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RESEARCH ARTICLE

Computational Prediction of the Adsorption Equilibrium for Ionic Surfactants at the Electrified Oil/Water Interface

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Dedicated to Prof. Hubert Girault on the occasion of his 65th birthday

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Abstract: In a previous study (Somekawa et al., *Langmuir* **2019**, *35*, 11345-11350) a non-Bornian solvation model was successfully applied to computational prediction of the adsorption equilibrium for nonionic surfactants at the oil (O)/water (W) interface. In this study we have extended the method to the adsorption of "ionic" surfactants at the polarized O/W interface. In this extension, the electrostatic potential of an ionic surfactant in the electric double layer formed at the O/W interface is taken into account together with the chemical potential estimated using the non-Bornian solvation model. The calculation results clearly show that a cationic surfactant (hexadecyltrimethylammonium ion) is adsorbed at the nitrobenzene/W interface, when the interfacial potential is negative. This prediction is consistent with the previous experimental observation using electrocapillary measurements.

Introduction

The adsorption of molecules or ions at the oil (O)/water (W) interface is an important phenomenon for understanding various colloidal systems, such as emulsions, liposomes, and micelles.[1–3] Thus far, surfactant adsorption at the O/W interface has extensively been studied by measuring interfacial tension,[4–7] capacitance,[7] and spectroscopic responses.[8–11] In addition to these experimental studies, molecular dynamics simulation has been applied to study the adsorption behaviors of surfactants at O/W interfaces, e.g., those of alkyl alcohols at alkene/W interfaces.[12–14]

Our previous paper[15] reported that the standard Gibbs energy for adsorption of nonionic surfactants at the O/W interface could be estimated theoretically by using the non-Bornian solvation model, which was recently proposed by our group.[16–22] An important feature of this model is that the relatively small contribution from the long-range electrostatic interaction is daringly ignored, and the solvation or resolvation energy of ions or neutral molecules can be formulated based on short-range or vicinal solute–solvent interactions, including cavity formation, Coulomb, polarization, etc. The short-range interaction energy on a minute surface of the solute molecule is evaluated as a function of the local electric field (E_i; $i = 1,2,3\cdots$) on the minute surface, which is obtained through density functional theory (DFT) calculation.[20] In the previous paper,[15] we showed that the proposed solvation model was successfully used to estimate the adsorption energy of nonionic surfactants (alkyl alcohols) at the O/W interface, by considering the adsorption process as a "partial" transfer of the surfactant molecule across the interface.

In this study we have extended this method to the adsorption of "ionic" surfactants at the polarized O/W interface. It is generally known that the interfacial adsorption of ionic surfactants is affected by the Galvani potential difference of the O/W interface.[8,23–25] Kakiuchi et al. conducted a series of studies on the potential-dependent adsorption of ionic surfactants at the polarized O/W interface.[23–26] They reported that the standard Gibbs energy of adsorption was linearly dependent on the Galvani potential difference of the O/W interface.[25,26] In this study we have extended our method to calculate the potential dependence of adsorption of ionic surfactants at the O/W interface. By incorporating the effect of the electric double layer of the O/W interface, the potential-dependent adsorption of a cationic surfactant (hexadecyltrimethylammonium; $HTMA^+$) at the nitrobenzene (NB)/W interface has been successfully reproduced by theoretical calculation. The effect of counter anions on the interfacial adsorption of $HTMA^+$ has also been discussed.

Calculation Methods

DFT Calculation

To obtain partial atomic charges of a surfactant molecule by the Merz–Kollman (MK) method,[27,28] we carried out a DFT calculation at the level of hybrid B3LYP/6-311++G(2d,p) using the Gaussian 09 program package. The previously developed subprogram[21] was employed to evaluate the values of E_i on minute molecular surfaces as well as their geometric area (S_i; $i = 1,2,3\cdots$) by using atomic van der Waals surfaces.

