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Journal of Colloid and Interface Science 279 (2004) 206–212
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Prediction of solid–fluid interfacial tension and contact angle

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Received 28 January 2004; accepted 17 June 2004

Available online 21 July 2004

Abstract

Two simple equations have been developed using the lattice theory and the regular solution assumption to predict the solid–vapor and solid–liquid interfacial tension. The required parameters are the liquid critical temperature and volume, the solid melting temperature and the molar volume of liquid and solid compounds. To confirm the models, the predicted solid–fluid interfacial tension values have been used to predict the contact angle of the liquid drop on the solid surface applying Young's equation. Agreement of the predicted contact angle with the experimental data reveals the reliability of the developed models.

Keywords: Contact angle; Solid–fluid; Interfacial tension; Surface tension

1. Introduction

Solid–liquid and solid–vapor interfacial tensions are two important properties of solid surfaces that cannot be determined experimentally. The difference in solid–liquid and solid–vapor interfacial tension values relates to the liquid surface tension and the contact angle of the liquid drop on the solid surface by Young's [1] equation. Since the liquid–vapor surface tension and the contact angle are measurable, it has been generally agreed that the most practical method of evaluating the solid surface energy is the measurement of the contact angle of the liquid drop on the solid surface.

The contact angle method of solid surface energy evaluation started, historically, with observations of Zismann and co-workers [2]. They found that the cosine of the contact angle, $\cos(\theta)$, decreases monotonically with increasing liquid–vapor surface tension. They extended the linear plot of $\cos(\theta)$ versus liquid–vapor surface tension to $\cos(\theta) = 1$ to find the corresponding liquid–vapor surface tension and they called it "critical surface tension." The liquids that have a lower surface tension than this critical value spread and completely wet the solid surface and those that have a higher value of surface tension can only partially wet the substrate, resulting in a three-phase contact point with an apparent contact angle. Experimental contact angles have been extensively used to develop models for estimation of solid surface energies [3–5] and some of them, such as the equation of state approach [4,6], have been subject of considerable controversy [7–12].

The observation of Zismann and co-workers suggests that the contact angle of a liquid drop on a particular solid surface can be determined solely by the liquid–vapor surface tension. Recently van Giessen et al. [13] found theoretically the same trend of $\cos(\theta)$ versus liquid–vapor surface tension by using a generalized van der Waals theory and concluded that "both the contact angle and the liquid–vapor surface tension depend on the properties of the fluids and one cannot simply be a function of the other."

This work aims to find a method for prediction of the contact angle. We employ the lattice theory and regular solution assumptions to develop two equations for prediction of solid–liquid and solid–vapor interfacial tension. The pre-

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2004.06.058

dicted values are then used in Young's equation to predict the contact angle.

2. Theory

2.1. Solid–liquid interfacial tension

We consider the liquid (α) and solid (β) phases totally immiscible, whereas both solid and liquid phases are pure systems of different compounds. We assume the interface ($\alpha\beta$), where solid and liquid phases meet, as a monomolecular plane composed of both liquid and solid compounds. Hence, the only mixture phase is the interface. We further consider the liquid and solid phases as a series of plains, each with the same number of molecules, parallel to the interface plain. Each molecule in the lattice interacts only with Z nearest neighbors, which lZ of them are situated in the same plain and mZ in the adjacent plain. Therefore,

$$l + 2m = 1. \tag{1}$$

The internal configurational energy of the interface plain due to interaction of molecules situated in the interface is

$$\begin{aligned} U_1 = {} & \frac{1}{2}\left(Nn^{\alpha\beta}X_1^{\alpha\beta}\right)\left(lZX_1^{\alpha\beta}\right)\varepsilon_{11} \\ & + \frac{1}{2}\left(Nn^{\alpha\beta}X_2^{\alpha\beta}\right)\left(lZX_2^{\alpha\beta}\right)\varepsilon_{22} \\ & + \left(Nn^{\alpha\beta}X_1^{\alpha\beta}\right)\left(lZX_2^{\alpha\beta}\right)\varepsilon_{12}, \end{aligned} \tag{2}$$

