

# A Molecular Thermodynamic Model for Interfacial Tension in Surfactant-Oil-Water System\*

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**Abstract** An interfacial equation of state based on perturbation theory for surfactant-oil-water system has been developed. By combining the interfacial equation of state with Boudh-Hir and Mansoori's model, a molecular thermodynamic model has been proposed. The interfacial tension of surfactant-oil-water systems can be calculated from the surface tensions of pure oil and water by this model. The interfacial tension data for sodium dodecyl sulphate-heptane-water system, polyoxyethylene *n*-octylphenol-heptane-water system and hexadecyl trimethyl ammonium bromide-heptane-water system have been correlated. By using the adjustable parameters obtained, the interfacial tensions of these systems at other temperatures have been predicted. Both the correlated and the predicted values are satisfactory.

**Keywords** interfacial tension, molecular thermodynamic model, perturbation theory, surfactant-oil-water system

## 1 INTRODUCTION

Liquid-liquid interface is a physical interface made up of two partially miscible liquids. Interfacial tension is a basic physical property in such systems. Surfactant-oil-water systems play an important role in industry. One of the basic properties in such systems is their small interfacial tension. However, few studies in this field have been made. So, a systematic study on interfacial tension of surfactant-oil-water systems is meaningful either in theory or in practice.

There are many models for predicting the interfacial tension of liquid-liquid system, such as Antonov equation<sup>[1]</sup>, Fowkes equation<sup>[2]</sup>, Girifalco-Good equation<sup>[3]</sup>, Owens equation<sup>[4]</sup>, Davis equation<sup>[5]</sup>, Fu-Li equation<sup>[6,7]</sup>. However, all the models mentioned above are empirical or semi-empirical models. Boudh-Hir and Mansoori<sup>[8]</sup> developed a mathematical relation between the interfacial tension of two partially miscible liquids with their pure liquid state surface tensions, but they did not use it for practical system.

Perturbation theory is a kind of statistical mechanical theories and has been widely used in molecular thermodynamics. We developed a surface equation of state to calculate the surface pressure in surfactant-water system by using the perturbation theory successfully<sup>[9]</sup>.

In this paper, besides the experimental work, an interfacial equation of state based on perturbation theory for surfactant-oil-water system is developed. By combining this equation with Boudh-Hir and Mansoori's model, a molecular thermodynamic model for interfacial tension of surfactant-oil-water systems is

proposed.

## 2 EXPERIMENTAL

The drop-volume method is applied to measure the surface tensions and interfacial tensions. To examine the reliability of this method, we measured the surface tensions and interfacial tensions of some systems. The results are shown in Table 1.

Table 1 Surface tensions and interfacial tensions of some systems

System	<i>T</i> , K	$\gamma_{\text{exp}}$ , mN·m <sup>-1</sup>	$\gamma_{\text{lit}}$ , mN·m <sup>-1</sup>	Sources
pentane	298.15	15.10	15.50	[10]
heptane	298.15	19.32	19.60	[10]
benzene	298.15	27.93	28.18	[10]
methanol	293.15	22.40	22.55	[11]
	303.15	21.25	21.69	[11]
ethanol	298.15	21.78	21.85	[11]
water	298.15	71.87	71.97	[11]
	303.15	71.03	70.93	[11]
	308.15	70.23	70.37	[11]
	313.15	69.41	69.44	[11]
	328.15	68.59	68.40	[11]
pentane-water	298.15	48.70	49.00	[6]
hexane-water	293.15	47.70	49.75	[6]
	298.15	49.60	49.70	[6]
heptane-water	298.15	49.50	50.20	[6]
benzene-water	298.15	33.60	34.10	[6]

From Table 1, it can be seen that our experimental results are reliable. In this paper, we also measured the interfacial tensions of heptane-water systems at 25°C, 30°C, 35°C, 40°C and 45°C, sodium dodecyl sulphate-heptane-water systems, polyoxyethylene

