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

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ABSTRACT: The non-Bornian solvation model has been applied for predicting the adsorption equilibrium for nonionic surfactants at the oil (O)/water (W) interface. In the non-Bornian model, the small contribution from the long-range electrostatic interaction is ignored, then the solvation or resolvation energy is formulated based on short-range solute molecule (or ion)–solvent interactions: cavity formation, Coulomb, polarization, charge transfer, etc. These interaction energies are given by zero, first, and second-order functions of the local electric field (E_i) on the molecular surface, which can be estimated by DFT calculation. In the present study, we considered an adsorption process as "partial" transfer of a molecule across the O/W interface. Using a non-Bornian, semi-empirical equation for the Gibbs energy of transfer of nonionic molecules, the adsorption states of alkyl alcohols (1-dodecanol, 1-octanol, and 1-hexanol) at the 1,2-dichloroethane/W interface were successfully predicted. The orientation angle (θ), the rotation angle (ω), and the penetration depth into the O phase (d) of the alcohols in the adsorption state could be estimated. Furthermore, the energies for the adsorption from O and W ($\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ and $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$) could be estimated theoretically. The values of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ for the alcohols studied were in good agreement with those determined experimentally by the drop-weight method.

INTRODUCTION

The adsorption of surface active species at the oil (O)/water (W) interface is basically important for understanding various interfacial processes, including heterogeneous charge transfer, phase-transfer catalysis, self-assembly of surfactants, emulsification, and so on.[1–3] Since olden times, experimental studies of the adsorption via interfacial tension have been conducted based on classical thermodynamics.[4–6] More recently, the potential-dependent adsorption of phospholipids,[7–9] surfactants,[10] proteins,[11,12] and dyes[13] at electrified or polarized O/W interfaces have been studied via interfacial tension, capacitance, and charge-transfer admittance. Furthermore, spectroelectrochemical techniques have breathed fresh life into this research field, for example, surface second-harmonic generation[14,15] (SHG) and potential-modulated fluorescence (PMF) spectroscopy.[16,17] Thus, various techniques have been effectively used to study adsorption phenomena at the O/W interface, however theoretical verification is still desirable for a deeper understanding about which interactions act significantly and why they do. In last two decades or so, molecular dynamics (MD) simulation has been applied to study the adsorption of anesthetics, surfactants, etc. at O/W interfaces.[18–22] MD simulation is a powerful technique and can provide detailed dynamic pictures of adsorption processes, though at the expense of higher computational cost, i.e., CPU time.

In this study, we propose a simple and reliable calculation method for understanding and predicting adsorption reactions occurring at the O/W interface. This method is comprised of density functional theory (DFT) calculation for adsorptive species and the calculation of the Gibbs energy change for the adsorption process across the O/W interface. For the latter calculation, we have applied a non-Bornian solvation model proposed by our group.[23–29] As described previously,[24] the contribution from the primary solvent layer, or, the short-range ion–solvent interaction should be much more significant than the Born-type, long-range electrostatic interaction. In the non-Bornian model, we have dared to ignore the small contribution from the long-range interaction. Then, we could find good agreement between experimental and theoretical values of the Gibbs energy of hydration or resolvation (i.e., phase transfer across the O/W interface) for various kinds of ions. For example, in a recent paper,[29] we employed ion-transfer voltammetry to determine the standard Gibbs energy ($\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}}$) of transfer from W to 1,2-dichloroethane (DCE) for 26 cations and 24 anions (mostly organic), and then applied the non-Bornian model to obtain semi-empirical equations of $\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}}$ for the cations and anions; the mean absolute error (MAE) was as small as 2–3 kJ mol^{-1}. The respective semi-empirical equation is comprised of seven terms, which are zero, first, or second order in the local electric field, E_i $(i = 1,2,3 \cdots)$, on an ionic surface. The seven terms are related to different kinds of short-range ion–solvent interactions (including cavity formation, Coulomb, polarization, charge transfer, etc.), showing their individual contributions to the total value of $\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}}$. It should here be noted that another semi-empirical equation of $\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}}$ has been provided for neutral or nonionic molecules by combining the two data sets for the cations and anions.[29]

