Selectivity and Stoichiometry Boosting of β-Cyclodextrin in Cationic/Anionic Surfactant Systems: When Host−Guest Equilibrium Meets Biased Aggregation Equilibrium

Lingxiang Jiang, Yun Yan, and Jianbin Huang*

Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Caifang Yu and Changwen Jin

Beijing NMR Center, College of Life Sciences, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Manli Deng and Yilin Wang*

*Institute of Chemistry, Chinese Academy of Sciences, Beijing, China*

Received: November 22, 2009; Revised Manuscript Received: December 28, 2009

Cationic surfactant/anionic surfactant/β-CD ternary aqueous systems provide a platform for the coexistence of the host−guest (β-CD/surfactant) equilibrium and the biased aggregation (monomeric/aggregated surfactants) equilibrium. We report here that the interplay between the two equilibria dominates the systems as follows. (1) The biased aggregation equilibrium imposes an apparent selectivity on the host−guest equilibrium, namely, β-CD has to always selectively bind the major surfactant (molar fraction > 0.5) even if binding constants of β-CD to the pair of surfactants are quite similar. (2) In return, the host−guest equilibrium amplifies the bias of the aggregation equilibrium, that is, the selective binding partly removes the major surfactant from the aggregates and leaves the aggregate composition approaching the electroneutral mixing stoichiometry. (3) This composition variation enhances electrostatic attractions between oppositely charged surfactant head groups, thus resulting in less-curved aggregates. In particular, the present apparent host−guest selectivity is of remarkably high values, and the selectivity stems from the bias of the aggregation equilibrium rather than the difference in binding constants. Moreover, β-CD is defined as a "stoichiometry booster" for the whole class of cationic/anionic surfactant systems, which provides an additional degree of freedom to directly adjust aggregate compositions of the systems. The stoichiometry boosting of the compositions can in turn affect or even determine microstructures and macroproperties of the systems.

1. Introduction

1.1. Host−Guest Equilibrium and Selectivity. The synthesis of crown ethers and subsequent studies on their selective ligation of alkali metal cations have led to the flourishing development of host−guest chemistry, which was recognized by the award of the Nobel Prize in Chemistry in 1987.[1] The selectivity of a host to different guests always plays a central role in host−guest chemistry due to its great importance in compound separation, molecular recognition, and construction of supramolecules, to name a few.[2] In this context, J. E. Trend et al. gave an impressive example by solving a stubborn clinical problem of assaying blood K^+ (inevitably coexisting with excess Na^+) with a cryptand/chromophore conjugated molecule.[3] Its cryptand portion can selectively bind K^+ ions over Na^+ ions, and the binding with K^+ will trigger the fluorescence emission of its chromophore portion. Consequently, the emission intensity is proportional to $[K^+]$ even in the presence of highly excess Na^+, allowing for specific determination of K^+ concentrations.

In the above case and other typical cases, the host−guest equilibrium can be described by the classical solution-phase model

$$\text{Host} + \text{Guest} \overset{K^b}{\rightleftharpoons} \text{Complex}$$
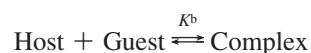
where the binding constant $K^b = [\text{Complex}]/([\text{Host}][\text{Guest}])$ for dilute solutions. The magnitude of K^b reflects the matching degree of a host−guest pair. When two guest species are presented, the selectivity of the host to one guest is exclusively governed by the ratio of binding constants ($S_{\text{Guest1}} = K^b_{\text{Guest1}}/K^b_{\text{Guest2}}$). This simple situation could, however, be complicated by the emergence of a coexisting equilibrium, which may raise issues concerning the adequacy of the simple solution-phase model and the dependence of selectivity on binding constants.

1.2. Biased Aggregation Equilibrium in Cationic/Anionic Surfactant Systems. Recently, cationic/anionic surfactant systems[4] have attracted increasing attention because of their advantages in synergism,[5] spontaneous formation of vesicles,[6] and aggregate polymorphism.[7] The above features, especially the aggregate polymorphism, are closely related to surfactant compositions in aggregates. With the compositions approaching

* To whom correspondence should be addressed. E-mail: yilinwang@iccas.ac.cn. Fax/Tel: 86-10-82615802 (Y.W.); E-mail: jbhuang@pku.edu.cn. Fax: 86-10-62751708. Tel: 86-10-62753557 (J.H.).

2166 *J. Phys. Chem. B, Vol. 114, No. 6, 2010*

Jiang et al.

the electroneutral mixing stoichiometry, electrostatic attractions between the oppositely charged head groups increase, transforming the aggregates into less-curved ones (typically in a micelle-to-vesicle-to-precipitate sequence). The aggregate transformations, in turn, greatly influence macroproperties of the solutions such as absorbance, viscosity, and phase separation.[8] In this sense, the aggregate composition is a deterministic parameter for this kind of system.

Several theories were successfully developed to model aggregation equilibria in mixed surfactant systems.[9] The Rubingh theory,[9a,b] a handy and broadly applicable one among them, treats a mixed surfactant solution as two pseudophases, where the monomeric surfactant aqueous phase is in equilibrium with the aggregated surfactant phase. Meanwhile, it introduces an interaction parameter β to describe the nonideal mixing of different surfactants in the aggregation phase. This theory was proven to be quite effective for cationic/anionic surfactant systems[9a,b,10] because (1) aggregation numbers of such systems are usually very large, ensuring the validity of the pseudophase separation assumption and (2) electrostatic attractions between oppositely charged head groups are properly quantified by the interaction parameter β. As theoretically predicted and experimentally determined,[4,6,9] nonstoichiometric cationic/anionic surfactant systems are characterized by a great bias in the aggregation equilibrium, that is, the charged aggregates considerably prefer the countercharged, minor surfactant (molar fraction < 0.5) over the cocharged, major one (molar fraction > 0.5) due to electrostatic reasons. The bias causes aggregate compositions to derivate from bulk compositions by getting close to electroneutral mixing.