Prediction of Adsorption State and Energy

A program has been written in Visual Basic 6.0 for predicting the adsorption state and energy of an ionic surfactant at the polarized O/W interface. To determine the orientation of $HTMA^+$ at the NB/W interface, the following three parameters have been defined: the distance of the charge center from the interface (d), the orientation angle with respect to the normal line of the interface (θ), and the rotation angle around the molecular axis (ω) (see Figure 1a). Figure 1b shows the long and short axes of the $HTMA^+$ molecule for determining the values of θ and ω. The long axis (i.e., molecular axis) is defined as the line connecting the midpoint of the head-part carbons C1 and C2 with that of the tail-part carbons C15 and C16; the center between the two midpoints is assigned as reference point RP1, from which an orthogonal line

crosses the dashed line between C1 and C2 at reference point RP2. Then, the line connecting RP1 and RP2 is regarded as the short axis of the molecule. Under these definitions, the normal line of the O/W interface coincides with the long axis at $\theta = 0°$. At $\omega = 0°$, the short axis lines parallel to the figure plane (Figure 1a). At $d = 0$ Å, the center of charge around the center of the C1–N bond is located on the O/W interface.

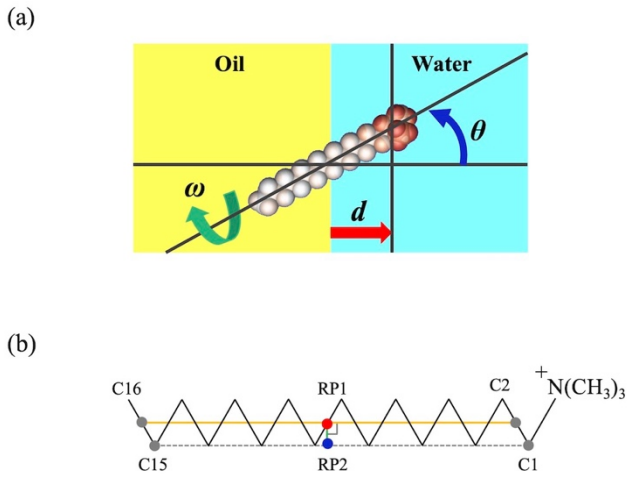

Figure 1. (a) Three parameters (d, ω, and θ) representing the orientation of $HTMA^+$ at the O/W interface. (b) Long and short axes of $HTMA^+$.

To predict the Gibbs energy profile in the adsorption–desorption processes, we changed θ ($0° - 180°$), ω ($0° - 180°$), and d (from –20 Å to 30 Å), respectively, by 1°, 1°, and 0.2 Å, and then obtained the combination of θ and ω that minimizes the Gibbs energy for each d. In this calculation, the Gibbs energy was evaluated as the sum of the chemical potential (G°_{chem}) estimated by the non-Bornian solvation model and the electrostatic potential (G°_{el}) for the charged species in the electric double layer:

$$G^\circ = G^\circ_{\mathrm{chem}} + G^\circ_{\mathrm{el}} \quad (1)$$

Another program was written for this calculation in Visual Basic 6.0.

Calculation of Chemical Potential

The chemical potential has been calculated by using the following semi-empirical equation for the standard Gibbs energy of ion transfer from W to O:

$$\Delta_{\mathrm{tr}}G^\circ_{\mathrm{W}\to\mathrm{O}} = \Delta A \sum S_i + \Delta B^*_+ \sum_{E_i \geq \xi_+} S_i E_i + \Delta B_+ \sum_{\xi_+ > E_i > 0} S_i E_i + \Delta C_- \sum_{E_i < 0} S_i {E_i}^2 \quad (2)$$

which is a modification of the previously reported equation for cations at the NB/W interface.[21] In Equation (2), ΔA, ΔB^*_+, ΔB_+, and ΔC_- are E_i-independent coefficients, being obtained as adjusting parameters in the regression analysis with the dataset of $\Delta_{\mathrm{tr}}G^\circ_{\mathrm{W}\to\mathrm{O}}$.[22] The first term of the r.h.s. of Equation (2) is proportional to the molecular surface area ($\sum S_i$), which is mainly related to the so-called cavity formation energy, though being influenced by the E_i-independent terms of short-range ion–solvent interactions. The second term represents the contribution from much positively charged surfaces with $E_i \geq \xi_+$ (threshold value). Such surfaces are known to be selectively hydrated in the O phase,[29,30] and the effects have been included in this term. The third term shows the contributions from moderately positively charged surfaces with $\xi_+ > E_i > 0$. These contributions are mainly from ion–dipole (Coulomb) interactions, though should include possible ion–induced dipole (polarization) interactions. Similarly, the last term shows the contributions from negatively charged surfaces with $E_i < 0$, which should include ion–dipole (and ion–induced dipole) interactions. Thus, Equation (2) consists of four different terms, while the previously reported equation consists of as many as seven terms.[22] In the previous equation, however, there are some pairs of strong correlations among the coefficients in the identical E_i-ranges, namely, multicollinearity was observed. Accordingly, we have reduced three terms to obtain Equation (2), in which more reliable prediction or analysis can be performed for $\Delta_{\mathrm{tr}}G^\circ_{\mathrm{W}\to\mathrm{O}}$. Table 1 shows the regression coefficients optimized anew in this study.