where N is Avogadro's number, $n^{\alpha\beta}$ is the number of moles situated in each plain, $X^{\alpha\beta}$ is the mole fraction in the interface and ε is the interaction energy. The subscripts 1 and 2 refer to the liquid and solid compounds, respectively. The configurational energy of the interface due to interaction of interface molecules with molecules situated on the adjacent plains is

$$\begin{aligned} U_2 = {} & \left(Nn^{\alpha\beta}X_1^{\alpha\beta}\right)(mZ)\varepsilon_{11} + \left(Nn^{\alpha\beta}X_1^{\alpha\beta}\right)(mZ)\varepsilon_{12} \\ & + \left(Nn^{\alpha\beta}X_2^{\alpha\beta}\right)(mZ)\varepsilon_{12} + \left(Nn^{\alpha\beta}X_2^{\alpha\beta}\right)(mZ)\varepsilon_{22}. \end{aligned} \tag{3}$$

Similarly to Eqs. (2) and (3) we can show the internal configurational energy of the bulk phases in each plain, U_3 and U_4, and the adjacent plains, U_5 and U_6, as follows:

$$U_3 = \frac{1}{2}Nn^{\alpha\beta}lZ\varepsilon_{11}, \tag{4}$$

$$U_4 = \frac{1}{2}Nn^{\alpha\beta}lZ\varepsilon_{22}, \tag{5}$$

$$U_5 = Nn^{\alpha\beta}mZ\varepsilon_{11}, \tag{6}$$

$$U_6 = Nn^{\alpha\beta}mZ\varepsilon_{22}. \tag{7}$$

We suppose the liquid phase comprises k^{α} layers and the solid phase k^{β} layers. The total internal configurational energy of the system is the summation of all these energies, using some algebraic simplification, as

$$\begin{aligned} U^{\text{total}} = {} & \frac{1}{2}Nn^{\alpha}Z\varepsilon_{11} + \frac{1}{2}Nn^{\beta}Z\varepsilon_{22} + \frac{1}{2}Nn^{\alpha\beta}Z\sum_{i=1}^{2}\left(X_i^{\alpha\beta}\varepsilon_{ii}\right) \\ & + \frac{1}{2}n^{\alpha\beta}l\left(X_1^{\alpha\beta}X_2^{\alpha\beta}\right)\alpha_{12} + \frac{1}{2}n^{\alpha\beta}m\alpha_{12}, \end{aligned} \tag{8}$$

where

$$\alpha_{12} = NZ\left(2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}\right). \tag{9}$$

n^{α} ($= k^{\alpha}n^{\alpha\beta}$) and n^{β} ($= k^{\beta}n^{\alpha\beta}$) are the number of moles in the bulk liquid and solid phases, respectively. The first two terms in Eq. (8) are the internal configurational energies of bulk phases and the third term is that of interface as a perfect solution. Therefore the last two terms in Eq. (8) are the excess internal configurational energy of the system attributed to the interface. Assuming zero excess volume and zero excess entropy, we obtain equality of the excess free energy and the excess internal configurational energy. Consequently, the activity coefficient of compounds in the interface is determined as

$$\begin{aligned} RT\ln\left(\gamma_i^{\alpha\beta}\right) = {} & l\frac{\partial}{\partial n_i^{\alpha\beta}}\left(\frac{1}{2}n^{\alpha\beta}X_1^{\alpha\beta}X_2^{\alpha\beta}\alpha_{12}\right)_{T,P,n_j^{\alpha\beta}} \\ & + \frac{1}{2}m\alpha_{12}, \quad i = 1, 2. \end{aligned} \tag{10}$$

Analogously to regular solutions we assume

$$RT\ln\left(\gamma_i^{\alpha\beta}\right) = \frac{\partial}{\partial n_i^{\alpha\beta}}\left(\frac{1}{2}n^{\alpha\beta}X_1^{\alpha\beta}X_2^{\alpha\beta}\alpha_{12}\right)_{T,P,n_j^{\alpha\beta}}. \tag{11}$$