1.3. Host−Guest Equilibrium versus Biased Aggregation Equilibrium. CDs are donut-like oligosaccharides with hydrophobic cavities and hydrophilic outer surface. The hydrophobic cavities allow CDs to include various surfactants with high binding constants.[11] The hydrophilic outer surface leads to the fact that the surfactant/CD complexes disfavor forming aggregates and are quite dissolvable in water.[11] Many efforts were devoted to the relation between the structure of surfactants (such as Gemini, bola, and double-chain surfactants) and the structure of CDs (such as α-, β-, γ-, and modified CDs).[12] Most of the work was performed in CD/single surfactant systems, whereas little work was conducted on CD/mixed surfactants systems. For example, β-CD prefers the fluorinated surfactant in a fluorinated /hydrogenated surfactant mixture due to size matching.[13]

Herein, we attempt to realize the coexistence of the host−guest and biased aggregation equilibria in cationic surfactant/anionic surfactant/β-cyclodextrin (β-CD) ternary aqueous systems. In a recent paper,[14] we reported that addition of β-CD to nonstoichiometric cationic/anionic surfactant systems will result in growth of surfactant aggregates, typically from micelles to vesicles. This observation is in contrast to the well-accepted "aggregate-breaking" effect[11] of CDs, thereby promoting us to unveil its origin. In this work, a thermodynamic model is established to describe the cationic surfactant/anionic surfactant/β-CD ternary aqueous systems, the validity of which is confirmed by surface tension, pulse-gradient spin−echo nuclear magnetic resonance (PGSE-NMR), and isothermal titration calorimetry (ITC) measurements. We find that the β-CD-induced aggregate growth is a direct consequence of the combination of the host−guest and biased aggregation equilibria. The biased aggregation equilibrium imposes an apparent selectivity on

the host−guest equilibrium by forcing β-CD to selectively bind the major surfactant. The host−guest equilibrium, in return, amplifies the bias of the aggregation equilibrium by facilitating the depletion of the major surfactant from the surfactant aggregates. Concomitantly, the aggregate composition gets closer to the electroneutral mixing stoichiometry. Eventually, the composition variation leads to the aggregate growth, as we recently observed. Due to its remarkable effect on aggregate compositions, β-CD could be a promising additive to control cationic/anionic surfactant systems.
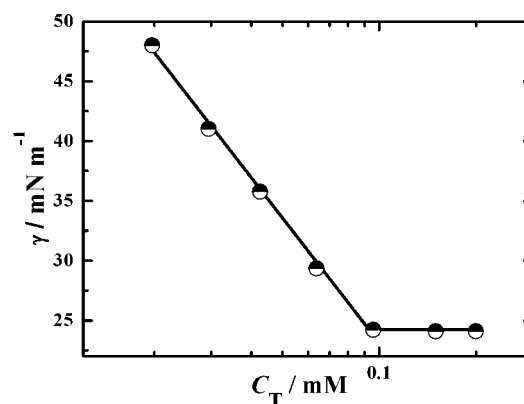
2. Experimental Section

2.1. Materials. Dodecyltriethylammonium bromide (DEAB) was prepared by reactions of 1-bromododecane with triethylamine, followed by recrystallizing five times from ethanol/acetone. ^{1}H NMR: δ 3.32 (q, 6H), 3.18 (t, 2H), 1.69 (m, 2H), 1.30 (m, 27H), 0.90 (t, 3H) ppm. Elementary analysis: found N 3.90%, C 60.95%, H 11.60%; calculated N 4.00%, C 61.70%, H 11.51%. Sodium dodecyl sulfate (SDS, 99%) was purchased from Acros Organics Co. and used as received. The purity of the surfactants was verified by the absence of minima in their surface tension curves (see the Supporting Information). β-Cyclodextrin (β-CD) was purchased from Sinopharm Chemical Reagent Co. with a water content of 14%. For NMR diffusion measurements, we dehydrated β-CD powder by heating it at 80 °C for 2 h before preparing its D_2O solution. Otherwise, β-CD was used without further treatment. D_2O (99.9%) was purchased from Cambridge Isotope Laboratories Inc. Water (H_2O) was redistilled from potassium permanganate.

2.2. Surface Tension. Surface tension γ measurements were conducted using the drop volume method at 25.0 °C. In a typical surface tension−surfactant concentration curve, three regions can be identified; region I, the surface tension slightly changes with the surfactant concentration; region II, a steep, linear decline; region III, an abrupt leveling at the critical aggregation concentration (CAC) where γ reaches its minimum, γ^{CAC}.[15] The surface tension is related to the surfactant concentration by the Gibbs adsorption equation

$$d\gamma = -\Gamma RT d \ln C \qquad (1)$$

where the Gibbs adsorption amount Γ is a surface excess quantity denoting the number of moles of the surfactant adsorbed per unit area at the surface, $R = 8.314$ J mol^{-1} K^{-1}, and T is the absolute temperature. In region II (also known as the saturated adsorption region), the linear decline indicates that Γ reaches its maximum (Γ^∞) and keeps constant.

Figure 1. The experimental surface tension curve of the SDS/DEAB (molar ratio 3/1) system upon dilution.

Host−Guest versus Biased Aggregation

J. Phys. Chem. B, Vol. 114, No. 6, 2010 **2167**

TABLE 1

	basic data		surface tension data[d]		diffusion coefficients[e]		enthalpy changes[f]	
CMC_{SDS}	8.3 ± 0.5 mM[a]	γ^{CAC}	24.8 ± 0.2 mN/m	D_{SDS}^{m}	$5.12 \pm 0.08 \times 10^{-10}$ m²/s	$\Delta H_{SDS}^{m \to c}$	−11.6 ± 0.2 kJ/mol
CMC_{DEAB}	14 ± 1 mM[a]	CAC	0.95 ± 0.05 mM	D_{DEAB}^{m}	$4.52 \pm 0.08 \times 10^{-10}$ m²/s	$\Delta H_{DEAB}^{m \to c}$	−8.3 ± 0.2 kJ/mol
K_{SDS}^{b}	$2.30 \pm 0.08 \times 10^{4}$ M⁻¹ [b]	Γ^{∞}	$6.4 \pm 0.5 \times 10^{-6}$ mol m⁻²	D_{SDS}^{c}	$2.62 \pm 0.04 \times 10^{-10}$ m²/s	$\Delta H_{SDS}^{a \to m}$	∼0 kJ/mol
K_{DEAB}^{b}	$2.54 \pm 0.08 \times 10^{4}$ M⁻¹ [b]			D_{DEAB}^{c}	$2.61 \pm 0.04 \times 10^{-10}$ m²/s	$\Delta H_{DEAB}^{a \to m}$	20.1 ± 0.2 kJ/mol
β	-13 ± 1[c]						