Table 1. Optimized coefficients in Equation (2)[a] and their standard deviations.

Coefficient	Optimized[b]
ΔA	-12.11 (0.52)[c]
ΔB^*_+	2.211 (0.080)
ΔB_+	0.9495 (0.0592)
ΔC_-	0.1349 (0.0116)
n[d]	63
R^2 [e]	0.963
MAE[f]	2.5

[a] Where $\Delta_{\mathrm{tr}}G^\circ_{\mathrm{W}\to\mathrm{O}}$ is in kJ mol^{-1}, S_i in nm^2, and E_i in V nm^{-1}. [b] Optimized values with ξ_+ = +27 V nm^{-1}. [c] The values in the parentheses are the standard deviations, [d] Number of data, [e] Square of the correlation coefficient. [f] Mean absolute error in kJ mol^{-1}.

By applying Equation (2) to the molecular surface located in the O phase, we can calculate G°_{chem} as the standard Gibbs energy of the partial transfer of the molecule from W to O (here, it is defined that $G^\circ_{\mathrm{chem}} = 0$ in the bulk O phase).

Calculation of Electrostatic Potential

To obtain the electrostatic potential, we have calculated the potential distribution at the O/W interface by applying Verwey–Niessen model.[31] In this model, ions in the respective phases form back to back diffuse layers at the O/W interface. The potential change occurring over the diffuse layers can be estimated by the analogy of the Gouy–Chapman model for metal electrode surfaces. Here, the following assumptions have been made: ions are considered as point charges; the distribution of ions follows Boltzmann's statistics; the interfacial adsorption of ions does not affect the potential profile across the O/W interface, which is determined only by the ions added to the O and W phases. Then, in the case of two 1:1 electrolytes in contact, by solving the Poisson–Boltzmann equation, the potential $\phi(x)$ in the W phase ($0 < x < +\infty$) is obtained as[32]

$$\tanh\left[\frac{e}{4kT}(\phi(x) - \phi^{\mathrm{W}})\right] = \exp\left(-\left[\frac{2N^{\mathrm{W}}e^2}{\varepsilon_0\varepsilon_{\mathrm{W}}kT}\right]^{1/2}x\right)\tanh\left[\frac{e}{4kT}(\phi(0) - \phi^{\mathrm{W}})\right] \quad (3)$$

and that in the O phase ($-\infty < x < 0$) is as

$$\tanh\left[\frac{e}{4kT}(\phi(x)-\phi^{O})\right] = \exp\left(\left[\frac{2N^{O}e^{2}}{\varepsilon_{0}\varepsilon_{O}kT}\right]^{1/2}x\right)\tanh\left[\frac{e}{4kT}(\phi(0)-\phi^{O})\right] \quad (4)$$

In these equations, ϕ^{W} or ϕ^{O} is the potential at the bulk of the W or O phase, N^{W} or N^{O} is the bulk volume concentration of the 1:1 electrolyte in the respective phase, $\phi(0)$ is the potential at the interface ($x = 0$), ε_0 is the dielectric constant of vacuum, ε_W or ε_O is the permittivity of water or organic solvent ($\varepsilon_W = 78$; $\varepsilon_O = 34.8$ for NB), and e, k, and T have their usual meanings. Figure 2 shows an example of the potential profile obtained for the electric double layer of the NB/W interface. In this figure is shown the variation of the potential profile for different Galvani potential of the interfaces ($\Delta_O^W\phi = \phi^W - \phi^O$). The concentration conditions used in the present study are as in the caption of Figure 2.