Substitution of Eq. (11) in Eq. (10) and then employing Eq. (1) yield

$$RT\ln\left(\gamma_i^{\alpha\beta}\right) = \frac{1}{4}\alpha_{12}, \quad i = 1, 2. \tag{12}$$

Equation (12) enables us to find the chemical potential of components in the interface. The chemical potential of ith component in the interface is

$$\mu_i^{\alpha\beta} = \mu_i^{0,\alpha\beta}(T, P) + RT\ln\left(X_i^{\alpha\beta}\gamma_i^{\alpha\beta}\right) - \sigma^{\alpha\beta}a_i, \tag{13}$$

where $\mu_i^{0,\alpha\beta}$ is the standard chemical potential of pure component i at the interface, a_i is the partial molar surface area of that compound and $\sigma^{\alpha\beta}$ is the solid–liquid interfacial tension. Since the system is in equilibrium, the chemical potential of each component has the same value in all phases. Using the equality of chemical potentials along with Eq. (12) and Eq. (13) yields

$$X_1^{\alpha\beta} = \exp\left(\frac{\sigma^{\alpha\beta}a_1 - \frac{1}{4}\alpha_{12} - \left(\mu_1^{0,\alpha\beta} - \mu_1^{\alpha}\right)}{RT}\right), \tag{14}$$

where μ_1^{α} is the chemical potential in the liquid phase.

The expression for concentration of the solid compound in the interface, $X_2^{\alpha\beta}$, is of the same form as Eq. (14), but changing the subscript 1 to 2 and μ_1^{α} to μ_2^{β}.

Employing $X_1^{\alpha\beta} + X_2^{\alpha\beta} = 1$ results in

$$\exp\left(\frac{\sigma^{\alpha\beta}a_1 - \frac{1}{4}\alpha_{12} - (\mu_1^{0,\alpha\beta} - \mu_1^{\alpha})}{RT}\right) + \exp\left(\frac{\sigma^{\alpha\beta}a_2 - \frac{1}{4}\alpha_{12} - (\mu_2^{0,\alpha\beta} - \mu_2^{\beta})}{RT}\right) = 1. \quad (15)$$

For practical purposes, we simplify Eq. (15) by making the following two assumptions:

(a) The partial molar surface area of the liquid compound in the interface is equal to that of solid compound, that is, $a_1 = a_2 = a_{sl}$. In applying the method, however, we use $a_{sl} = 0.5(a_s + a_l)$. This assumption will be the case if the solid and liquid compounds are of the same molecular size.

(b) The difference between the chemical potential of liquid compound in the bulk liquid phase and the standard chemical potential in the interface is the same as that of solid compound, that is,

$$\mu_1^{0,\alpha\beta} - \mu_1^{\alpha} = \mu_2^{0,\alpha\beta} - \mu_2^{\beta} = M. \quad (16)$$

The above assumptions will become more valid as the solid and liquid compounds become more similar, that is, similar in molecular size, lattice point distance, molecular packing and interaction potential model.

Using these two assumptions Eq. (15) simplifies to

$$\sigma^{\alpha\beta} = \frac{1}{a_{sl}}\left(\ln(0.5)RT + \frac{1}{4}\alpha_{12} + M\right). \quad (17)$$

We assume the solid–liquid potential, ε_{12} in Eq. (19), obeys the Berthelot's [14] rule:

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}. \quad (18)$$

The Berthelot's rule applies when the forces between molecules are of dispersion types [16,25,26]. Since in our model we characterize the compounds by their interaction potential and molecular size, the model will predict no interface (zero interfacial tension) when the interaction potential and the molecular size are the same for both compounds. We have already assumed that the partial molar surface area of solid and liquid compounds is the same. If we apply the model to a system composed of molecules of equal interaction potentials, Eq. (17) should result in zero interfacial tension and

$$M = -\ln(0.5)RT. \quad (19)$$

Equation (19) along with Eq. (9) and Eq. (17) yields

$$\sigma^{\alpha\beta} = \frac{1}{2}\frac{NZ}{a_{sl}}\left(\varepsilon_{12} - \frac{\varepsilon_{11} + \varepsilon_{22}}{2}\right). \quad (20)$$

Equation (20) is the final equation to be used for prediction of solid–liquid interfacial tension. The required parameters are the molar surface area of solid–liquid interface, the coordination number and the interaction potentials. In the last section we will discuss how to approximately obtain these parameters.