Thus, using the non-Bornian model, in which long-range electrostatic interaction is ignored, we can evaluate the resolvation energy for local molecular surfaces. Then, we can estimate the adsorption energy simply by considering an adsorption process as "partial" transfer of a molecule across the O/W interface. As shown in Figure 1, if a molecule (or ion) partially crosses an interface and shows an energy minimum, the resolvation energy of the molecular surface dipping in the O phase can be assumed as the Gibbs energy of adsorption from W to the interface, $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\to\mathrm{I}}$ (where "I" denotes interface). This assumption is applicable when the O/W interface is sharp; previous MD simulation[30,31] of the DCE/W interface supported the molecular sharpness. In the present study, we have assessed the usefulness of the non-Bornian solvation model in the prediction of adsorption behaviors of neutral molecules (i.e., 1-dodecanol, 1-octanol, and 1-hexanol) at the DCE/W interface.

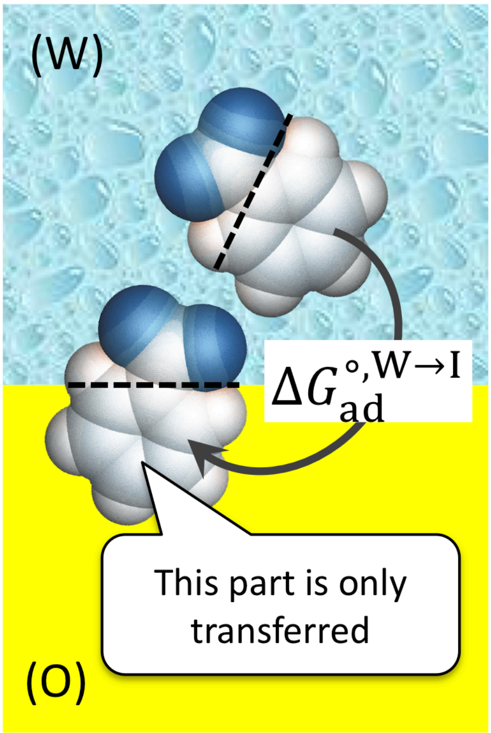

Figure 1. The Gibbs energy of adsorption of a molecule (benzoate ion as an example) from water to the interface, $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$, which is defined as "partial" transfer of the molecule across the O/W interface.

METHODS

DFT Calculation. The Gaussian 09 program package was used for DFT calculation. Using the B3LYP hybrid DFT method with the 6-311++G(2d,p) basis set, geometries of the above alkyl alcohols in vacuum were optimized and partial atomic charges were computed by Merz-Kollman (MK) method.[32,33] Then, the values of E_i on minute molecular surfaces as well as their geometric area (S_i; $i = 1,2,3\cdots$) were evaluated by using the previously reported subprogram.[28] In this study, according to the previous results,[29] the van der Waals (vdW) surface was used for the evaluation. The vdW radii of atoms (C, H, and O for the alkyl alcohols) were listed in a previous paper.[27]

Prediction of Adsorption States. A program has been written in Visual Basic 6.0 for predicting the adsorption state of a molecule at the O/W interface. In order to determine the geometry of an adsorptive species, the orientation angle with respect to the normal line of the O/W interface (θ), the rotation angle around the molecular axis (ω), and the penetration depth into the O phase (d) have been defined for the alkyl alcohols, as shown in Figure 2a. Note that the geometrics of the molecules were optimized in advance by DFT calculation. As exemplified by 1-dodecanol in Figure 2b, the long axis (i.e., molecular axis) is defined as the line connecting the midpoint of the head-part carbons 1 and 2 (C1 and C2) with that of the tail-part carbons 11 and 12 (C11 and C12), and the center between the two midpoints is assigned as reference point 1 (RP1), from which an orthogonal line crosses the line between C1 and C11 at reference point 2 (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 lies parallel to the figure plane (Figure 2a). At d = 0 Å, a hydrogen atom at the end of the alkyl chain touches the O/W interface by its vdW surface.