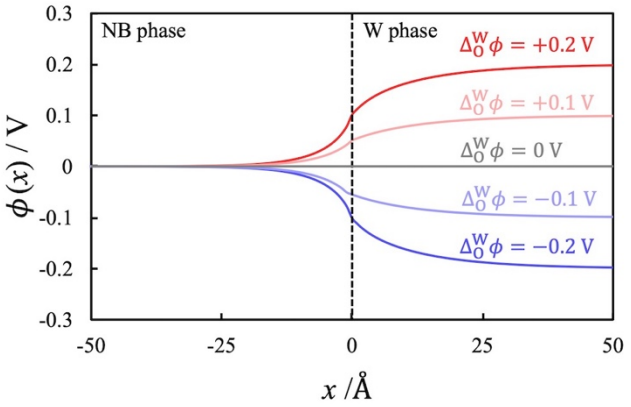

Figure 2. Potential profiles obtained for the electric double layer of the interface between NB (100 mM 1:1 electrolyte) and W (50 mM 1:1 electrolyte).

Finally, the electrostatic potential has been calculated by

$$G^{\circ}_{el} = \sum_j q_j F\phi(x) \quad (5)$$

where q_j is the partial atomic charge of each constituent atom j ($= 1,2,3\cdots$) of a surfactant molecule, being obtained from the DFT calculation, and F is the Faraday constant.

Results and Discussion

Prediction of Adsorption–Desorption Processes

Figure 3 shows the theoretically predicted Gibbs energy (G°) profile in the adsorption–desorption process for HTMA$^+$ at the NB/W interface. In this figure is shown the variation of G° for eight different values of $\Delta_O^W\phi$. As seen, when $\Delta_O^W\phi$ is positive, HTMA$^+$ is energetically most stable in the bulk NB phase ($d < -20$ Å). The energy profile has no minimum, indicating that HTMA$^+$ does not adsorb at the interface in the positive potential region. On the contrary, when $\Delta_O^W\phi$ is negative, the energy profile has a minimum value near the interface ($d \approx 0$ Å). This shows that HTMA$^+$ may adsorb at the negatively polarized NB/W interface. Such adsorption properties of HTMA$^+$ is in good agreement with the experimental results obtained from interfacial tension measurements.[23,24] In the electrocapillary curves reported, the interfacial tension was depressed by the specific adsorption of HTMA$^+$ only in the negative potential region.

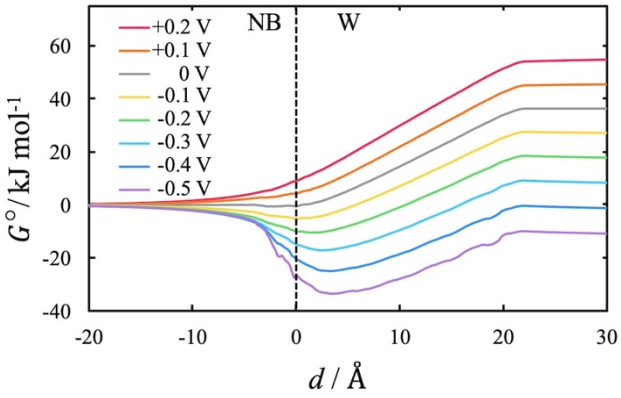

Figure 3. Theoretically predicted Gibbs energy profiles in the adsorption–desorption process for HTMA$^+$ at the NB/W interface. The variation of the Gibbs energy profile is shown for eight different values of $\Delta_O^W\phi$ (= +0.2, +0.1, 0, –0.1, –0.2, –0.3, –0.4, –0.5 V).