2.2. Solid–vapor interfacial tension

We consider the lattice of solid to be covered by a monomolecular interface plane. The molecules of the vapor phase are far from each other (at low pressure conditions); therefore, their interaction with the interface plain is ignored. The same procedure, described above, used for solid–liquid will result in the activity coefficients of solid and vapor compounds at the interface as follows,

$$RT\ln\left(\gamma_1^{\gamma\beta}\right) = \frac{1}{2}NZ(\varepsilon_{12} - \varepsilon_{11}) - \frac{1}{4}NZ\varepsilon_{22} \quad (21)$$

and

$$RT\ln\left(\gamma_2^{\gamma\beta}\right) = -\frac{1}{4}NZ\varepsilon_{22}, \quad (22)$$

where the superscript γ denotes the vapor phase. Since the liquid and vapor compounds are the same substance, the subscript number 1 denotes the vapor compound as well as the liquid compound. Using Eq. (22) to evaluate the chemical potential of the solid compound at the solid–vapor interface, we obtain

$$RT\ln\left(X_2^{\gamma\beta}\right) = \sigma^{\gamma\beta}a_2 - \left(\mu_2^{0,\gamma\beta} - \mu_2^{\beta}\right) + \frac{1}{4}NZ\varepsilon_{22}. \quad (23)$$

It has been well demonstrated that the solid–vapor interfacial tension is independent of the vapor type (e.g., see Refs. [4,6]). Therefore it is reasonable to assume that the solid–vacuum surface tension has the same value as the solid–vapor interfacial tension, σ^S. Hence, from the definition of the standard state chemical potential, we obtain

$$\mu_2^{0,\gamma\beta} - \mu_2^{\beta} = \sigma^S a_2 = \sigma^{\gamma\beta}a_2. \quad (24)$$

Equations (24) and (23) result in the mole fraction of solid compound at the interface, as

$$X_2^{\gamma\beta} = \exp\left(\frac{1}{4}\frac{NZ}{RT}\varepsilon_{22}\right). \quad (25)$$

Evaluation of the chemical potential of the vapor compound at the interface, using Eq. (21) and remembering that $X_1^{\gamma\beta} = 1 - X_2^{\gamma\beta}$, and substitution $X_2^{\gamma\beta}$ from Eq. (25) give us the equation

$$RT\ln\left(1 - \exp\left[\frac{1}{4}\frac{NZ}{RT}\varepsilon_{22}\right]\right) - \frac{1}{4}NZ\varepsilon_{22} - \sigma^S a_1 = \mu_1^{\gamma} - \mu_1^{0,\gamma\beta} - \frac{1}{2}NZ(\varepsilon_{12} - \varepsilon_{11}). \quad (26)$$

Considering our assumption that the solid surface tension is independent of the vapor type and our assumption on the vapor lattice points, the right-hand side of the Eq. (26) should be zero. The molar surface areas of both compounds are considered to be the same, in accord with the assumption we made for the solid–liquid interface, and equal to the molar solid surface area. These assumptions make the left-hand side of the Eq. (26) independent of vapor compound. Hence,

Eq. (26) reduces to the final equation of the solid–vapor interfacial tension, as

$$\sigma^S = -\frac{1}{4}\frac{NZ}{a_s}\varepsilon_{22} + \frac{RT}{a_s}\ln\left(1 - \exp\left(\frac{1}{4}\frac{NZ}{RT}\varepsilon_{22}\right)\right). \quad (27)$$

This simple equation enables us to evaluate the solid surface tension at any temperature. The required parameters are the interaction potential of the solid, the coordination number and the molar solid surface area.