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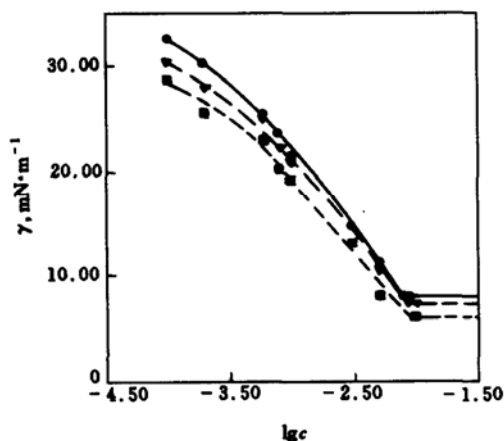
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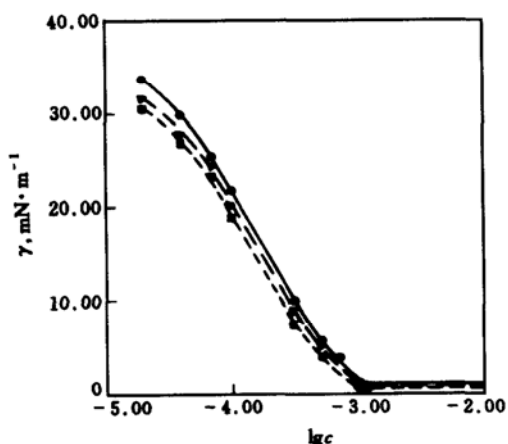
*n*-octylphenol-heptane-water systems and hexadecyl trimethyl ammonium bromide-heptane-water systems at 25°C, 30°C and 35°C by using the drop-volume method. The experimental results show that the interfacial tension decreases rapidly until it reaches a constant as the concentration of surfactant increases and the interfacial tension decreases as the temperature increases. The results are shown in Table 2 and Figs. 1–3.

**Table 2** Experimental data and calculated results of interfacial tension in heptane-water systems at different temperature

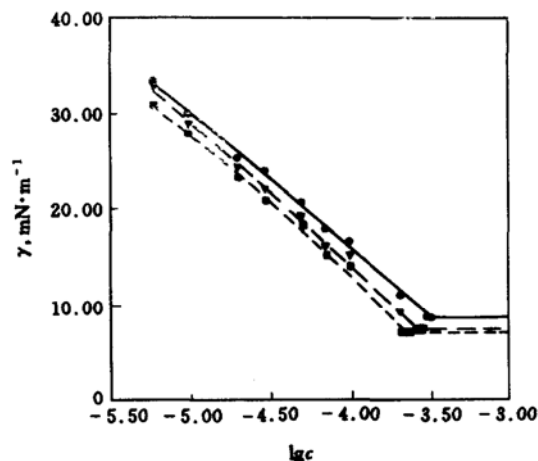
<i>T</i> , K	$\gamma_{exp}$ , mN·m <sup>-1</sup>	$\gamma_{cal}$ mN·m <sup>-1</sup>	ARD, %
298.15	49.50	49.45	0.10
303.15	48.60	49.00	-0.72
308.15	47.65	47.60	0.11
313.15	46.41	46.30	0.24
318.15	45.50	45.30	0.44



**Figure 1** Interfacial tension for C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na-H<sub>2</sub>O-C<sub>7</sub>H<sub>16</sub> system  
 ● experimental, — calculated, at 25°C;  
 ▼ experimental, - - - calculated, at 30°C;  
 ■ experimental, - - - - calculated, at 35°C



**Figure 2** Interfacial tension for C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>Br-H<sub>2</sub>O-C<sub>7</sub>H<sub>16</sub> system  
 ● experimental, — calculated, at 25°C;  
 ▼ experimental, - - - calculated, at 30°C;  
 ■ experimental, - - - - calculated, at 35°C



**Figure 3** Interfacial tension for C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>O(OC<sub>2</sub>H<sub>4</sub>)<sub>10</sub>O-H<sub>2</sub>O-C<sub>7</sub>H<sub>16</sub> system  
 ● experimental, — calculated, at 25°C;  
 ▼ experimental, - - - calculated, at 30°C;  
 ■ experimental, - - - - calculated, at 35°C