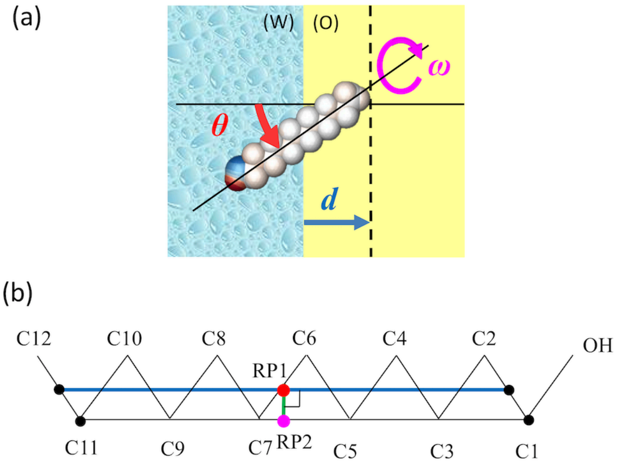

Figure 2. (a) Three parameters (θ, ω, and d) representing the orientation of an alkyl alcohol at the O/W interface. (b) Long and short axes of 1-dodecanol as an example. For further details, see the text.

To know the adsorption state of alkyl alcohols at the DCE/W interface, we have changed θ (0°–180°), ω (0°–180°), and d (from 0 Å to a value larger than the molecular length) by 1°, 1°, and 0.1 Å, respectively, and then performed the following energy calculation to find the best combination of θ, ω, and d representing an energy minimum.

The energy calculation has been performed by applying the following semi-empirical equation of $\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}}$, which was previously provided for neutral molecules at the DCE/W interface.[29] Note that eq S1 in the Supporting Information of ref 29 is inaccurate and should be revised as follows:

$$\begin{aligned}\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}} &= \Delta A \sum S_i + \Delta B_+^* \sum_{E_i \geq \xi_+} S_i E_i \\ &+ \Delta C_+^* \sum_{E_i \geq \xi_+} S_i {E_i}^2 + \Delta B_-^* \sum_{E_i \leq \xi_-} S_i E_i + \Delta C_-^* \sum_{E_i \leq \xi_-} S_i {E_i}^2 + \Delta B_+ \sum_{\xi_+ > E_i > 0} S_i E_i \\ &+ \Delta C_+ \sum_{\xi_+ > E_i > 0} S_i {E_i}^2 + \Delta B_- \sum_{\xi_- < E_i < 0} S_i E_i + \Delta C_- \sum_{\xi_- < E_i < 0} S_i {E_i}^2\end{aligned} \tag{1}$$

The first term of the r.h.s. of this equation is proportional to the molecular surface area ($\sum S_i$), which is mainly related to the hydrophobic interaction or the so-called cavity formation energy. The second and third terms represent the contributions from much positively charged surfaces with $E_i \geq \xi_+$ (threshold value). Such surfaces are selectively hydrated in the O phase,[34,35] and their effects are included in the two terms. Similarly, the fourth and fifth terms represent the contributions from much negatively charged surfaces with $E_i \leq \xi_-$ (threshold value). The sixth and seventh terms show the contributions from moderately positively charged surfaces with $\xi_+ > E_i > 0$. The respective terms are mainly due to ion–dipole (Coulomb) and ion–induced dipole (polarization) interactions. In a similar manner, the last two terms show the contributions from moderately negatively charged surfaces with $\xi_- <$

$E_i < 0$. Thus, the respective terms in eq 1 correspond to various ion–solvent interactions (for further details, see refs 28 and 29). However, it is difficult to obtain the coefficients of these terms, i.e., ΔA, ΔB_{+}^{*}, ΔC_{-}, etc., in any rigorous theoretical manner. In the previous study,[29] we performed a regression analysis with experimental data to determine these coefficients as adjusting parameters (Table 1).

