potential calculated from eqs A.2 and A.3 ((▲) $m = 0.25$, (○) $m = 0.50$, (□) $m = 1$, (◇) $m = 1.5$), and eq A.5 (—) for a perturbation of maximum coupling, respectively. (d) Effective $a(z)$ variation under the condition of maximum coupling.

representing the bulk phase, the energy stored in a subsurface results from the expansion or contraction of these effective springs. The variation of a_W would then represent the degree of softening or hardening of the springs due to the interfacial coupling of the two nets of springs representing the separate fluids. For low values of *m* (far from the triple point) and for a profile of density of the interface with an effective width thickness Δ, $\rho(z)$ is given by the expression[48] (see continuous curve in Figure 4a)

$$\rho(z) = (1/2)\left[(\rho^{liq} + \rho^{vap}) + (\rho^{liq} - \rho^{vap})\tanh\left(\frac{z\ln(9)}{\Delta}\right)\right] \quad (A.4)$$

As can be observed in Figure 4b, the variation of $a_W(z)$ with respect to *z* exposes the presence of two sub-phases, a liquid and gaseous one. Furthermore, the softening effect of the liquid sub-phase is also evident along with hardening effect of the gaseous sub-phase. The spatial dependence of $a_W(z)$ provides a criterion for the clear location of the plane of Gibbs (Figure 4b).

Let us further assume that the variation of $\Phi(z)$ in passing from the vapor to the liquid phase could be represented as an aggregation process. In such a process, the many-body contributions to the potential of mean force can be mimicked employing an arbitrary function of population growth where the time variable *t* is substituted by the space variable *z*. This function has the form

$$\Phi(z) = -\frac{1}{2}\frac{a_W^\infty \rho^{vap} e^{-q(z-(L/2))}}{1 + \frac{\rho^{vap}}{\rho^{liq}}(e^{-q(z-(L/2))} - 1)} \qquad (A.5)$$
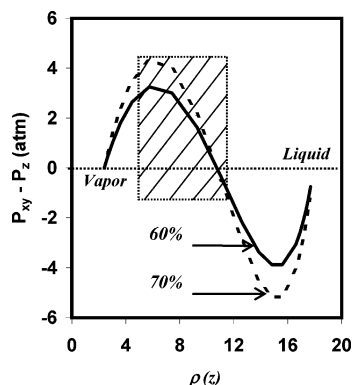
Figure 5. z-Axis pressure profile calculated from eqs A.2, A.5, and A.6, considering percentages of 60% and 70% of the maximum coupling. The shaded region indicates the possible meta-stability regions occurring under extreme conditions of isothermal expansion of the liquid or compression of the vapor.

Here L is the width of the interface, superscripts liq and vap are used to indicate that the property is evaluated in the liquid or the vapor phase, respectively, and q is a parameter that depends on the level of "saturation" of the system.

If it is supposed that (1) there are an infinite number of molecules inside each mesoscopic interfacial plane located at position z inside the subsurface of a fluid and (2) the configuration of the molecules is approximately uniform within that plane, the mean field approximation should be satisfactorily fulfilled. Consequently, a van der Waals equation for $\Phi(z)$ can be formulated

$$-\Phi(z) = \frac{2}{\rho(z)}\left[\left(\frac{RT\rho(z)}{1 - b\rho(z)}\right) - P_z\right] \qquad (A.6)$$

From the function of population growth $\Phi(z)$ given by the equation A.5, one can obtain the profile of superficial density $\rho(z)$ given by the broken line in Figure 4a. This profile is very similar to the one described by the eq A.4.

As can be observed in Figure 4c, changes of $a(z)$ as a function of parameter m generate sizable differences in the dependence of the mean field potential with z. It is possible to calculate an "effective energy" $a(z)_{100}$ from eqs A.5, A.6, and A.2, under the condition of maximum coupling (100%). That is, the condition where the density profile is only due to the softening of the liquid network and the hardening of the gaseous one in the vicinity of the interface, and not due to the z-pressure profile. Figure 4d suggests the possible variation of $a(z)$ with the density. As expected, it is lower in the liquid region and higher in the vapor one.

Figure 5 shows the difference in the components of the stress tensor in the interfacial region, in the axial direction z and perpendicular to it (xy). As shown by Kirwood and Buff,[49] the integration of this difference (interfacial pressure P^σ) across the interface is equal to the interfacial tension. The axial component of the stress tensor is equal to the bulk pressure of the fluid bulks, whereas the transverse component is different. According to Figure 5 there is a particular coordinate z for which $P_z = P^\sigma = P_{xy}$. The density variation in this region (calculated from eq A.6) is produced by a softening of the field caused by the coupling of the interfaces. However, the condition of minimization of the Helmholtz free energy produces the appearance of tensions of different magnitude in the planes P_{xy} of the liquid region even under conditions of very strong coupling. Important differences are observed among the components of the surface
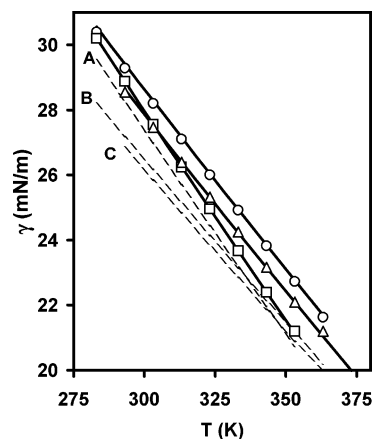