### 3 MODEL

#### 3.1 Interfacial tension of oil-water systems

Boudh-Hir and Mansoori deduced an equation of the interfacial tension of two partially miscible liquids composed of molecule *a* and *b* as<sup>[8]</sup>

$$\begin{aligned} \gamma_{ab} &= \left( \frac{\partial F}{\partial A} \right)_{V,T,\mu} \\ &= \frac{1}{2} \int dr_1 dr_2 \rho_{aa}(1,2) \left( \frac{\partial w_{aa}(1,2)}{\partial A} \right)_V \\ &\quad + \frac{1}{2} \int dr_1 dr_2 \rho_{bb}(1,2) \left( \frac{\partial w_{bb}(1,2)}{\partial A} \right)_V \\ &\quad + \int dr_1 dr_2 \rho_{ab}(1,2) \left( \frac{\partial w_{ab}(1,2)}{\partial A} \right)_V \end{aligned} \quad (1)$$

where  $w_{aa}$  and  $w_{bb}$  are the interactions between two particles of the same species;  $w_{ab}$  is the interaction between two particles of different species,  $\rho_{aa}(1,2)$ ,  $\rho_{bb}(1,2)$  and  $\rho_{ab}(1,2)$  denote the two-particle densities.

By some proper assumptions and necessary simplifications, Boudh-Hir and Mansoori got their model which can be expressed as

$$\begin{aligned} \gamma_{ab} &= (\Delta\rho_a/\Delta\rho_a^0)^2 \gamma_a + (\Delta\rho_b/\Delta\rho_b^0)^2 \gamma_b \\ &\quad - 2(\Delta\rho_a/\Delta\rho_a^0)(\Delta\rho_b/\Delta\rho_b^0)(d_{aa}d_{bb}/\sigma_{ab}^2)^2 \\ &\quad (\gamma_a \gamma_b)^{1/2} \end{aligned} \quad (2)$$

$$\begin{aligned} \Delta\rho_a &= \rho_{a/A} - \rho_{a/B}, & \Delta\rho_b &= \rho_{b/B} - \rho_{b/A} \\ \Delta\rho_a^0 &= \rho_a^L - \rho_a^V, & \Delta\rho_b^0 &= \rho_b^L - \rho_b^V \end{aligned}$$

where  $\rho_{a/A}$ ,  $\rho_{a/B}$ ,  $\rho_{b/A}$  and  $\rho_{b/B}$  denote the number densities of molecules *a* and *b* in phases A and B,

respectively;  $\rho_a^L$ ,  $\rho_b^L$ ,  $\rho_a^V$  and  $\rho_b^V$  stand for the number densities of pure molecules a and b in liquid and vapor phases, respectively;  $d_{aa}$  and  $d_{bb}$  are the hard-sphere diameters of molecules a and b, respectively;  $\rho_{ab}$  is the cross diameter, which can be calculated by the following combining rule

$$\sigma_{ab} = \frac{1}{2}(d_{aa} + d_{bb})(1 + \delta_{ab}) \quad (3)$$

where  $\delta_{ab}$  is the unlike interaction parameter.

At room temperature, compared with the density in liquid phase, the density in vapor phase is so small that it can be ignored, so we have

$$\Delta\rho_a^0 = \rho_a^L - \rho_a^V \approx \rho_a^L, \quad \Delta\rho_b^0 = \rho_b^L - \rho_b^V \approx \rho_b^L \quad (4)$$

then Eq. (2) can be predigested as follows<sup>[12]</sup>

$$\begin{aligned} \gamma_{ab} = & (\Delta\rho_a/\rho_a^L)^2\gamma_a + (\Delta\rho_b/\rho_b^L)\gamma_b \\ & - 2(\Delta\rho_a/\rho_a^L)(\Delta\rho_b/\rho_b^L)(d_{aa}d_{bb}/\sigma_{ab}^2)^2(\gamma_a\gamma_b)^{1/2} \end{aligned} \quad (5)$$

where  $\gamma_a$  and  $\gamma_b$  are surface tensions of pure molecules a and b, respectively.