[a] Determined by surface tension measurements (see the Supporting Information). Reference value: $CMC_{SDS} = 8.0$ mM.[16] [b] Determined by ITC measurements (see Figure 2). Reference value: $K_{SDS}^{b} = 2.1 \times 10^{4}$ M⁻¹.[17] [c] Determined by PGSE-NMR for the SDS/DEAB (15/5 mM, β-CD-free) system. The calculation of the β involves $\beta = \ln(C_1^m/CMC_1 x_1^a)/(x_2^a)^2 = \ln(C_2^m/CMC_2 x_2^a)/(x_1^a)^2$, which is derived from eqs 15−17. This value of −13 is used to predict the SDS/DEAB/β-CD system when different amounts of β-CD are added. [d] Determined by surface tension measurements for the SDS/DEAB (molar ratio 3/1, β-CD-free) system. For details, see section 2.2. [e] Determined by PGSE-NMR. For details, see section 2.3. Reference value: $D_{SDS}^{m} = 4.2 \times 10^{-10}$ m²/s,[18a] 5.8×10^{-10} m²/s.[18b] [f] Determined by ITC. For details, see section 2.4.
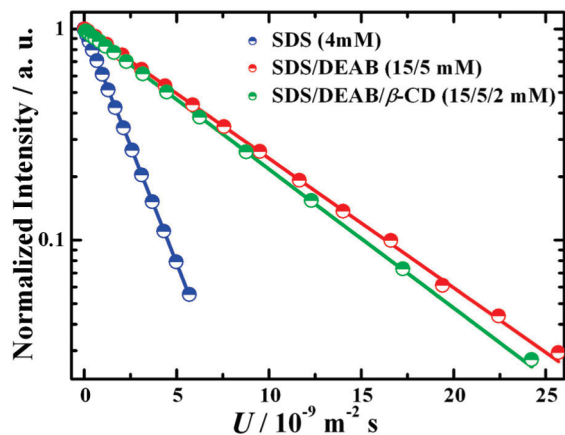

Figure 2. A semilog plot of the decays of the SDS signal in different systems, where $U = \lambda^2 G^2 \delta^2(\Delta - \delta/3)$.

Thus, Γ^{∞} can be obtained according to the slope in this region, and the integration of the Gibbs adsorption equation

$$\gamma - \gamma^{CAC} = -\Gamma^{\infty} RT(\ln C - \ln CAC) \quad (2)$$

can give γ for any C as long as γ^{CAC}, Γ^{∞}, and CAC are available. Figure 1 shows the surface tension curve of the SDS/DEAB (molar ratio 3/1) system, where the γ^{CAC}, Γ^{∞}, and CAC are shown in Table 1. These data will be used to derive surface tension values for SDS/DEAB/β-CD systems.

2.3. Pulse-Gradient Spin−Echo Nuclear Magnetic Resonance (PGSE-NMR). The NMR diffusion measurements were performed on a Bruker 400 NMR spectrometer at 25 °C. Samples were prepared using D_2O as the solvent. For molecules undergoing unhindered random motion, the attenuation of the signal intensity is given by[19]

$$I = I_0 \exp[-D\lambda^2 G^2 \delta^2(\Delta - \delta/3)] \quad (3)$$

where I is the observed intensity, I_0 the intensity without the gradient pulse, D the diffusion coefficient of the molecules, λ the magnetogyric ratio of protons, G the gradient strength, Δ the time interval, and δ the duration time of the gradient pulse. A LED bipolar pulse sequence was used here, where G was changed from 0 to 32 G/cm, δ was set as 6 ms, and Δ was typically chosen as 300 ms. For DEAB and SDS, the peaks at ∼3.2 and 3.9 ppm were selected, respectively. For all of the samples, single-exponential decays of the echo amplitude were always observed, indicating that the exchanges of the species between different states are rapid with respect to the NMR time scale. Figure 2 displays three representative decays (intensity

versus U, $U = \lambda^2 G^2 \delta^2(\Delta - \delta/3)$) of the SDS signal in different systems, all of which are clearly single-exponential. Fitting of the data to eq 3 will yield the diffusion coefficient D. The PGSE-NMR measurements in this work serve to determine concentrations of surfactants in monomeric, complexed, and aggregated states, where diffusion coefficients of surfactants in the two former states need to be preobtained. For SDS, DEAB, and their complexes with β-CD, their diffusion coefficients are preobtained from control experiments and are listed in Table 1.

2.4. Isothermal Titration Calorimetry (ITC). Calorimetric measurements were conducted by a TAM 2277-201 microcalorimetric system (Thermometric AB, Jarfalla, Sweden) at 25.00 °C. A 1 mL stainless steel sample cell was initially loaded with the titrand solution, and the titrant solution was injected into the sample cell via a 250 μL Hamilton syringe controlled by a 612 Thermometric Lund pump. The system was stirred at 50 rpm with a gold propeller. For the calibration constant of ITC measurements, please see the Supporting Information. The observed heat was obtained by integration over the peak of each injection in the plot of heat flow P against time t. For Q^{obs}, the dilution heat $Q^{dilution}$ always contributes, and this contribution needs to be corrected. The $Q^{dilution}$ was evaluated from control experiments and was subtracted from Q^{obs}, giving the dilution-corrected heat Q. This Q was then weighed by the mole number of the added titrant, giving ΔH in kJ mol⁻¹.

First, ITC was employed to determine binding constants of SDS/β-CD and DEAB/β-CD. Figure 3 gives the ΔH curves for
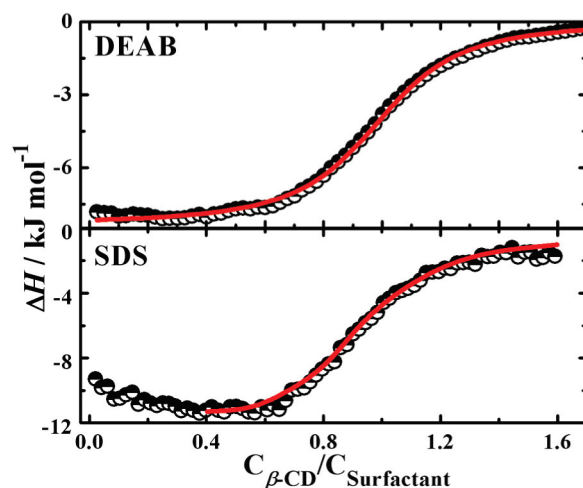

Figure 3. Calorimetric curves of titrations of a concentrated β-CD solution into dilute surfactant solutions. Red solid lines are fitting curves. Please note that the fitting of SDS/β-CD was commenced from 0.4 (SDS/β-CD molar ratio) because (1) the more endothermic plateau shows a significant change in the enthalpy and (2) the sigmoid part of the data is most related to the binding process.

the titrations of a β-CD (12 mM) aqueous solution into SDS (2 mM, below its CMC) and DEAB (2 mM, below its CMC) aqueous solutions, respectively. The software Ligand Binding was used to fit the curves to a 1:1 surfactant/β-CD model. The fitting yielded binding constants K_i^b and enthalpy changes in the transfer of surfactant **i** from monomeric to complexed states $\Delta H_i^{m\rightarrow c}$ (or equivalently, the complexation enthalpy ΔH_i^b), which are listed in Table 1.