Figure 6. Surface tension of ($\square$) benzene, ($\bigcirc$) ethyl-benzene, and ($\triangle$) p-xylene, as a function of temperature. The continuous lines illustrate the predictions of the present methodology using $A_w(T)$. The broken lines were calculated using the same procedure but employing the constant value of $V_c^{2/3}$ for each compound: (A) benzene, (B) ethyl-benzene, and (C) p-xylene.

pressure of both phases (Figure 5), considering perturbations of 60% and 70% in $a(z)$, which correspond to a strong coupling case.

The CI model satisfactorily explains the presence of tensions in the liquid region, which are relatively assimilated by this phase due to its finite elasticity. Yet, an excess of pressure should occur in the gaseous phase in order to guarantee the continuous profile of density. The compression may show values as high as the absolute value of the expansion in the liquid phase (Figure 5), and this would lead to possible in-homogeneities in the shaded region of Figure 5. To avoid such phenomena, the effect of the coupling on the vapor phase should be larger than that of the liquid phase.[48] This indicates that m (which corresponds to the parameter κ which equates the free energy of an inhomogeneous system to the density gradient in the van der Waals theory) decreases from low (gas) to high densities (liquid) in an isothermal expansion. As a consequence, the tension at the interface will have its larger contribution in the liquid sub-phase as suggested by our mesoscopic model.

Appendix B: Suitability of $A_w(T)$ and $V_c^{2/3}$ for the Calculation of the Interfacial Tension

As shown by Rice and Teja,[12] use of $V_c^{2/3}$ for the calculation of the interfacial tension in the context of corresponding states generates very good results. For simple alkanes or molecules with small ramifications, that methodology[12] is equally successful for the prediction of the surface tension than the present one. For more complex cases, that might not be the case. One of the most important differences between these two approaches is the use of $V_c^{2/3}$ (Rice and Teja) or $A_w(T)$ (present work) for the evaluation of the tension. Figure 6 shows how the scaling of the interfacial energy with $A_w(T)$ is more successful for the prediction of γ in the case of aromatic compounds. All curves were computed with the formalism described in this work. Yet, $V_c^{2/3}$ was used for the calculation of the broken lines, and $A_w(T)$ was used for the computation of the continuous ones. It is observed that, at least for this limited set of aromatic compounds, the present theory improves the fitting of the experimental data.

It should be kept in mind, however, that despite the practical advantages of this theory, the present article does not intend to provide a better method for the prediction of the surface tension. There are several empirical formulas in the literature that might
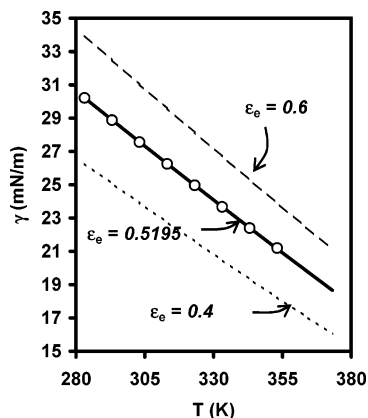
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Figure 7. Effect of the fraction of empty volume (ϵ_e) on the prediction of the surface tension by means of eq 26. The best fit correspond to ϵ_e = 0.5195. Average percentages of absolute deviation (%AAD) of 13.4 and 12.6 are obtained for ϵ_e = 0.4 and 0.6, respectively.

be more suitable for this purpose. The object of the manuscript is to show that when the interfacial energy is considered for scaling under the principle of corresponding states, the resulting predictions of the tension are at least as accurate as currently accepted formalisms. Furthermore, the use of this magnitude for scaling was suggested by the theory published in refs 18 and 19 regarding the accumulation of elastic energy in the subphase regions of the interface.

Figure 7 shows the variation of the surface tension of benzene as a function of temperature for three different fractions of empty volume ϵ_e. The solid line corresponds to the best fitting of the experimental data (empty circles) obtained for ϵ_e = 0.5195. As previously remarked, the fraction of empty volume at the boiling point is around 0.5 for all molecules studied (see Table 2). Large deviations of the surface tension are obtained otherwise. The predictions of the theory for ϵ_e = 0.4 and 0.6 are illustrated with dashed lines (Figure 7). The high sensitivity of the equations with respect to the departure of ϵ_e from the value of 0.5 is clearly observed.

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