From the theoretically predicted G° vs. d plot in Figure 3, we obtained the standard Gibbs energy of adsorption of HTMA$^+$ from O to the interface (I), $\Delta_{ad}G^{\circ}_{O\to I}$, as the minimum value of G° measured from the bulk O phase (where $G^{\circ} = 0$). In the present case, the adsorption energy could be determined in the negative range of $\Delta_O^W\phi$ in which the energy minimum appeared. In Figure 4, blue plots show the calculated values of $\Delta_{ad}G^{\circ}_{O\to I}$ in the range of $\Delta_O^W\phi$ between –0.25 V and –0.15 V. Here, it should be noted that the $\Delta_{ad}G^{\circ}_{O\to I}$ values have been obtained by assuming one-molecule adsorption, i.e., no intermolecular interaction among the adsorbed HTMA$^+$ ions. In the figure are also shown the experimental values of $\Delta_{ad}G^{\circ}_{O\to I}$ by yellow, green, and orange plots, which were reported when LiF, LiCl, and LiBr were used, respectively, for the electrolytes in W. As seen in the figure, the theoretically predicted $\Delta_{ad}G^{\circ}_{O\to I}$ linearly depends on $\Delta_O^W\phi$ with the slope of 60 kJ mol^{-1}. Such potential dependence is in harmony with the experimental results; the slopes are 50, 50, and 38 kJ mol^{-1} for LiF, LiCl, and LiBr, respectively, being close to the theoretical slope of 60 kJ mol^{-1}. Nevertheless, the experimental linear plots are located below the theoretical plot, shifting to the lower energy side in the order of LiF < LiCl < LiBr. Most probably, these shifts can be ascribed to the ion-pair formation of HTMA$^+$ with halide ions, as discussed by Kakiuchi et al.[24] It has also been discussed that the more weakly hydrated Br$^-$ has larger association constants than Cl$^-$ in W, in line with the Hofmeister series of anions.[33] These results clearly indicate that the present theoretical prediction is valid for the one-molecular adsorption of HTMA$^+$ in the absence of ion-pair formation.

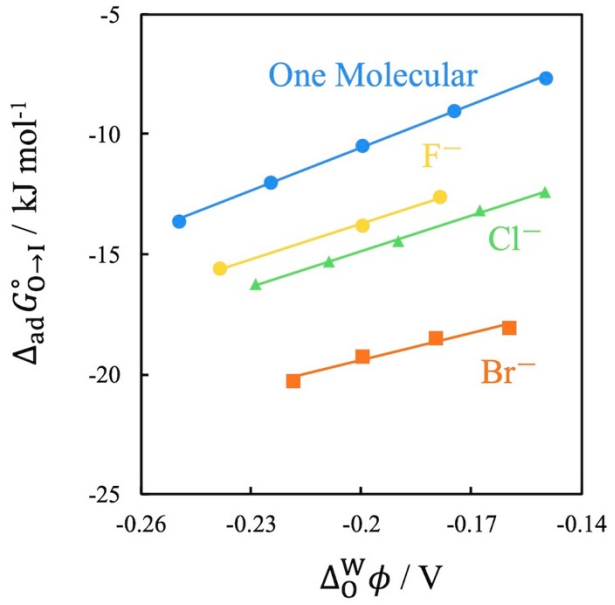

Figure 4. Potential dependence of $\Delta_{ad}G^{\circ}_{O\to I}$ for HTMA$^+$ at the NB/W interface. Blue plots show the values theoretically predicted by assuming one-molecular adsorption. Yellow, green, and orange plots show the experimental values in the presence of LiF, LiCl, and LiBr, respectively, in W.[24]

Table 2 shows the values of $\Delta_{ad}G^{\circ}_{O\to I}$ and also $\Delta_{ad}G^{\circ}_{W\to I}$ (for the adsorption from W to I), which were theoretically predicted in a wide range of $\Delta^{W}_{O}\phi$ from 0 V to –0.5 V. As shown in the table, $\Delta_{ad}G^{\circ}_{O\to I}$ becomes negatively larger with the change of $\Delta^{W}_{O}\phi$ to the negative values. On the contrary, $\Delta_{ad}G^{\circ}_{W\to I}$ becomes negatively smaller with the negative change of $\Delta^{W}_{O}\phi$. The potential dependence of $\Delta_{ad}G^{\circ}_{W\to I}$ is similar to that experimentally shown for decylammonium ion at the 1,2-dichloroethane/W interface.[25] Table 2 also shows the parameters (d, θ, and ω) representing the orientation of HTMA$^+$ adsorbed at the interface, which are dependent on $\Delta^{W}_{O}\phi$. As seen in the change of d, the charge center of HTMA$^+$ tends to be pulled from the interface to the W-phase side with the negative change of $\Delta^{W}_{O}\phi$. This is depicted in Figure 5. Such effect is also evident on the potential dependence of θ. The electrostatic attraction toward the W phase and the lipophilicity of the alkyl chain seem to make the HTMA$^+$ molecule stand at the interface. (i.e., $\theta \to 0°$). On the other hand, ω is insensitive to $\Delta^{W}_{O}\phi$, being either lower ($0° - 20°$) or higher ($\sim 180°$) depending on the small energy difference. The orientation of HTMA$^+$ corresponding these two ω values are almost identical except for a $180°$ rotation of the polar head group. This is due to the high symmetry and linearity of the optimized structure of HTMA$^+$.