3. Results and discussion

3.1. Application

Application of Eqs. (20) and(27) requires the values of energy parameter and molar surface area of all the compounds. According to the assumption (b), described in the solid–liquid section, the same interaction potential model should be used for both liquid and solid molecules. The interaction between two molecules has been supposed to be independent of their orientation and only depends on their distances and their molecular sizes. Any potential model that considers only these two parameters can be used to calculate the interaction energies. The parameters of the model may also be calculated from thermodynamic properties of the compounds using lattice models. For simplicity we consider the liquid and the solid phases to be reasonably adequately described by the Lennard–Jones model, which is

$$\varepsilon = 4\varepsilon_0\left[\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6}\right], \quad (28)$$

where ε_0 is the absolute value of the well depth potential and δ is the distance at zero potential energy. The parameters of Lennard–Jones model for many compounds have been determined, using methods such as matching the predicted viscosity or the second virial coefficient to experimental data, and reported in the literature. They can also be determined simply from available correlations, particularly in the absence of reported data, such as the ones suggested by Chung et al. [15]:

$$\varepsilon_0 = k\frac{T_c}{1.2593} \quad (29)$$

and

$$\delta = 0.809(V_c)^{1/3}, \quad (30)$$

where k is the Boltzmann's constant, T_c is the critical temperature in Kelvin and V_c is the critical molar volume in $\mathrm{cm^3\,mol^{-1}}$.

The distances of the adjacent molecules at the lattice can be found by the following expression [16],

$$r = 10^8\lambda(V)^{1/3}(N)^{-1/3}, \quad (31)$$

where V is the molar volume in $\mathrm{cm^3\,mol^{-1}}$, λ is a constant coefficient related to the geometry of the molecular packing at the lattice and r is in Å.

Since the critical volume of the solid compound may not be available, mostly, we may use the molar volume of solid, instead of the critical volume, to calculate the δ parameter. We further suppose the distance of the molecules at the solid phase such that the solid potential falls to the well depth potential of the Lennard–Jones model, that is, $\varepsilon_{22} = \varepsilon_0$.

Equation (29) can be used to calculate the energy parameters of both solid and liquid systems but since some solid compounds may have no critical point (e.g., polymers) a similar approach that correlates the solid energy parameter to the melting point may be used. Recently Morris and Song [17] calculated the equilibrium melting line of Lennard–Jones fluids by molecular dynamic simulation and concluded, using different truncation potentials, that

$$T_m\frac{k}{\varepsilon_{22}} = 0.654\ldots0.683. \quad (32)$$

The above values have been obtained at zero pressure, but may be extended to the atmospheric melting point, as the melting temperature change with pressure is small.

To ensure the reliability of the above approach, the Lennard–Jones energy parameters of some simple liquids such as Ar, Kr, Ne, Xe, N_2 and methane, determined from the viscosity data [18], were selected and a least squares fit was employed to find the right-hand side value of Eq. (32) at atmospheric pressure. The obtained value was 0.75, which was close to the values at zero pressure but as expected slightly higher.

The molar surface area can be estimated from the molar liquid and solid volume, V_i. In this work we used the simplest relation, proposed by Sprow and Prausnitz [19],

$$a_i = V_i^{2/3}N^{1/3}. \quad (33)$$

The coordination number, Z, can vary between 4 and 12 subject to the packing structure of the lattice. For the face-centered cubic, which is the densest lattice, the coordination number is 12 and for the least dense lattice, i.e., the diamond structure, the coordination number is 4. The liquid surface tension can enable us to estimate the coordination number as follows.

Although Eq. (27) has been developed for solid–vapor, it can be reasonably generalized for determination of the surface tension of any condensed phase, as the assumption used for the solid phase is mostly general and applicable to the liquid phase.

Table 1 shows the results of the predicted surface tension values for some hydrocarbons and two polar liquids, water and glycerol, using Eq. (27). It is noted that Eq. (27) does not have any solution for nondense packing, that is, the simple cube and diamond structure, for the tested compounds except for water.