### 3.2 Interfacial equation of state for surfactant-oil-water systems

Interfacial pressure  $\Pi$  is expressed as

$$\Pi = \gamma_0 - \gamma_\infty \quad (6)$$

where  $\gamma_0$  is the interfacial tension of oil-water system and  $\gamma_\infty$  is the interfacial tension of surfactant-oil-water system.

Interfacial pressure  $\Pi$  can also be calculated from Helmholtz free energy

$$\Pi = -\left(\frac{\partial F}{\partial A}\right)_{N,T} \quad (7)$$

According to perturbation theory, the interfacial pressure can be expressed as

$$\Pi = -\Pi^{hs} + \Pi^{per} \quad (8)$$

where  $\Pi^{hs}$  and  $\Pi^{per}$  are the hard-sphere reference term and perturbation term of interfacial pressure, respectively.

Hard-sphere term  $\Pi^{hs}$  can be expressed by the equation of Henderson *et al.*<sup>[13]</sup>

$$\Pi^{hs} = \frac{kT}{A} \frac{(1 + \xi^2/8)}{(1 - \xi)^2} \quad (9)$$

where

$$\xi = \frac{A_h}{A} \quad (10)$$

where  $A_h$  is cross-sectional area and  $A$  is the average area of each surfactant molecule on the interface.

The perturbation term can be expressed as follows

$$\Pi^{per} = -\left(\frac{\partial F^{per}}{\partial A}\right)_{N,T} \quad (11)$$

Because every surfactant is made up of hydrophobic group and hydrophilic group which stretch into oil phase and water phase, respectively, we divided  $\Pi^{hs}$  and  $\Pi^{per}$  into two parts, one for hydrophobic group and the other for hydrophilic group

$$\Pi^{hs} = \frac{kT}{A} \frac{(1 + \xi_1^2/8)}{(1 - \xi_1)^2} + \frac{kT(1 + \xi_2^2/8)}{A(1 - \xi_2)^2} \quad (12)$$

$$\xi_1 = \frac{A_{h,1}}{A}, \quad \xi_2 = \frac{A_{h,2}}{A} \quad (13)$$

where  $A_{h,1}$  and  $A_{h,2}$  are the cross-sectional areas of hydrophobic group and hydrophilic group, respectively.

$$A_{s,1} = \alpha_1^2 A_{h,1}, \quad A_{s,2} = \alpha_2^2 A_{h,2} \quad (14)$$

where  $A_{s,1}$  and  $A_{s,2}$  are the soft-areas of hydrophobic group and hydrophilic group, respectively;  $\alpha = \frac{\sigma}{d}$ ,  $\sigma$  and  $d$  are the soft-sphere and hard-sphere diameters, respectively. According to the equation of Cotterman *et al.*<sup>[14]</sup> based on perturbation theory, it is

$$\frac{\sigma}{d} = \frac{1 + 0.33163kT/\varepsilon + 0.01047(kT/\varepsilon)^2}{1 + 0.2977kT/\varepsilon} \quad (15)$$

#### 3.2.1 Non-ionic surfactant-oil-water systems

For non-ionic surfactant-oil-water systems,  $\Pi^{per}$  can be expressed as the sum of Lennard-Jones term and dipole-dipole term<sup>[9]</sup>

$$\Pi^{per} = \Pi^{LJ} + \Pi^{dd} \quad (16)$$

$$F^{LJ} = \frac{16\varepsilon A_s}{A} \left[ \sigma^{10} \int_0^\infty \frac{g^{hs}(r)}{r^{11}} dr - \sigma^4 \int_0^\infty \frac{g^{hs}(r)}{r^5} dr \right] \quad (17)$$