Table 2. Theoretically predicted standard adsorption energies and the orientation parameters for HTMA$^+$ at the NB/W interface.

$\Delta^{W}_{O}\phi$ [V]	$\Delta_{ad}G^{\circ}_{O\to I}$ [kJ mol^{-1}]	$\Delta_{ad}G^{\circ}_{W\to I}$ [kJ mol^{-1}]	d [Å]	θ [°]	ω [°]
0	–0.562	–36.9	–22	44	179
–0.1	–5.21	–31.9	0.2	24	1
–0.2	–10.5	–27.5	1.4	11	179
–0.3	–17.1	–24.5	2.4	15	0
–0.4	–25.0	–22.7	3.2	1	20
–0.5	–33.5	–21.6	3.4	3	179

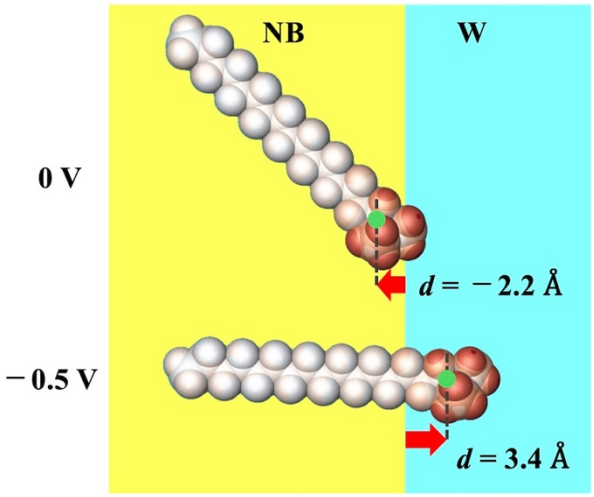

Figure 5. Theoretically predicted adsorption states of HTMA$^+$ at the NB/W interface for two different interfacial potentials: 0 V and –0.5 V.

Energy Decomposition

One important merit of the present theoretical method is that energy decomposition can be performed to evaluate the contributions from chemical and electrostatic potentials (G°_{chem} and G°_{el}) in the adsorption–desorption process and also those from different intermolecular interactions in G°_{chem}.

In Figure 6a, the change of the total Gibbs energy (G°) in the adsorption–desorption process at –0.2 V is divided into G°_{chem} and G°_{el}. As shown in the figure, the minimum of G° is caused by the balance between G°_{chem} and G°_{el}. In the adsorption process of HTMA$^+$ from O to I ($d = -\infty$ to ~ 0 Å), the G°_{chem} remains almost zero and the adsorption energy, $\Delta_{ad}G^{\circ}_{O\to I}$, is mostly due to the lowering of G°_{el}. When d exceeds 1.4 Å, the part of the HTMA$^+$ molecule penetrating the interface becomes unstable in W and a considerable increase in G°_{chem} overcomes the stabilization by G°_{el}. Thus, G° has a minimum value.

Figure 6b shows the changes of four energy terms in the r.h.s of Equation (2) (in the following, the respective terms called A-term, B^{*}_{+}-term, B_{+}-term, and C_{-}-term). As shown in Figure 6b,

in the process of the head group's penetration into the W phase ($d = -4$ to ~ 1.4 Å), A- and B_+-terms cancel out each other, and thus the chemical potential hardly changes in this d range. The head group of $HTMA^+$, i.e., tetramethylammonium group, does not seem to have strong hydrophilicity, since the group is relatively bulky and the surface field strength is lower.