Table 1: Optimized Coefficients in Equation 1[a]

coefficient	optimized[b]	SD[c]
ΔA	−14.60	2.2
ΔB_{+}^{*}	3.095	2.4
ΔC_{+}^{*}	0.01718	0.077
ΔB_{-}^{*}	1.058	1.3
ΔC_{-}^{*}	0.1313	0.040
ΔB_{+}	1.945	0.81
ΔC_{+}	−0.03134	0.057
ΔB_{-}	−0.3169	0.70
ΔC_{-}	0.04849	0.032
n [d]	50	
R^2 [e]	0.942	
MAE [f]	3.9	

[a] Where $\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\to\mathrm{O}}$ is in kJ mol^{-1}, S_i in nm^2, and E_i in V nm^{-1}. [b] Optimized values with ξ_{+} = +20 V nm^{-1} and ξ_{-} = –29 V nm^{-1}. [c] Standard deviation. [d] Number of data. [e] Square of the correlation coefficient. [f] In kJ mol^{-1}. Adapted with permission from the Supporting Information of ref 29. 2018 © The Japan Society for Analytical Chemistry.

By applying eq 1 to molecular surfaces located in the O phase, we can calculate the standard Gibbs energy of a molecule partially transferred across the O/W interface ($G°$; with $G° = 0$ in the bulk W phase). The combination of θ, ω, and d showing a minimum of $G°$ represents the most stable adsorption state of the molecule at the interface.

Energy Calculation for Adsorption–Desorption Processes. For simplicity, we have assumed that the values of θ and ω determined for the adsorption state are kept constant during an adsorption–desorption process, and then have calculated the Gibbs energy profile using eq 1 as above, by changing d by 0.1 Å in a certain range. For this calculation, another program was written in Visual Basic 6.0.

Determination of Interfacial Tensions. Analytical grade of 1-dodecanol, 1-octanol, and 1-hexanol (Kishida Chemical Co.) and DCE (for HPLC; Wako Pure Chemical Industries) were purchased and used as received. The drop-weight or drop-volume method[36,37] was used to determine the interfacial tension (γ) for the DCE/W interface with the addition of 0 – 0.500 M (=mol dm^{-3}) alkyl alcohol in DCE. A water drop was formed at the end of a stainless capillary (i.d., 0.69 mm; o.d., 1.08 mm) immersed in the DCE solution that was contained in a water-jacketed glass column to keep the temperature at 15, 20, 25, 30, and 35 °C. By sending purified water to the capillary using a syringe pump (SP100i, World Precision Instruments) with a Hamilton 1010TLL syringe, the drop time (i.e., the time for one drop to grow and detach itself) was measured with a stopwatch. In this measurement, the solution sending speed was set low enough (v = 200 μL h^{-1}) to ensure the interfacial adsorption equilibrium. Each measurement was repeated five times, and the averaged drop time (t) was used to determine the drop volume ($V = vt$). Then, γ can be obtained from V as[36,37]

$$\gamma = \frac{V(\Delta\rho)g}{2\pi r}\phi \tag{2}$$

where $\Delta\rho$ is the density difference between the DCE and W phases,[38] g the acceleration of gravity, r the inner radius of the capillary (here, $r = 0.35$ mm; measured by a microscope), and ϕ is the empirically derived correction factor. Harkins and Brown[36] found ϕ to be independent of the nature of the liquids or the material of the capillaries and to depend only on r and V, giving a smooth plot against $r/V^{1/3}$. Based on their reported data, we have found that ϕ can be evaluated by a polynomial of $r/V^{1/3}$ (=X):

$$\phi = 1 + 1.8136X - 2.6972X^2 + 3.6186X^3 - 2.4511X^4 - 0.0054X^5 + 0.3619X^6 \quad (3)$$