Second, ITC was used to obtain enthalpy changes in the transfer of surfactants from aggregated to monomeric states $\Delta H_i^{a\rightarrow m}$. A SDS (5 mM) or DEAB (2 mM) aqueous solution was titrated into a SDS/DEAB (4/1 mM) aqueous solution. These titrations involve the transfer of surfactant molecules from monomeric to aggregated states, a reverse of the objective process ($\Delta H_i^{m\rightarrow a} = -\Delta H_i^{a\rightarrow m}$). After accounting for the fraction of the transferred surfactant molecules, we can obtain $\Delta H_i^{a\rightarrow m}$ as listed in Table 1.

3. Thermodynamic Model

Consider a given aqueous mixture of surfactant **1**, surfactant **2**, and β-CD, where their respective bulk concentrations are C_1, C_2 ($C_1 + C_2 = C_T$), and $C_{\beta\text{-CD}}$. In a 1:1 surfactant/β-CD binding model, the host−guest equilibrium is governed by

$$K_i^b = \frac{C_i^c}{C_i^m C_{\beta\text{-CD}}^f} \qquad (4)$$

where K_i^b is the binding constant of CD to surfactant **i** (**i** = **1** or **2**) and C_i^c, C_i^m, and $C_{\beta\text{-CD}}^f$ are the concentrations of the **i**/β-CD complex, monomeric (uncomplexed and unaggregated) **i**, and free (uncomplexed) β-CD, respectively. The mass balance of β-CD gives

$$C_{\beta\text{-CD}}^f + C_1^c + C_2^c = C_{\beta\text{-CD}} \qquad (5)$$

It is reasonable to use the ratio of C_i^c weighed by C_i to measure the apparent selectivity of β-CD to **i**, S_i, which yields

$$S_1 \equiv \frac{C_1^c C_2}{C_2^c C_1} = \frac{K_1^b C_1^m C_2}{K_2^b C_2^m C_2} \qquad (6)$$

$$S_2 = 1/S_1 \qquad (7)$$

Clearly, $S_1 \gg 1$, $S_1 \ll 1$, and $S_1 \approx 1$ correspond to a high selectivity to **1**, a high selectivity to **2**, and a low selectivity, respectively. Moreover, this selectivity S will depend on the nature of a specific binary surfactant mixture and the amount of added β-CD (i.e., $C_{\beta\text{-CD}}$). To eliminate the effect of $C_{\beta\text{-CD}}$, we define the initial selectivity S^* in the limit of $C_{\beta\text{-CD}} \rightarrow 0$, that is

$$S_1^* \equiv \lim_{C_{\beta\text{-CD}}\rightarrow 0} \frac{C_1^c C_2}{C_2^c C_1} = \lim_{C_{\beta\text{-CD}}\rightarrow 0} \frac{K_1^b C_1^m C_2}{K_2^b C_2^m C_2} \qquad (8)$$

If $C_T <$ critical aggregation concentration (CAC), the mass balance of surfactant **i** is given by

$$C_i^m + C_i^c = C_i \qquad (9)$$

and the mixed system can be fully described by the host−guest equilibrium (eq 4) and the mass balances of β-CD and surfactants (eqs 5 and 9). At the limit of $C_{\beta\text{-CD}} \rightarrow 0$, C_i^c is practically 0, $C_i^m = C_i$, and the selectivity S_1^* simply reads

$$S_1^* = K_1^b / K_2^b \qquad (10)$$

In this case, the selectivity S_1^* is identical to the classic selectivity that exclusively depends on binding constants.

If $C_T \geq$ CAC, the aggregation equilibrium emerges, and the surfactant mass balance is expressed by

$$C_i^m + C_i^c + C_i^a = C_i \qquad (11)$$

where C_i^a is the concentration of **i** in the mixed aggregates. Within the pseudophase separation model, the balance between chemical potentials of **i** in monomeric and aggregated states reads

$$\mu_i^{m\Theta} + RT \ln(C_i^m/55.5) = \mu_i^a \qquad (12)$$

where $\mu_i^{m\Theta}$ is the standard chemical potential of monomeric **i**, 55.5 the molar concentration of water, and μ_i^a the chemical potential of **i** in the mixed aggregation phase. According to the Rubingh theory, the mixed aggregation phase is treated as a regular solution, leading to

$$\mu_i^a = \mu_i^{a\Theta} + RT \ln(f_i^a x_i^a) \qquad (13)$$

where $\mu_i^{a\Theta}$ is the standard chemical potential of **i** in its own pure micelles, f_i^a the activity coefficient of **i** in the mixed aggregation phase, and x_i^a the mole fraction of **i** in the mixed aggregation phase ($x_1^a = C_1^a/(C_1^a + C_2^a)$). Then, $\mu_i^{a\Theta}$ is correlated to the critical micelle concentration of **i**, CMC_i, and $\mu_i^{m\Theta}$ by

$$\mu_i^{m\Theta} + RT \ln(CMC_i/55.5) = \mu_i^{a\Theta} \qquad (14)$$

Combining eqs 12, 13, and 14, one obtains

$$C_i^m = CMC_i f_i^a x_i^a \qquad (15)$$

Here, a dimensionless parameter β is introduced to correlate f_i^a and x_i^a by

$$f_1^a = \exp(\beta(x_2^a)^2) \qquad (16)$$

$$f_2^a = \exp(\beta(x_1^a)^2) \qquad (17)$$

where β is the interaction parameter of the two surfactants and represents a net energy difference between the mixed (**1** + **2**) aggregation phase and the pure (**1** or **2**) micellar phases. Now the ternary **1**/**2**/β-CD aqueous mixture can be described by the host−guest (eq 4) and aggregation (eqs 15−17) equilibria as well as the β-CD (eq 5) and surfactant (eq 11) mass balances.