$$\begin{aligned} \Pi^{LJ} = & -\frac{16\varepsilon_1 A_{s,1} [G'_1(5) - G'_1(11)]}{A^2} \\ & -\frac{16\varepsilon_2 A_{s,2} [G'_2(5) - G'_2(11)]}{A^2} \end{aligned} \quad (18)$$

$$G'(n) = \alpha^{n-1} G(n) \quad (19)$$

where  $G(n)$  is the integral function<sup>[15]</sup>

$$\begin{aligned} G(n) = & d^{n-1} \int_0^\infty \frac{g^{hs}(r)}{r^n} dr \\ = & \frac{1 + J_1 \Gamma^* + J_2 \Gamma^{*2}}{n + J_3 \Gamma^* + J_4 \Gamma^{*2}} \end{aligned} \quad (20)$$

where  $\Gamma^* = \Gamma d$ ,  $\Gamma$  is the adsorptive capacity. The universal constants  $J_1 - J_4$  in the above equation have been given from Ref. [16] by use of molecular simulation.

Because it is very small, the dipole moment of hydrophobic group is ignored and only the dipole moment of hydrophilic group is taken into account.

$$F^{dd} = -\frac{\pi\mu^4}{3AkT(4\pi\epsilon_0D)^2} \int_0^\infty \frac{g^{hs}(r)}{r^5} dr \quad (21)$$

$$\Pi^{dd} = -\frac{\pi\mu_2^4}{A^23kT(4\pi\epsilon_0D)^2} \frac{G_2^{hs}(5)}{d_2^4} \quad (22)$$

where  $D$  is relative dielectric constant of water.

The interfacial tension of non-ionic surfactant-oil-water system can be eventually expressed as

$$\begin{aligned} \Pi = & \frac{kT}{A} \frac{(1 + \xi_1^2/8)}{(1 - \xi_1)^2} + \frac{kT}{A} \frac{(1 + \xi_2^2/8)}{(1 - \xi_2)^2} - \\ & \frac{16\epsilon_1 A_{s,1} [G_1'(5) - G_1'(11)]}{A^2} - \\ & \frac{16\epsilon_2 A_{s,2} [G_2'(5) - G_2'(11)]}{A^2} - \\ & \frac{\pi\mu_2^4}{A^23kT(4\pi\epsilon_0D)^2} \frac{G_2(5)}{d_2^4} \end{aligned} \quad (23)$$

### 3.2.2 Ionic surfactant-oil-water system

For ionic surfactant-oil-water system, besides the Lennard-Jones term and dipole-dipole term, the ion-ion term and ion-dipole term must be taken into account also<sup>[9]</sup>.

$$\frac{\Pi^{cc}A}{kT} = 1 + \frac{\pi e^2 z^2 R}{3AkT(4\pi\epsilon_0D)} G(y) \quad (24)$$

where  $y = \frac{r}{R}$ ,  $r$  is the distance between particles,  $R$  presents molecular diameter and  $G(y)$  is another integral function

$$G(y) = \int_0^\infty g_{ij}^{el}(y) dy \quad (25)$$

The expression of  $g_{ij}^{el}(y)$  is given from Ref. [17].  $G(y)$  can be expressed as

$$G(y) = \frac{1 - 12.21 \frac{d_2^2}{A} + 10.7396 \left(\frac{d_2^2}{A}\right)^2}{38.2408 + 25.5281 \frac{d_2^2}{A} + 0.7322 \left(\frac{d_2^2}{A}\right)^2} \quad (26)$$

The above universal constants have been given from Ref. [9] also. The Holmholtz free energy and interfacial pressure terms due to ion-dipole interaction

are

$$F^{cd} = -\frac{\pi e^2 z^2 \mu^2}{3AkT(4\pi\epsilon_0D)^2} \int_0^\infty \frac{g^{hs}(r)}{r^3} dr \quad (27)$$

$$\Pi^{cd} = -\frac{\pi e^2 z^2 \mu^2}{A^23kT(4\pi\epsilon_0D)^2} \frac{G(3)}{d_2^2} \quad (28)$$

By combining Eq. (23) with Eqs. (24) and (28), the interfacial pressure,  $\Pi$ , for ionic surfactant-oil-water system can be calculated.