Although the results are sensitive to the lattice geometry, the experimental values fall into the predicted data

Table 1
Experimental liquid–vapor surface tension data [23] and the predicted values using Eq. (27) and different lattice geometries at 20 °C

Liquid	Exp. ($mN\,m^{-1}$)	Diamond structure, $Z = 4$ and $\lambda = 2^{-1}3^{1/2}$	Simple cubic, $Z = 6$ and $\lambda = 1$	Body-centered, $Z = 8$ and $\lambda = 2^{-2/3}3^{1/2}$	Face-centered, $Z = 12$ and $\lambda = 2^{1/6}$
Dodecane	25.40	–	–	26.42	41.44
Tetradecane	26.70	–	–	25.01	39.83
Hexadecane	27.60	–	–	18.80	35.67
Hexylbenzene	30.00	–	–	30.29	49.28
Decylbenzene	31.20	–	–	24.24	42.31
1-Methylnaphthalene	36.40	–	–	39.86	66.37
Octanoic acid	29.20	–	–	33.63	55.16
Nonanoic acid	29.5	–	–	31.95	52.61
Water	72.80	24.81	162.44	160.05	212.61
Glycerol	63.40	–	–	−25.64	80.47

ranges. According to Table 1, the body-centered cubic lattice reasonably represents the molecular packing geometry of the hydrocarbons and the alkanoic acids like octanoic and nonanoic acids. Furthermore, a coordination number between those of the diamond structure ($Z = 4$) and the simple cubic lattice ($Z = 6$) can represent water molecules. Interpolation between theses two geometrical structures to match the measured surface tension of water results in $Z = 4.7$, which is in a very good agreement with the numbers obtained by X-ray diffraction measurement [20,21]. The result obtained by Morgan and Warren [20] shows that the number of nearest neighbors in the liquid water increases from $Z = 4.4$ at 1.5 °C to $Z = 4.9$ at 83 °C while the later work of the Narten et al. [21] results in $Z = 4.4$ at all temperatures from 4 to 200 °C.

The above observation indicates the reliability of the developed model and our proposed method of using the liquid surface tension data for estimation of the coordination number. Application of Eq. (20) for prediction of liquid–liquid interfacial tension of two pure immiscible liquids, instead of solid–liquid, also leads to acceptable data, although the results are less sensitive to the coordination number.

The coordination number, Z, can be different for solid and liquids but since the same coordination number has been assumed during the derivation we suppose an average coordination number can be used for both phases. A coordination number of 8 is a reasonable value for the packing structure of liquids. Since the solid compound is denser than or as dense as the liquid, its coordination number could be 8 or higher. The model uses the same value for liquid and solid components, thus, typical average values of 8, 9, or 10 seem appropriate. The predicted solid–vapor interfacial tensions by these coordination numbers are 18, 20.5, and 22.8 $mN\,m^{-1}$ for *n*-octadecylamine solid surface, respectively, and are 18.6, 21, and 23.5 $mN\,m^{-1}$ for stearic acid solid surface. These values are close to each other and close to predicted values by the Li–Neumann model. We propose $Z = 10$ in the absence of data as this value has been used often successfully in some other liquid models (e.g., the UNIQUAC activity coefficient model). Moreover, the selected value of the coordination number is a reasonable value to calculate the solid–fluid interfacial tension, as solids are mostly dense compounds.

3.2. Evaluation

As pointed out previously, there are no experimental data on solid–vapor or solid–liquid interfacial tension to evaluate the predicted values. Hence, we employed Young's equation along with the predicted values of solid–vapor and solid–liquid interfacial tension to predict the contact angle, θ, of a liquid drop on the solid surface.

According to Young's equation the contact angle can be calculated as

$$\cos(\theta) = \frac{\sigma^{SV} - \sigma^{SL}}{\sigma^{LV}}. \tag{34}$$

However, to obtain some interpretation of predicted interfacial tensions, the predicted data of Eqs. (20) and (27) are compared with the data calculated by the Li–Neumann model [22].