Host−Guest versus Biased Aggregation

J. Phys. Chem. B, Vol. 114, No. 6, 2010 **2169**

At the limit of $C_{\beta\text{-CD}} \rightarrow 0$, the combination of eqs 8, 15, 16, and 17 gives

$$S_1^* = \lim_{C_{\beta\text{-CD}} \rightarrow 0} \frac{K_1^b \text{CMC}_1 x_1^a C_2}{K_2^b \text{CMC}_2 x_2^a C_1} \exp(\beta((x_2^a)^2 - (x_1^a)^2))$$

$$= \frac{K_1^b \text{CMC}_1 x_1^{a0} C_2}{K_2^b \text{CMC}_2 x_2^{a0} C_1} \exp(\beta((x_2^{a0})^2 - (x_1^{a0})^2)) \qquad (18)$$

in which x_i^{a0} is the molar fraction of **i** in the aggregates without β-CD addition (i.e., $C_{\beta\text{-CD}} = 0$).

It is worthy noting that 1) this model can be modified to account for systems involving 1:2 surfactant/β-CD complexation by re-establishing the complexation equilibria (in a 1:2 manner) and relevant mass balances, (2) β-CD here can be replaced by any member from the CD family, and (3) although this work focuses on cationic/anionic surfactant mixtures, this model is, in principle, operative for any other binary surfactant mixtures.

4. Results

In this section, several conclusions that can be directly drawn from the thermodynamic model are listed, and the correctness of them is experimentally checked in SDS/DEAB/β-CD systems. In the studied SDS/DEAB/β-CD systems, the molar ratio of SDS/DEAB was always selected to be 3/1 to avoid an equimolar ratio because a SDS/DEAB equimolar mixture is not stable and will precipitate over 1 to 2 weeks. A partial phase diagram of the SDS/DEAB system is presented in the Supporting Information.

4.1. Low Selectivity at $C_T < $ CAC. For $C_T < $ CAC, the aggregation equilibrium is not yet raised, and the selectivity is simply governed by binding constants. The thermodynamic model suggests quite low selectivity for SDS/DEAB/β-CD ($C_T < $ CAC) systems, which is not surprising since the binding constants of β-CD to SDS and DEAB are almost identical. The initial selectivity is always 0.91, and the apparent selectivity is even closer to 1 (Figure 4a) for mixtures of SDS/DEAB (molar ratio 3/1) and β-CD. The above prediction is tested by surface tension measurements, in which SDS/DEAB/β-CD solutions are diluted against β-CD buffers (the surfactant molar ratio is constant at 3/1, and $C_{\beta\text{-CD}}$ is kept at 3, 6, or 10 mM). The experimental results are shown as scatters in Figure 4b, while the predicted lines are obtained as follows. In the presence of β-CD, the effective total surfactant concentration related to the surface tension is actually the sum of monomeric surfactant concentrations. The Gibbs adsorption equation (in integral form, in the saturated adsorption region) then reads

$$\gamma - \gamma^{\text{CAC}} = -\Gamma^\infty RT[\ln(C_{\text{SDS}}^m + C_{\text{DEAB}}^m) - \ln \text{CAC}] \qquad (19)$$

The C_{SDS}^m and C_{DEAB}^m can be readily calculated according to the predicted selectivity for a given solution. The γ^{CAC}, Γ^∞, and CAC are determined from a β-CD-free control experiment (see the Experimental Section and Table 1). The consistency between the experimental and predicted results validates our thermodynamic model and the deduced low selectivity for the SDS/DEAB/β-CD ($C_T < $ CAC) systems.

4.2. High Selectivity toward the Major Surfactant at $C_T > $ CAC. With $C_T > $ CAC, the combination of the host−guest and aggregation equilibria dominates the systems. For the
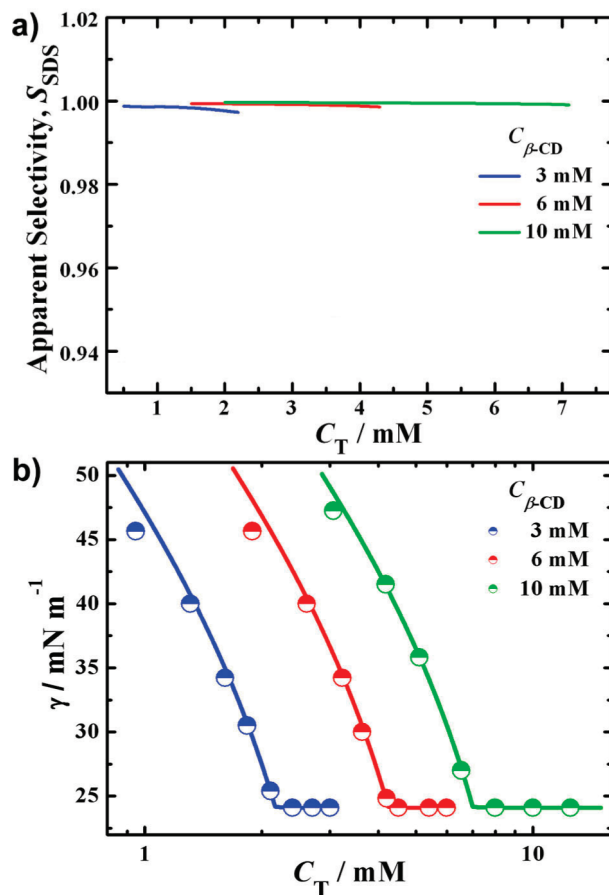
Figure 4. (a) Predicted selectivity for mixtures of SDS/DEAB (molar ratio 3/1) and β-CD. (b) Predicted (lines) and measured (scatters) surface tension curves for the dilution of SDS/DEAB/β-CD solutions against β-CD buffers, where the surfactant molar ratio is constant at 3/1 and $C_{\beta\text{-CD}}$ is kept at 3, 6, or 10 mM.

SDS/DEAB/β-CD systems, the thermodynamic model generally gives high selectivity of β-CD to the major surfactant regardless of the similarity between K_{SDS}^b and K_{DEAB}^b. Specifically, Figure 5a−c shows the predicted binding behavior of β-CD in the SDS/DEAB (15/5 mM) system upon addition of β-CD. The concentration of complexed SDS (C_{SDS}^c, the red curve in Figure 5a) is almost proportional to $C_{\beta\text{-CD}}$, whereas the concentration of complexed DEAB (C_{DEAB}^c, the red curve in Figure 5b) is always close to 0, qualitatively revealing a high selectivity to SDS (S_{SDS}). The quantitative value of S_{SDS} shows a maximum of ∼140 at $C_{\beta\text{-CD}} = 0$ mM (i.e., the initial selectivity S_{SDS}^*) and undergoes a progressive decrease to ∼25 (still ≫1) at $C_{\beta\text{-CD}} = 5$ mM (the black line in Figure 5c). The figures further manifest that (1) the added β-CD will bind the major surfactant SDS with a high selectivity, partly removing the excess SDS from aggregates (the green line in Figure 5a), (2) the concentration of DEAB in aggregates C_{DEAB}^a is not affected (the green line in Figure 5b), and (3) the net effect is clearly the shift of the aggregate composition toward 1:1 electroneutral mixing (the blue cure in Figure 5c).