RESULTS AND DISCUSSION

Experimental Determination of Adsorption Energies. From the experimental dependence of γ on the alkyl-alcohol concentration (c) in DCE, the adsorption energy of alkyl alcohols from DCE to the interface, i.e., $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$, was determined by referring to previous literatures.[39,40]

First, γ was plotted against $\ln c$, as shown in Figure S1 (the Supporting Information). The interfacial concentration (Γ) of the adsorptive species was then obtained by numerical differentiation of the approximate curve for the γ vs. $\ln c$ plot. This is based on a well-known relation:

$$\Gamma = -\frac{1}{RT}\left(\frac{\mathrm{d}\,\gamma}{\mathrm{d}\ln c}\right) \quad (4)$$

where R and T have their usual meanings.

Next, the thus obtained Γ values were plotted against c, as shown in Figure S2 (the Supporting Information). The Γ vs. c plots could be well fitted to Langmuir adsorption isotherm:

$$\theta = \frac{\Gamma}{\Gamma_\infty} = \frac{\beta c}{1+\beta c} \tag{5}$$

where θ is the interfacial coverage, Γ_∞ the saturated interfacial concentration, and β the adsorption coefficient. Then, Γ_∞ and β were obtained as adjusting parameters.

In the present analysis, we assumed an Arrhenius-type relation between β and $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\to\mathrm{I}}$:[41]

$$\beta = \beta_0 \exp\left(-\frac{\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\to\mathrm{I}}}{RT}\right) \tag{6}$$

where β_0 is a constant independent of T. Taking the logarithm of eq 6 yields

$$\ln\beta = \ln\beta_0 - \frac{\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\to\mathrm{I}}}{RT} \tag{7}$$

According to this equation, $\ln\beta$ was plotted against $1/T$, as shown in Figure S3 (the Supporting Information). From the slope of the linear plot, we could estimate $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\to\mathrm{I}}$ for three different alkyl alcohols at the DCE/W interface (Table 2).

Table 2: Experimental and Theoretical Values of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ for Alkyl Alcohols at the DCE/W Interface

	$\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ (kJ mol^{-1})	
	experimental	theoretical
1-dodecanol	−5.9	–5.21
1-octanol	–5.7	–5.21
1-hexanol	–6.8	–5.32

Theoretical Prediction of Adsorption States. Table 3 shows the parameters representing the adsorption states of three alkyl alcohols at the DCE/W interface. As seen, the values of θ and ω are not very dependent on the nature of alcohols. The value of θ (=34° or 33°) shows that the molecular axis leans considerably from the perpendicular of the interface. The value of ω (=0°) shows that the plane comprised of the long and short axes is perpendicular to the interface. In contrast, the value of d is changed in accordance with the alkyl chain length. At these geometries, only the hydroxyl group, whose oxygen and hydrogen atoms have strong electric fields, is located in the W phase and hydrated most efficiently therein (for example, see Figure 3). The Gibbs energy for the transfer of a hydroxyl group from O to W should be considered as $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$. As expected, the value of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ is not very dependent on the alkyl chain length, along with the experimental observation (Table 2). It should also be noted in the table that there is a reasonable agreement between the experimental and theoretical values of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ for the alkyl alcohols examined. Meanwhile, the theoretical value of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$, i.e., the Gibbs energy for adsorption from the W phase, becomes negatively larger with increasing the alkyl chain length. This energy corresponds to the transfer of an alkyl chain from W to O. Since the alkyl chains have weaker electric fields as shown in Figure 3, their surfaces are hydrophobic, leading to a negative contribution to $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$. The theoretical values of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$ shown in Table 3 has a linear correlation with the number of carbon atoms of the alkyl chains. From this relation, we have obtained the contribution of a methylene group ($-CH_2-$) to $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$, i.e., –2.97 kJ mol^{-1}. This value is in good agreement with the value of –3.05 kJ mol^{-1}, which has been estimated from the literature data of $\Delta G_{\mathrm{tr}}^{\circ,\mathrm{W}\rightarrow\mathrm{O}}$ for quaternary ammonium ions at the DCE/W interface.[42]

