Molecular Exchanging Energy of Anionic/Cationic Surfactants System on the Surface of Solution

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Abstract: In order to study synergism of the mixed surfactants system with molecular exchanging energy (ε), the Lennard-Jones formula has been firstly introduced to evaluate the ε of the mixed system, $CH_3(CH_2)_nOSO_3^-$ /$CH_3(CH_2)_nN^+(CH_3)_3$, directly from their molecular structure. The comparison of the calculated and the observed results showed that this method is practical.

Keywords: Surfactant, molecule exchanging energy, dimensional crystal model.

Mixed surfactants are often superior to a single one in reducing the surface energy of solution. This phenomenon is called synergism of mixed surfactants[1]. Synergism is very useful in many fields such as mining engineering, oil extraction, pharmaceutical production, cosmetic industry, and so on. The source of synergism is the existence of the molecular exchange energy (ε) of different surfactants.   Since ε is influenced by kinds of molecular interactions in the solution such as van der Waals force, Coulomb force and hydrogen bond and all these interactions are related to the molecular structure of surfactants, therefore, the study of the relationship between ε and the molecular structure of surfactants is very important.   However, because the molecular structure of surfactants is somewhat complicated, to our knowledge, no work has been reported in this field.

In our previous work, we have introduced the experimental method with the molecular interaction parameter (β) presented by Rubing, Rosen and their coworkers[2]. The present work is with a commonly used anionic/cationic surfactant mixture, $CH_3(CH_2)_nOSO_3^-$ /$CH_3(CH_2)_nN^+(CH_3)_3$, as an example, to introduce a method of evaluating ε directly from the molecular structure of mixed surfactants with the Lennard-Jones formula.

Determination of the molecular exchanging energy with the two-dimensional crystal model of mixed surfactants in monolayer

When the positions of two surfactants with different molecular structures are exchanged,

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the molecular exchanging energy often takes place because of the exchange of the intermolecular forces among them.   The molecular exchanging energy of mixed surfactants in monolayer can be determined with the two-dimensional crystal model[2] shown in **Figure 1** as

$$A\text{-}A + B\text{-}B \rightarrow 2A\text{-}B$$

$$\varepsilon = \varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2 \tag{1}$$

Here ε_{AB}, ε_{AA} and ε_{BB} are the interaction energies of molecules A and B forming the molecular pairs A-B, A-A and B-B, respectively.   With the help of the regular solution theory and the Flory-Huggins lattice theory we can obtain the experimental equation expressed by Rubing and Rosen's molecular interaction parameter β as

$$\varepsilon = \beta RT / g N_0 \tag{2}$$

were R, T, g and N_0 is the ideal gas constant, the temperature of system, the ligand number and the Avogadro's constant, respectively. β can be obtained by measuring the surface tension of the mixed surfactant solution.   Based on this two-dimensional crystal model, synergism can be judged with ε, *i.e.*, the higher the absolute value of ε when $\varepsilon < 0$, the better synergism will be.

Evaluation of ε from Molecular Structure of Surfactants with Lennard-Jones Formula

Since ε is the result of the exchange of intermolecular forces among surfactants, we can divide it into van der Waals force ε_V, Coulomb force ε_C and the hydrogen bonds ε_h as

$$\varepsilon = \varepsilon_C + \varepsilon_v + \varepsilon_h \tag{3}$$

If the Debye Hückel approximation is appointed to express the change of the electrostatic force and Lennard-Jones formula is appointed to express the change of the van der Waals force, we can calculate the molecular exchange energy directly from the molecular structure information of surfactants as

$$\varepsilon = \frac{e^2}{\eta}[\frac{z_A z_B}{l_{AB}} - \frac{1}{2}(\frac{z_A^2}{l_{AA}} + \frac{z_B^2}{l_{BB}})] + [n_{AB} + \frac{1}{2}(n_{AA} + n_{BB})]\varpi$$
$$+ \{[\sum_{i \neq j}^{n_A} \sum_{j}^{n_B} (\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}})]_{AB} - 0.5[\sum_{i \neq j}^{n_A} \sum_{j}^{n_A} (\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}})]_{AA} - 0.5[\sum_{i \neq j}^{n_B} \sum_{j}^{n_B} (\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}})]_{BB}\} \tag{4}$$

where e is the elementary charge, η is the dielectric constant, z_A and z_B are respectively the charge numbers of A and B. l_{AB}, l_{AA} and l_{BB}, are the distances between two neighbor molecules as shown in **Figure 1**. n_{AB}, n_{AA} and n_{BB} are the formed hydrogen bond numbers between two neighbor molecules and ϖ is the energy of single hydrogen bond. A_{ij} and B_{ij} are constants in the Lennard-Jones formula.   For some atomic pairs these constants have been computed with quantum mechanic method[3]. r_{ij} is the distance between two arbitrary atoms belonging to two neighbor molecules. n_A and n_B are the atomic numbers of the corresponding two neighbor molecules.