These predictions are examined by PGSE-NMR measurements. Figure 5d demonstrates the observed diffusion coefficients of tetramethylsilane (TMS), DEAB, and SDS with the addition of β-CD to the SDS/DEAB (15/5 mM) solution. TMS is added to the solutions to label the diffusion coefficient of the surfactant aggregates D^a. Because the strongly
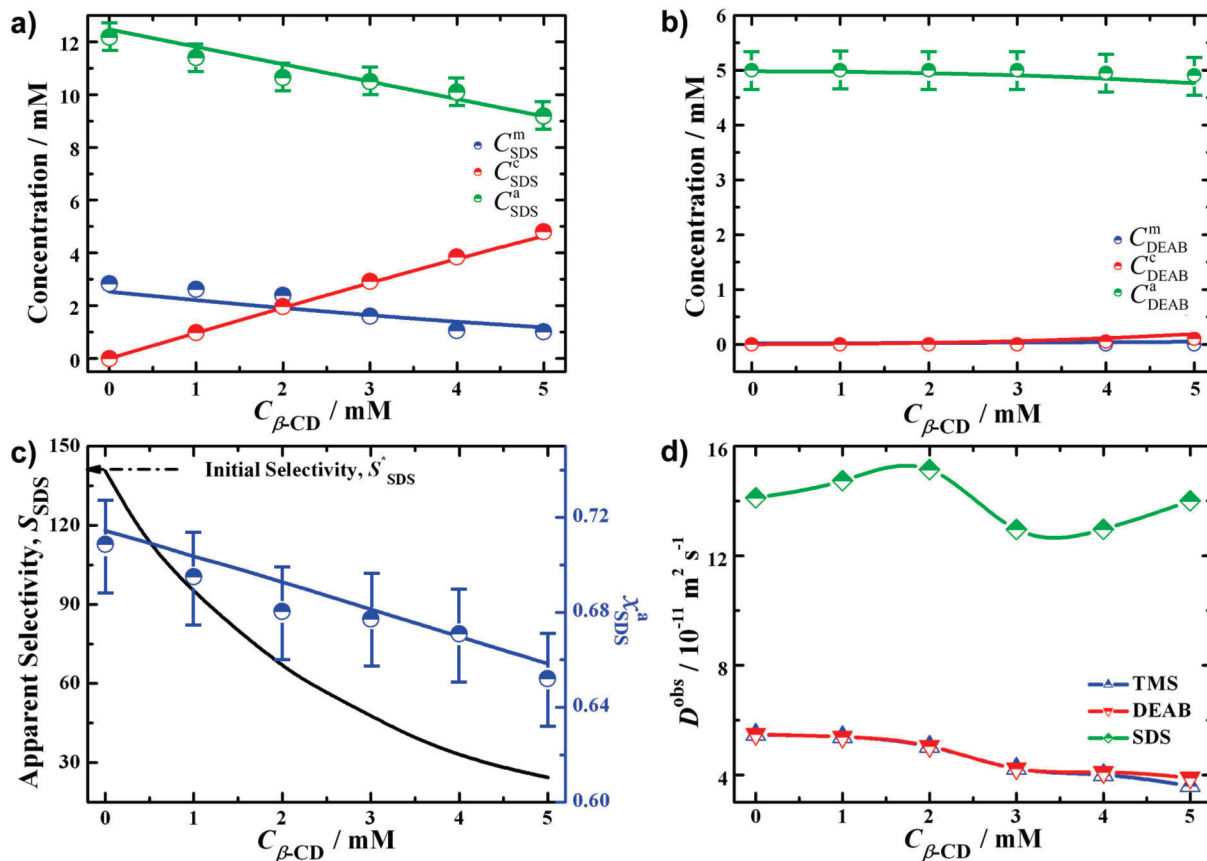
Figure 5. The selective binding of β-CD upon its addition to a SDS-rich SDS/DEAB (15/5 mM) system as predicated by the thermodynamic model and experimentally confirmed by PGSE-NMR. (a) and (b) Variations of concentrations of SDS and DEAB in different states. (c) Variations of the selectivity and aggregate composition. In (a−c), the lines are predicted, while the scatters are measured. (d) Variations of diffusion coefficients of TMS, DEAB, and SDS.

hydrophobic TMS will be fully solubilized into the aggregates, D^a is simply given by $D^a = D^{obs}_{TMS}$. As shown in Figure 5d, the aggregates diffuse more slowly with β-CD addition, in line with the previously observed β-CD-induced aggregate growth. The D^{obs}_{DEAB} and D^{obs}_{SDS} are related to the concentrations of SDS or DEAB in different states by the n-state exchange model. The validity of this model in this case is confirmed by the fact that the echo amplitude of SDS or DEAB always follows single-exponential decays (Figure 2). In the n-state exchange model, the observed diffusion coefficient of surfactant **i** (**i** = DEAB or SDS) is a concentration-weighed average of the diffusion coefficients in different states

$$D^{obs}_i = (C^m_i D^m_i + C^c_i D^c_i + C^a_i D^a)/C_i \qquad (20)$$

where D^m_i and D^c_i are the diffusion coefficients of **i** in monomeric and complexed states, respectively, and can be obtained from separate experiments (see the Experimental Section and Table 1). According to this equation, the mass balances of β-CD and surfactants (eqs 5 and 11), and the complexation equilibrium (eq 4), we experimentally determined C^m_i, C^c_i, and C^a_i, which are shown as scatters in Figure 5a−c. Obviously, the experimental data is in good agreement with the predicted data, verifying the highly selective binding to SDS and the approaching of 1:1 electoneutral mixing.