Table 3: Theoretical Parameters Representing the Adsorption States of Alkyl Alcohols at the DCE/W Interface

	θ (degree)	ω (degree)	d (Å)	$\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$ (kJ mol^{-1})	$\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ (kJ mol^{-1})
1-dodecanol	34	0	14.4	–34.9	–5.21
1-octanol	33	0	10.2	–23.2	–5.21
1-hexanol	34	0	8.0	–17.0	–5.32

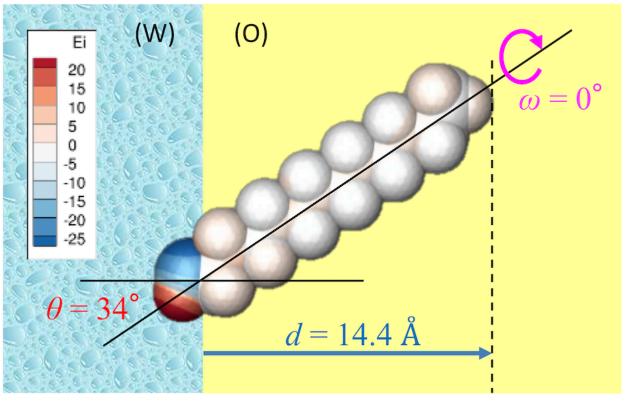

Figure 3. Theoretically predicted adsorption state for 1-dodecanol at the DCE/W interface.

Theoretical Prediction of Adsorption–Desorption Processes. Figure 4 shows the theoretically predicted Gibbs energy change in the adsorption–desorption process for 1-dodecanol at the DCE/W interface. As described above, it has here been assumed that the orientation and rotation angles, i.e., θ and ω, are kept constant in the transfer process. By changing only d by 0.1 Å, the change of $G°$ has been calculated on the basis of eq 1. Similar energy profiles have been obtained for 1-octanol and 1-hexanol, as shown in Figures S4 and S5 (the Supporting Information).

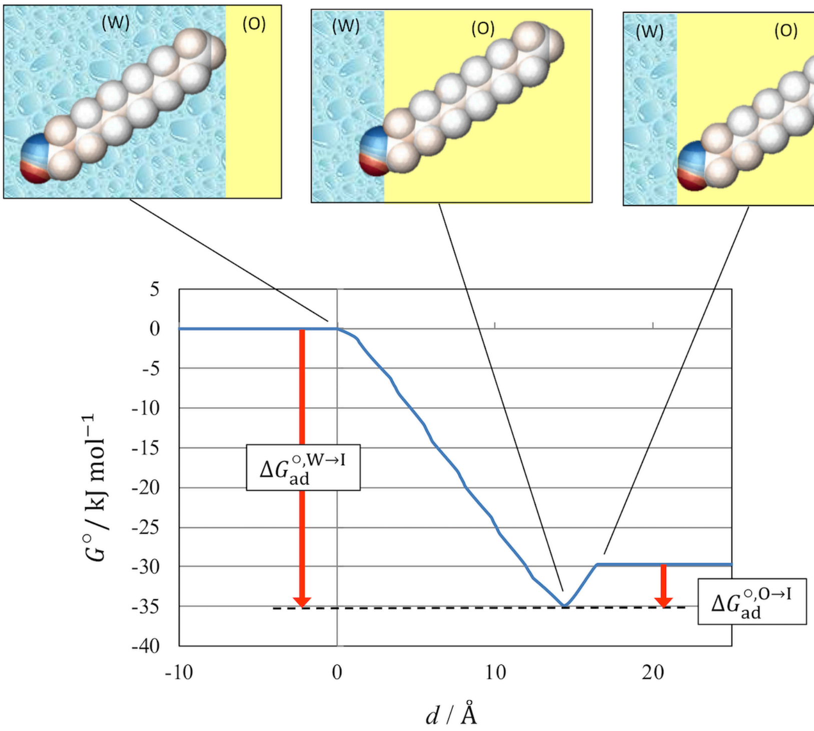

Figure 4. Theoretically predicted Gibbs energy change in the adsorption–desorption process for 1-dodecanol at the DCE/W interface.