The proposed universal equation of Li–Neumann relates the solid–vapor interfacial tension with the solid–liquid and liquid–vapor interfacial tensions as

$$\sigma^{SL} = \sigma^{LV} + \sigma^{SV} - 2\sqrt{\sigma^{LV}\sigma^{SV}}\,e^{-\beta(\sigma^{LV}-\sigma^{SV})^2}. \tag{35}$$

Using Eqs. (34) and (35), along with experimental data on contact angles, Li and Neumann obtained a constant value of $\beta = 0.0001247$ $(m^2\,mJ^{-1})^2$. Equation (35) has been subjected to considerable criticism as explained in Refs. [7–12]. However, it can be used along with Young's equation and experimental contact angle data to calculate the solid–fluid interfacial tension.

Recently Kwok and Neumann [23] reported the contact angle of a large number of liquid compounds on several solid surfaces. We chose two solid surfaces for which their physical properties were available, namely, *n*-octadecylamine and stearic acid.

In our calculations we used a constant value of 0.75 in Eq. (32) to calculate the solid energy parameter from the melting temperature. Equation (29) was used for evaluation of the liquid energy parameter, except for polar liquids such

Table 2
Experimental contact angle [23] and predicted solid–liquid interfacial tension and contact angle on two solid surfaces

Solid surface	Liquid	σ^{SL}, Li–Neumann	σ^{SL}, this work	θ, exp. [23]	θ, predicted	AAD %
n-Octadecylamine	Nonane	0.01	0.05	13	5.7	56.1
	Decane	0.04	0.10	18	18.0	0.2
	Dodecane	0.16	0.21	30	27.1	9.8
	Tetradecane	0.30	0.32	34	32.5	4.3
	Hexadecane	0.47	0.08	38	34.5	9.3
	Hexylbenzene	0.95	0.33	39	41.4	6.1
	Decylbenzene	0.97	0.34	44	43.9	0.3
	α-Methylnaphthalene	2.61	0.71	55	52.6	4.4
	Water	36.76	0.47	102	72.1	29.3
	Glycerol	23.50	1.83	90	70.7	21.5
Stearic acid	Octanoic acid	0.62	0.16	40	37.1	7.4
	Nonanoic acid	0.81	0.21	43	38.0	11.7
	Glycerol	24.68	2.24	92	70.4	23.4
Total						14.1%

as water. We used the reported energy parameter of 809.1k for water, calculated from viscosity data [18], and 873.12k for glycerol calculated from surface tension [24]. It should be noted that the energy parameters obtained from Eqs. (18), (29), and (32) are the absolute values and must be used in the equations as negative values. The average value of the solid and liquid surface areas was used for evaluation of a_{sl} in Eq. (20), according to our assumption (a).

The predicted values of the solid–vapor interfacial tension of the above two solids by Eq. (27) are 22.8 and 23.5 mN m^{-1}, respectively, which are very close to the values found, 22.6 mN m^{-1} for both, using the Li–Neumann model and the experimental contact angle data [23]. Table 2 shows the predicted values of solid–liquid interfacial tension and contact angle of some liquid drops on these two solid surfaces as well as the experimental contact angles. The solid–liquid interfacial tension values found using the Li–Neumann model and the average absolute percentage deviation (AAD %) of predicted contact angles from the experimental values are also included in Table 2.

Fig. 1 shows the impact of coordination number on predicted contact angle of some hydrocarbon compounds on the *n*-octadecylamine solid surface. The contact angle does not show a smooth trend with the interfacial tension as the compounds belong to different hydrocarbon families. Note the changes in predicted contact angles with the coordination number, but the predicted trend of the contact angle versus the liquid surface tension is very similar to that of experimentally observed values by Zismann et al. [23]. We propose a coordination number of 10 in the absence of any measured data. However, the prediction can be improved by selecting Z (and or the solid energy parameter) as an adjustable parameter using any available data.

The predicted contact angles are in a very good agreement with the experimental data, although our proposed model is simple and the tested systems are far from our assumptions (e.g., the solid and the liquids have very different molecular sizes, the solid systems deviate from the Lennard–Jones fluid). The deviations of the predicted contact angles from the experimental data are higher for polar compounds, which can be attributed to deterioration of the solid–liquid interfacial tension model for polar systems.