## 4 CORRELATION AND PREDICTION

### 4.1 Oil-water system

By using Eq. (5), interfacial tensions of heptane-water system at 25°C, 30°C, 35°C, 40°C and 45°C have been correlated. The parameters obtained are:  $\sigma_{water} = 0.292$  nm;  $\sigma_{heptane} = 0.602$  nm;  $\delta = 0.097$ . The average relative deviation (ARD) is 0.32%. The experimental data and calculated results are shown in Table 2.

### 4.2 Surfactant-oil-water system

By using Eqs. (5), (6), (23), (24) and (28), the interfacial tensions of sodium dodecyl sulphate-heptane-water ( $C_{12}H_{25}SO_4Na-C_7H_{16}-H_2O$ ) system, polyoxyethylene *n*-octylphenol-heptane-water [ $C_8H_{17}C_6H_4O(OC_2H_4)_{10}O-C_7H_{16}-H_2O$ ] system and hexadecyl trimethyl ammonium bromide-heptane-water [ $C_{16}H_{33}N(CH_3)_3Br-C_7H_{16}-H_2O$ ] system at 25°C have been correlated. The average relative deviations and the adjustable parameters obtained are shown in Table 3. The calculated results are shown in Figs. 1—3 also. These figures and Table 3 indicate that the calculated results are very close to the experimental data, which proves that our model has good correlation function.

By using the adjustable parameters obtained from correlation, the interfacial tensions of these three systems mentioned above at 30°C and 35°C have been predicted. The predicted results are also close to the experimental ones, The average relative deviations are shown in Table 4.

The calculated and predicted results show that the interfacial tensions of surfactant-heptane-water systems decline when temperature or concentration of surfactant becomes higher. It coincides with the experimental results and shows again that our model is reliable.

Table 3 Average relative deviations and adjustable parameters

System	$(\epsilon_1/k)$	$(\epsilon_2/k)$	$A_{s,1}$	$A_{s,2}$	$\mu_1 \times 10^{30}$	$\mu_2 \times 10^{30}$	ARD, %
	K	K	nm <sup>2</sup>	nm <sup>2</sup>	C·m	C·m	
$C_{12}H_{25}SO_4Na-C_7H_{16}-H_2O$	290.00	300.00	25.20	27.85	0.00	3.50	4.07
$C_8H_{17}C_6H_4O(OC_2H_4)_{10}O-C_7H_{16}-H_2O$	300.00	320.00	26.51	29.55	0.00	8.35	5.26
$C_{16}H_{33}N(CH_3)_3Br-C_7H_{16}-H_2O$	350.00	380.00	30.11	34.07	0.00	3.17	3.78

Table 4 Predicted results at different temperatures

System	T, K	Data points	ARD, %
C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na-C <sub>7</sub> H <sub>16</sub> -H <sub>2</sub> O	303.15	8	4.59
	308.15	8	5.16
C <sub>8</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> O(OC <sub>2</sub> H <sub>4</sub> ) <sub>10</sub> O-C <sub>7</sub> H <sub>16</sub> -H <sub>2</sub> O	303.15	9	3.77
	308.15	9	3.90
C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br-C <sub>7</sub> H <sub>16</sub> -H <sub>2</sub> O	303.15	7	2.46
	308.15	7	3.97

## 5 CONCLUSIONS

A molecular thermodynamic model is developed based on perturbation theory and Boudh-Hir and Mansoori equation. The interfacial tension in surfactant-oil-water system can be calculated from the surface tensions of pure oil and water by using this model. The interfacial tensions of three surfactant-heptane-water systems at 30°C and 35°C have been predicted from the correlated parameters obtained at 25°C. All the average relative deviations of correlation and prediction are less than 6%. It shows that our model has good correlation and prediction functions.