Now let us consider the case in which a 1-dodecanol molecule initially existing in the bulk W phase is transferred to the bulk O phase via the adsorption state at the O/W interface. Until the end of the alkyl chain touches the interface (i.e., for $d < 0$ Å), there is no change in $G°$. With increasing d positively, or, with penetration of the alkyl chain into the O phase, the Gibbs energy decreases almost constantly until it reaches a minimum at d = 14.4 Å (the adsorption state). The large energy change for this process should correspond to $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\to\mathrm{I}}$. We would like to add that the almost monotonous decrease of $G°$ still contains small fluctuations, which are due to the atomic-level roughness of the alkyl chain.

After d exceeds 14.4 Å, the Gibbs energy turns to increase until the hydrophilic hydroxyl group crosses the interface and detaches itself therefrom to the O phase. The relatively small change in G° should be $-\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$, the value of which has been found to agree well with the experimental value (Table 2).

Energy Decomposition. One important merit of the non-Bornian solvation model is that energy decomposition can be performed for theoretically predicted phase-transfer energies.[29] In this study we have evaluated the contributions from the respective terms in the r.h.s. of eq 1 to the Gibbs energy change in the adsorption–desorption process shown in Figure 4. For simplicity, in the following, the first to ninth terms and the total energy change are denoted by A, B_{+}^{*}, C_{+}^{*}, B_{-}^{*}, C_{-}^{*}, B_{+}, C_{+}, B_{-}, C_{-}, and ΔG, respectively.

As shown in Figure S6 (the Supporting Information), we could estimate the contributions to ΔG from the nine different terms. However, as described previously,[29] it is difficult to discuss concisely the magnitude relation between a B-term (here, B_{+}^{*}, B_{-}^{*}, B_{+}, or B_{-}) and a C-term (C_{+}^{*}, C_{-}^{*}, C_{+}, or C_{-}, respectively), because the terms have relatively large uncertainties. Nevertheless, as shown by the previous analysis,[29] the sums of B-term and C-term (i.e., $\mathrm{B}_{+}^{*} + \mathrm{C}_{+}^{*}$, $\mathrm{B}_{-}^{*} + \mathrm{C}_{-}^{*}$, $\mathrm{B}_{+} + \mathrm{C}_{+}$, and $\mathrm{B}_{-} + \mathrm{C}_{-}$) are available for a clearer discussion on the respective contributions from differently charged surfaces. Then we have evaluated the above four $\mathrm{B} + \mathrm{C}$ sums as well as A-term for the adsorption–desorption process of 1-dodecanol (Figure 4).

As shown in Figure 5, for the penetration of the alkyl chain into the O phase, the monotonous decrease of the total energy (marked by ΔG; for $0 < d < 14.4$ Å) is mainly due to the change in A-term (cavity formation energy), though there is some contribution from $\mathrm{B}_{+} + \mathrm{C}_{+}$, i.e., from the moderately positively charged surface of the alkyl chain with ξ_{+} (+20 V nm^{-1}) $> E_i > 0$. The latter contribution to ΔG is positive, suggesting that the alkyl-chain surface should have a certain electrostatic affinity to water, though the cavity formation effect is more significant.

For the process of desorption from the interface to the O phase (for $d > 14.4$ Å), the main contributions to the energy change in ΔG are those from $B^*_+ + C^*_+$ and $B_- + C_-$. The former contribution is due to the much positively charged H atom of the hydroxyl group in the alkyl alcohol; it is suggested that the H atom should extract some water molecule(s) to the O phase in the desorption process from the interface.[34,35] The latter contribution from $B_- + C_-$ is due to the moderately negatively charged O atom of the hydroxyl group. Both the contributions are positive, showing that the transfer of the hydrophilic hydroxyl group to the O phase is energetically unfavorable. We would like to add that because the alkyl alcohol does not have any strongly negatively charged surface, there is no contribution from $B^*_- + C^*_-$ (also see Figure 5).