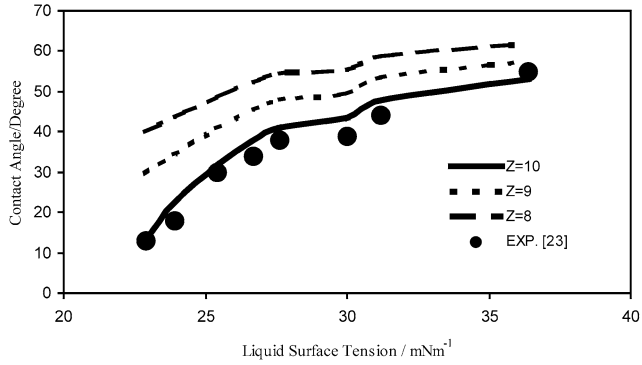

Fig. 1. Experimental contact angle of hydrocarbon compounds on the *n*-octadecylamine solid surface and its prediction using different coordination numbers.

As we mentioned before Berthelot's rule (Eq. (18)) is applicable when the molecular forces are of the dispersion type [16,25,26], and may not be applicable to polar systems. Hence, we use a more appropriate mixing rule for such systems [24]:

$$\varepsilon_{12} = \left(\frac{4\delta_1\delta_2}{(\delta_1+\delta_2)^2}\right)\sqrt{\varepsilon_{11}\varepsilon_{22}}. \tag{36}$$

It is notable that the use of above mixing rule will not change Eq. (19).

Also simple averaging of molar surface areas of liquid and solid will require modification for such systems. For *n*-octadecylamine–water and *n*-octadecylamine–glycerol interfaces we suppose that water and glycerol molecules orient themselves at the interface by their OH groups and therefore the interface contains one OH group of the liquid and one hydrogen bond of the solid compound. That is, the area

Table 3
Predicted values of solid–liquid interfacial tension and contact angle accounting for polar effects

Solid surface	Liquid	σ^{SL}, predicted	θ, predicted	θ, measured	AAD %
n-Octadecylamine	Water	43.80	106.8	102	4.7
	Glycerol	8.48	76.9	90	14.5
Stearic acid	Glycerol	10.28	78.0	92	15.2
Total					11.5%

of the interface for *n*-octadecylamine solid is the same as the water surface area. A similar discussion can be made for the stearic acid solid–glycerol interface. We can suppose that both the solid and the liquid compounds approach the interface by their OH groups so that for each molecule of stearic acid the glycerol interface contains two groups of OH; that is, the surface area is twice the previous case. Table 3 shows the solid–liquid interfacial tension and the predicted contact angles for these systems using the above modifications. Note that our revised assumptions have significantly improved the predicted values especially for water.

4. Summary

The interface between two immiscible pure solid and fluid compounds was considered as a monomolecular plain in which the molecules mix with each other. Using the lattice theory, with short-range forces acting between molecules, and regular solution assumptions we developed two simple equations to predict the solid–liquid and solid–vapor interfacial tension. The required parameters are the molar surface area of the compounds and the interaction energy potentials of the solid and the liquid molecules. The critical temperature and volume of the liquid and the melting temperature of the solid along with their molar volumes can be used to estimate the liquid and the solid interaction energy potential, respectively. The developed equations were used to determine the solid–fluid interfacial tension of two solid surfaces and a large number of fluids. To validate the predicted values we employed them in Young's equation to predict the contact angle of liquid drops. A good agreement of the predicted contact angles with experimental data confirmed the reliability of the predicted interfacial tension, although the systems conditions were not totally compatible with our assumptions. A discussion has been presented for prediction of solid–liquid interfacial tension when the liquid is a polar compound. It seems that the solid–liquid molecular interaction and the orientation of the molecules near the interface play important rules when one or both of the compounds are polar. Considering our assumptions the developed models are limited to systems at low pressure and away from the liquid critical point.

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