The thermodynamic model and its predictions are further evaluated by ITC measurements, where a β-CD (5 mM)

solution is titrated into a SDS/DEAB (4/1 mM) solution. The experimental result is that $\Delta H = \sim -12$ kJ/mol, while predicted data are generated by the following procedure. When a β-CD solution is titrated into a SDS/DEAB ($C_T >$ CAC) solution, the dilution-corrected heat Q for each injection can be divided into four parts
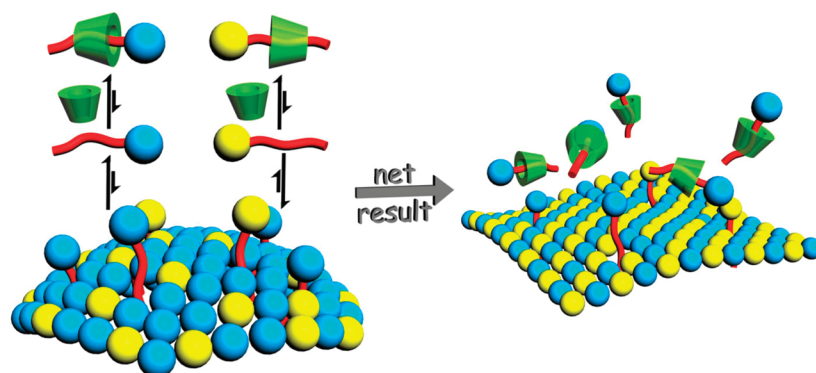
$$Q = Q^{m \to c}_{SDS} + Q^{a \to c}_{SDS} + Q^{m \to c}_{DEAB} + Q^{a \to c}_{DEAB} \qquad (21)$$

where $Q^{m \to c}_i$ and $Q^{a \to c}_i$ (**i** = SDS or DEAB) are the heats due to the transfers of **i** from water and the aggregates to β-CD cavities, respectively. Equation 21 can be expressed by molar enthalpy changes

$$\Delta H \Delta n_{\beta\text{-}CD} = \Delta H^{m \to c}_{SDS} n^{m \to c}_{SDS} + \Delta H^{a \to c}_{SDS} n^{a \to c}_{SDS} +$$
$$\Delta H^{m \to c}_{DEAB} n^{m \to c}_{DEAB} + \Delta H^{a \to c}_{DEAB} n^{a \to c}_{DEAB} = \Delta H^{m \to c}_{SDS}(-\Delta n^m_{SDS}) +$$
$$\Delta H^{a \to c}_{SDS}(-\Delta n^a_{SDS}) + \Delta H^{m \to c}_{DEAB}(-\Delta n^m_{DEAB}) +$$
$$\Delta H^{a \to c}_{DEAB}(-\Delta n^a_{DEAB}) \qquad (22)$$

The $\Delta n_{\beta\text{-}CD}$, Δn^m_{SDS}, Δn^a_{SDS}, Δn^m_{DEAB}, and Δn^a_{DEAB} are molar changes of corresponding species in the titrand solution during an injection, where the last four molar changes are predictable for a given $\Delta n_{\beta\text{-}CD}$. Noteworthily, the transfer of surfactant **i** from aggregates into β-CD cavities can be conceptually broken down into two steps, the transfer of **i**

Host−Guest versus Biased Aggregation

J. Phys. Chem. B, Vol. 114, No. 6, 2010 **2171**

SCHEME 1

from the aggregates to water and then to β-CD cavities, which leads to

$$\Delta H_i^{a \rightarrow c} = \Delta H_i^{a \rightarrow m} + \Delta H_i^{m \rightarrow c} \qquad (23)$$

The $\Delta H_i^{a \rightarrow m}$ and $\Delta H_i^{m \rightarrow c}$ can be determined from separate experiments (see the Experimental Section and Table 1), eventually enabling the prediction of ΔH. The predicted ΔH is -11.4 kJ/mol, consistent with the experimental data.

Taken together, the PGSE-NMR and ITC measurements confirm the validity of the present thermodynamic model and identify the high selectivity toward SDS for the SDS-rich SDS/DEAB systems. As to DEAB-rich SDS/DEAB systems, high selectivity to DEAB ($\sim 10^2$) is predicted by our model and confirmed experimentally by PGSE-NMR and ITC. Therefore, it is suggested that in the present cases, the added β-CD will always bind the major surfactant with high selectivity, consequently shifting the aggregate composition toward electroneutral mixing.
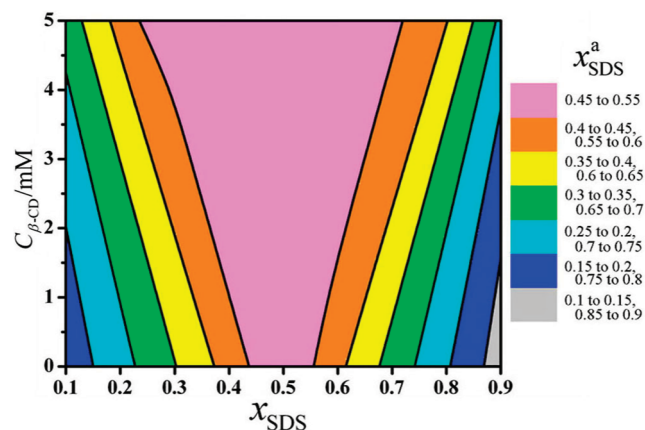
5. Discussion

5.1. The Selectivity and Stoichiometry Boosting Effect of β-CD. For $C_T <$ CAC, the aggregation equilibrium is not yet raised, the host−guest equilibrium governs the systems, and the selectivity of β-CD is simply determined by the difference in binding constants as in the classical cases. For the SDS/DEAB pair with similar binding constants, the selectivity is, not surprisingly, quite low. The situation gets complicated for C_T > CAC, where the two equilibria coexist and are coupled through

Figure 6. Predicted contour map for SDS/DEAB ($C_T = 10$ mM) and β-CD mixed systems; x_{SDS}^a against the surfactant composition in bulk solution (x_{SDS}) and against $C_{\beta\text{-CD}}$.

the bridging of surfactant monomers. Before the discussion on how the combination of the two equilibria dominates the systems, we attempt to clarify the bias of the aggregation equilibrium, which always plays a central role in nonstoichiometric cationic/anionic surfactant systems with or without the presence of β-CD. The bias is that the aggregation of the minor surfactant is much more preferred than that of the major surfactant even if the two surfactants are of close CMCs. This is reasonable considering that the net charge of the aggregates will favor the countercharged, minor surfactant and repel the cocharged, major surfactant electrostatically. In the case of the SDS-rich SDS/DEAB mixture, the bias is evidenced by the remarkable difference in the aggregation enthalpy changes (-20 kJ/mol for DEAB, favored; -0.1 kJ/mol for SDS, disfavored) as well as by the β parameter of -13.