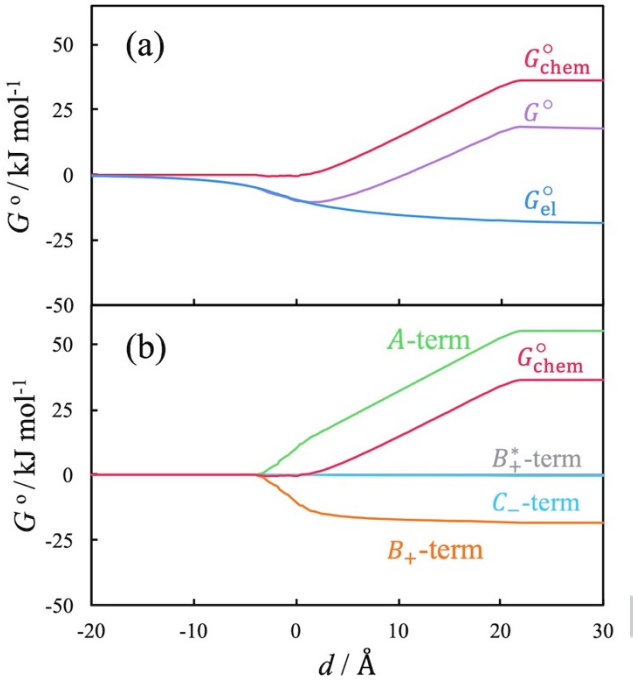

Figure 6. (a) Division of G° into G°_{chem} and G°_{el} (at $\Delta^W_O\phi = -0.2$ V). (b) Energy decomposition of G°_{chem}.

For the desorption process from I to W (for $d > \sim 1.4$ Å), the main contribution to the energy change in G° is from the A-term. In this process, the A-term increases with a constant slope until the alkyl chain crosses the interface and detaches itself therefrom to W. Because the alkyl chain has a lower electric surface field, the A-term (relating to the so-called "cavity formation energy") mainly contributes to the energy change, and its value becomes positively larger in the W-phase side where cavity formation requires large energy. A similar calculation has also been carried out for six *n*-alkyltrimethylammonium ions including $HTMA^+$ ($[C_nH_{2n+1}N(CH_3)_3]^+$; n = 8, 10, 12, 14, 16, 18). It has been found that the standard Gibbs desorption energy, $\Delta_{des}G^\circ_{I\to W}$ ($= -\Delta_{ad}G^\circ_{W\to I}$), linearly depends on the carbon number of the alkyl group: $\Delta_{des}G^\circ_{I\to W}/\text{kJ mol}^{-1} = 2.55n - 3.9$ ($R^2 = 1.00$). Thus, the contribution of a methylene group (–CH_2–) to $\Delta_{des}G^\circ_{I\to W}$ has been estimated to be 2.55 kJ mol^{-1}. This value is in good agreement with the experimental value of 2.45 kJ mol^{-1}.[34] This result shows that the present theoretical prediction is valid for not only the adsorption process but also the desorption process.

Conclusion

The non-Bornian solvation model allows us to predict the adsorption equilibrium of ionic surfactants at the electrified O/W interface in a simple and accurate manner. The adsorption energies of an ionic surfactant from the O- and W-phase sides, nemely, $\Delta_{ad}G^\circ_{O\to I}$ and $\Delta_{ad}G^\circ_{W\to I}$, have been shown to depend on the interfacial potential. The linear potential dependence of $\Delta_{ad}G^\circ_{O\to I}$, being theoretically predicted for a negative potential range, is in good agreement with the previously observed experimental data.[23,24] Furthermore, the proposed calculation method enables us to predict the orientation state (i.e., d, θ, and ω) for the adsorbed surfactant, which should be influenced by the change of the interfacial potential. The present method is also useful to know how the chemical and electrostatic potentials contribute to the potential-dependent adsorption, respectively, and how the decomposed chemical energies for differently charged molecular surfaces contribute to the adsorption–desorption process.

Acknowledgements

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Keywords: ionic surfactant • oil/water interface • adsorption • calculation

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"Tetradecyltrimethylammonium" in the title should read "Hexadecyltrimethylammonium".

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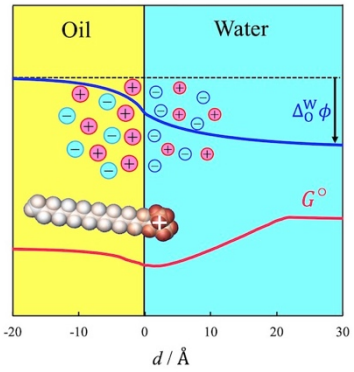

Potential dependent adsorption: A new calculation method based on a non-Bornian solvation model has been proposed for predicting the adsorption equiliblium for ionic surfactants at the polarized oil (O)/water (W) interface. The electrostatic potential of an ionic surfactant in the electric double layer of the O/W interface is successfully considered together with the chemical potential.