## NOMENCLATURE

$A$	interfacial area, nm <sup>2</sup>
$A_h$	cross-sectional area, nm <sup>2</sup>
$A_s$	soft-sphere area, nm <sup>2</sup>
$c$	concentration of surfactant, mol·L <sup>-1</sup>
$D$	relative dielectric constant of water
$d$	hard-sphere diameter, nm
$e$	unit electric charge, C
$F$	Helmholtz free energy, J
$G$	integral function
$G'$	integral function defined in this paper
$g(r)$	radial distribution function
$k$	Boltzmann constant, J·K <sup>-1</sup>
$n$	natural number, $n \geq 2$
$R$	molecular diameter, nm
$r$	distance between particles, nm
$T$	absolute temperature, K
$V$	volume, m <sup>3</sup>
$y$	reduced distance
$z$	ionic valence
$\alpha$	ratio between hard-sphere diameter and soft-sphere diameter
$\Gamma$	adsorptive capacity, mol·cm <sup>-2</sup>
$\gamma$	interfacial tension, mN·m <sup>-1</sup>
$\gamma_0$	interfacial tension of oil-water system, mN·m <sup>-1</sup>
$\gamma_\infty$	interfacial tension of surfactant-oil-water system, mN·m <sup>-1</sup>
$\delta$	unlike interaction parameter
$\epsilon$	dispersion parameter, J
$4\pi\epsilon_0$	dielectric constant of vacuum, C <sup>2</sup> ·N <sup>-1</sup> ·m <sup>-2</sup>
$\mu$	dipole moment, C·m
$\xi$	reduced area
$\Pi$	interfacial tension, mN·m <sup>-1</sup>
$\rho$	number density
$\sigma$	soft-sphere diameter, nm

## Superscripts

cc	charge-charge
cd	charge-dipole
dd	dipole-dipole
el	static
hs	hard sphere
L	liquid
LJ	Lennard-Jones
per	perturbation
V	vapor
*	reduced parameter

## Subscripts

A,B	phases
a,b	molecules
cal	calculated values
exp	experimental values
lit	data from literature
N	number of particles
1	hydrophobic group
2	hydrophilic group

## REFERENCES

- Antonov, G. J., *Chem. Phys.*, **5**, 372 (1907).
- Fowkes, F. M., *J. Chem. Phys.*, **66**, 382 (1962).
- Girifalco, L. A., Good, R. J., *J. Phys. Chem.*, **61**, 904 (1957).
- Owens, D. K., Uy, K. Q., *J. Adhesion*, **2**, 50 (1970).
- Davis, H. T., *J. Chem. Phys.*, **62** (9), 3412 (1975).
- Fu, J. F., Li, B. Q., Wang, Z. H., *Chem. Eng. Sci.*, **41** (10), 2673 (1986).
- Li, B. Q., Fu, J. F., *Chem. Eng. Sci.*, **44** (7), 1519 (1989).
- Boudh-Hir, M. E., Mansoori, A. G., *Physica. A.*, **179**, 219–231 (1991).
- Fu, D., Bao, T. Z., Lu, J. F., Li, Y. G., Li, X. S., *J. Chem. Ind. & Eng. (China) (in Chinese)*.
- Galiant, R. W., *Hydrocarbon Process*, **46** (7), 121 (1987).
- Jasper, J. J., *J. Phys. Chem. Ref. Data*, **1**, 841–1009 (1972).
- Li, Z. B., Ph. D. Thesis, Chem. Eng. Dept., Tsinghua Univ., Beijing (1998).
- Henderson, D., *Molecular Physics*, **30**, 971–972 (1975).
- Cotterman, R. L., Schwarz, B. J. and Prausnitz, J. M., *AIChE J.*, **32**, 1787–1798 (1986).
- Henderson, D., Blum, L. and Tani, A., *Am. Chem. Soc. Symp. Ser.*, **30**, 281–296 (1986).
- Li, C. X., Ph. D. Thesis, Chem. Eng. Dept., Tsinghua Univ., Beijing (1996).
- Hirata, F., Arakawa, K., *Bull. Chem. Soc. Japan*, **48** (7), 2139–2144 (1975).