As thus exemplified, the proposed method enables us to examine quantitatively the contributions from different modes of intermolecular interactions in the adsorption–desorption processes at the O/W interface.

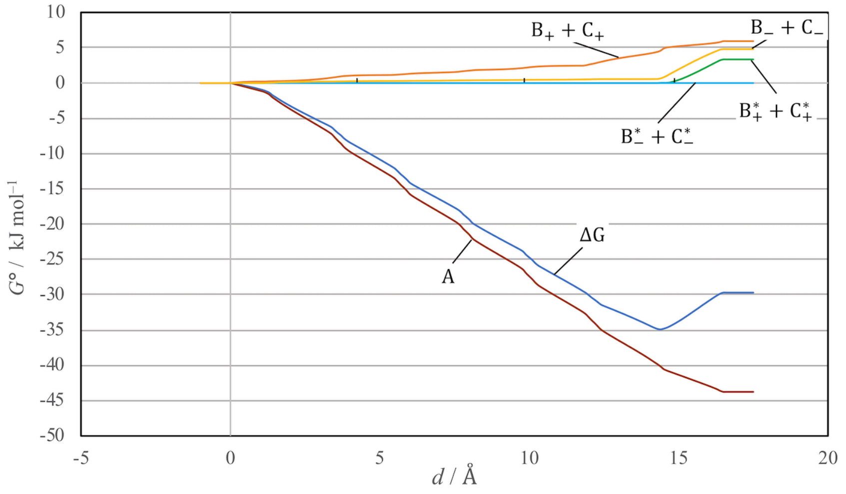

Figure 5. Result of energy decomposition for the adsorption–desorption process (1-dodecanol) shown in Figure 4. For further details, see the text.

SUMMARY AND CONCLUSIONS

The non-Bornian solvation model provides a simple and reliable method for prediction of the adsorption equilibrium of nonionic surfactants at the O/W interface. This has been successfully exemplified in the adsorption of alkyl alcohols (1-dodecanol, 1-octanol, and 1-hexanol) at the DCE/W interface. The parameters (θ, ω, and d) representing the orientation of the alcohols at the interface and the adsorption energies from O and W (i.e., $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ and $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{W}\rightarrow\mathrm{I}}$) can be obtained from a relatively simple theoretical calculation. The theoretical values of $\Delta G_{\mathrm{ad}}^{\circ,\mathrm{O}\rightarrow\mathrm{I}}$ are in good agreement with the experimentally determined values. Furthermore, energy decomposition is useful for evaluating the respective contributions of differently charged molecular surfaces in the adsorption–desorption processes.

It should be noted that in this paper, the effect of the electric double layer[43] formed around the O/W interface has not been taken into account, because we have herein dealt with “nonionic” surfactants having lower electrical sensitivity. However, the electric double layer should affect significantly the interfacial adsorption of “ionic” surfactants such as dodecylsulfate. An extended application of our approach to ionic species will be reported in a subsequent paper.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.???????.

Plots of γ vs. $\ln c$; adsorption isotherms; plots of $\ln \beta$ vs. $1/T$; Gibbs energy changes in adsorption–desorption processes; and a result of energy decomposition (PDF)

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Notes

The authors declare no competing financial interest.

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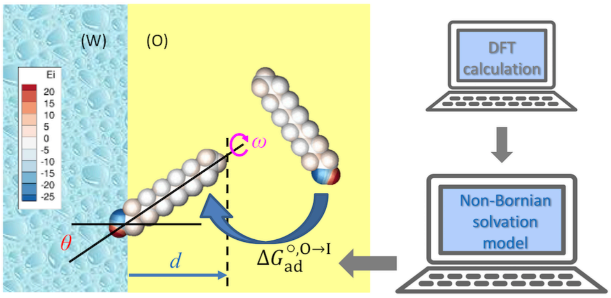
TOC graphic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