Simplification of the calculation of ε from molecular structure of surfactants

There are two difficulties in the calculation of ε with equation (4). One is that the

calculation is very complicate in the last term of the equation for surfactant molecules. The other is that the existence of varies kinds of movements in a molecule, such as the extension, compression, winding and rotation of all kinds of bonds, the collision among atoms, and so on, makes the position of atoms can not be precisely determined and consequently, the distance r_{ij} in Lennard-Jones formula can not be determined. Therefore, in order to obtain a practical analytical expression of calculating ε, we present a few approximations as follows:

i. The shape of the hydrophobic segment of a surfactant molecule is considered as a cylinder with height h and radius r and the hydrophilic segment as a sphere with a radius R. The arrangement of surfactants in the monolayer is parallel (**Figure 1**).

ii. All the charge of ionic surfactant evenly distributes on the surface of hydrophilic segment and the charge on the hydrophobic segment is neglected[4].

iii. After the consideration of all kinds of their movement, the atoms having the same properties in surfactant molecules can be thought distributing with an even probability in a certain space.

iv. Since ε_V is a short-range force, as a simplified method, the inner atoms can be neglected in dealing with the molecular interaction. Even for the H atoms on the cylinder surface, only the interaction of atoms in the faced cirques belonging to the separated molecules is considered.

Under the above approximations, the atoms contributing to the molecule exchanging energy will distribute on the cirques of the tail or on the surface of the head with some certain atomic number densities, and this distribution will make the position between any two neighbor surfactant molecules can be mathematically determinable. As the results of this determination of the position of atoms, the additive operation in the last term of equation (4) can be easily simplified by transforming it into integral operation, and the calculation of the Coulomb force ε_C also can be further simplified.

As an example, for the commonly used binary anionic/cationic mixture, (A=$CH_3(CH_2)_{11}OSO_3^-$ and B=$CH_3(CH_2)_{11}N^+(CH_3)_3$), the molecular volumes of A and B can be evaluated from the following parameters:

(1) van der Waals radii of atoms (Å): H, 1.20; O, 1.40;

(2) Lengths of covalent bonds (Å): C—H, 1.11; C—C, 1.52; N—C, 1.54; C—O, 1.42; S—O, 1.52;

(3) Bond angles: bond angles in tail C—C—C, 111.4^o; C—C—H, 110.0^o and the others being simply evaluated from the tetrahedral configuration as O—S—O, C—O—S, N—C—C and C—N—C $109.5\,^o$.

The molecular volume parameters with the above parameters are: r=1.80Å, R_A=2.13Å, R_B=2.53Å. From the experimental minimum surface areas[1]: S_{AA} =53 Å^2 and S_{BB} =72 Å^2, the values of l_{AA} and l_{BB} are calculated as 8.2 Å and 9.6Å, respectively. By substituting these values of r, R_O, R_H, l_{AA} and l_{BB} into equations (4), we finally obtain the expression of ε in Joule for $CH_3(CH_2)_{11}OSO_3^-$ /$CH_3(CH_2)_{11}N^+ (CH_3)_3$ mixture in the monolayer of solution as

$$\varepsilon(J) = 2.03 \times 10^{-21} + \frac{1.07 \times 10^{-106}}{l_{AB}^{12}} - \frac{3.40 \times 10^{-63}}{l_{AB}^{6}} - \frac{4.00 \times 10^{-43}}{l_{AB}^{3}} \qquad (5)$$

The variation of ε *versus* the distance between A and B is shown in **Figure 2**. The value of ε in adsorption equilibrium is the minimum value of the curve, which is -2.6 $\times 10^{-20}$ J and the corresponding distance between A and B is 6.3×10^{-10} m. The observed values of β and l_{AB} at 298.16K are –27.8 J and 6.2×10^{-10} m, respectively. For the saturated adsorption, $g=6$ (see **Figure 1**), then equation (2) gives the observed $\varepsilon = -1.9 \times 10^{-20}$ J. The comparison of the calculated and the observed values of ε and l_{AB} illustrated that the molecular exchanging energy and further the determination of the synergism of mixed surfactants can be directly evaluated from the molecular structures of the surfactants.

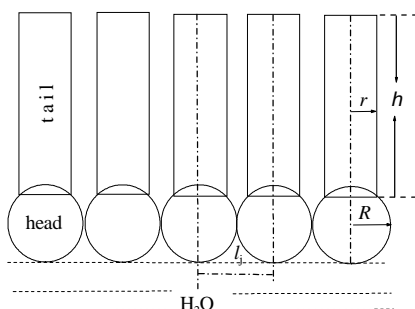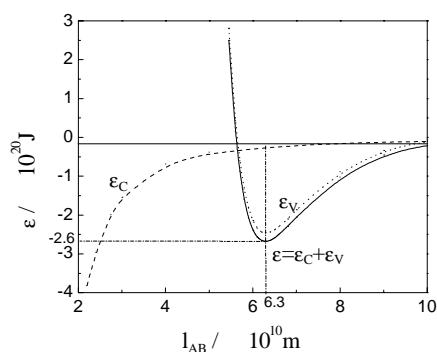**Figure 1**   Schematic representation of the adsorption of surfactants on the surface of aqueous solution.

Figure 2   Variation of molecular exchange energy between surfactants A and B *vs.* the distance of their head centers.

"$---$" Coulomb force ε_C, "$\cdots$" van der Waals force ε_V and "$\underline{\quad}$" the molecular exchange energy ε.

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