As a result of the bias, there is a tendency for the aggregates to deplete all of the excess part of the major surfactant and to finally reach electroneutral mixing stoichiometry. In the absence of β-CD, the major surfactant can be solely depleted into water, an environment that disfavors the hydrophobic moiety of the surfactant and that can only accommodate a limited amount of the major surfactant. In the presence of β-CD, the major surfactant can also be depleted in β-CD cavities, an environment quite comfortable with the hydrophobic moiety of the surfactant. Therefore, β-CD has to accept the major surfactant, the less aggregatable and more available one, although β-CD may exhibit no preference to the major or minor surfactants on its own. In this context, the bias gives rise to a kind of apparent K_b-independent host−guest selectivity. Considering the high binding constants of β-CD to surfactants, the β-CD cavities can act as efficient vessels for the depleted major surfactant molecules. Upon the addition of β-CD, an increasing amount of the major surfactant is removed from the aggregates to β-CD cavities, leaving the aggregate composition approaching electroneutral mixing stoichiometry. The approaching to electroneutrality promotes transitions of aggregates into low-curved ones, which answers for the recently observed β-CD-induced aggregate growth.[14] The above description is summarized in Scheme 1.[20,21]

On account of its influence on aggregate compositions, β-CD is defined as a stoichiometry booster for nonstoichiometric cationic/anionic surfactant systems. This stoichiometry boosting effect is further profiled in a contour map (Figure 6) for SDS/DEAB/β-CD systems, where x_{SDS}^a (the aggregate composition; its value is denoted by different colors) is predicted according to input values of x_{SDS} (the bulk composition) and $C_{\beta\text{-CD}}$. Along the y axis, the relation between $C_{\beta\text{-CD}}$ and x_{SDS}^a at a constant x_{SDS} is demonstrated. Taking $x_{SDS} = 0.8$ as an instance, one observes the approach of x_{SDS}^a to the 1:1 stoichiometry (from

TABLE 2: Factors that Affect the Initial Selectivity[a]

					S_1	
systems (tail length) **1/2**	$K_1^b/K_2^{b\ b}$	$CMC_1/CMC_2{}^c$	$K_1^b CMC_1/K_2^b CMC_2$	β^d	$x_1^{a0} = 0.7$	$x_2^{a0} = 0.3$
SDS/DTAB(12/12)	$2.30 \times 10^4/2.37 \times 10^4$	8.3/16	0.50	−25	2.6×10^3	1.0×10^{-5}
SOS/DTAB(8/12)	$2.56 \times 10^3/2.37 \times 10^4$	$1.4 \times 10^2/16$	0.91	−19	4.3×10^2	2.0×10^{-3}
SDSO₃/DTAB(12/12)	$1.61 \times 10^4/2.37 \times 10^4$	9.7/16	0.42	−19	1.9×10^2	9.1×10^{-3}
DTAB/DPyB(12/12)	$2.37 \times 10^4/1.87 \times 10^4$	16/12	1.7	0.0	1.7	1.7

[a] DTAB, dodecyl trimethyl ammonium bromide. DPyB, dodecyl pyridinium bromide. SOS, sodium octyl sulfate. SDSO₃, sodium dodecyl sulfonate. The DTAB/DPyB system is a cationic/cationic surfactant system, while all of the other systems are cationic/anionic surfactant systems. [b] References 11c and 17b. [c] Reference 9a. [d] Reference 22.

cyan via green to yellow) with the $C_{\beta\text{-CD}}$ increase. Along the x axis, the connection between x_{SDS} and x_{SDS}^a at a constant $C_{\beta\text{-CD}}$ is displayed. For β-CD-free samples ($C_{\beta\text{-CD}} = 0$), x_{SDS}^a is basically determined by input x_{SDS} (i.e., their values are close); x_{SDS}^a falls in the near-stoichiometry region (0.45−0.55, magenta) only for x_{SDS} from 0.43 to 0.56. However, for samples with $C_{\beta\text{-CD}} = 5$ mM, x_{SDS}^a shows a strong resistance to variations of x_{SDS}; x_{SDS}^a remains near stoichiometry for a highly broadened range of x_{SDS} from 0.27 to 0.72. This figure clarifies two equivalent features of stoichiometry boosters, (1) altering aggregate compositions to stoichiometry for samples at a fixed bulk composition as well as (2) resisting variations of bulk compositions and maintaining aggregate compositions near stoichiometry for samples at a fixed total bulk concentration. These features manifest that the stoichiometry booster is analogous to a pH buffer which always adjusts the ratio of H⁺/OH⁻ to a certain value. Considering the deterministic role of aggregate compositions in cationic/anionic systems, the present stoichiometry booster β-CD could be a powerful additive for this kind of systems.

**5.2. Factors that Affect the Initial Selectivity at $C_T > CAC$.** These factors will be evaluated one by one in terms of eq 18, which is rewritten here for convenience

$$S_1^* = \frac{K_1^b CMC_1 x_1^{a0} C_2}{K_2^b CMC_2 x_2^{a0} C_1} \exp(\beta((x_2^{a0})^2 - (x_1^{a0})^2)) \quad (18)$$

As listed in Table 2, for a mixture of cationic/anionic surfactants with equal tails, both K_1^b/K_2^b and CMC_1/CMC_2 are close to 1. As for a mixture of catanionic surfactants with unequal tails, $K_1^b CMC_1/K_2^b CMC_2$ is close to 1, as well due to a "compensation effect" between K_1^b/K_2^b and CMC_1/CMC_2. This compensation effect is understandable since surfactants with longer tails (more hydrophobic) are easier to bind with β-CD (higher K^b) and to aggregates (lower CMC). Thus, the two terms can hardly contribute to the initial selectivity.

The dependence of S_1^* on x_1^{a0} is plotted by predicted curves in SDS/DEAB systems (Figure 7). For the SDS-rich systems (x_{SDS}^{a0} or $x_{SDS} > 0.5$), S_{SDS}^* is larger than 1 and increases abruptly with the composition moving from 0.5 to 1. As for the DEAB-rich systems (x_{SDS}^{a0} or $x_{SDS} < 0.5$), S_{SDS}^* is lower than 1 and decreases precipitously upon shifting the composition from 0.5 to 0. Alternatively, the poorer the selectivity to SDS, the better the selectivity to DEAB ($S_{DEAB}^* = 1/S_{SDS}^*$). It is also noticeable that the deviation of a x_{SDS} curve from the x_{SDS}^a curve is aggravated by C_T decrease, which is associated with the fact that, in nonstoichiometric cationic/anionic surfactant systems, aggregate compositions always depart farther from bulk compositions (i.e., gets closer to 1:1) with C_T decrease. Overall, the selectivity exhibit near-exponential dependence on the aggregate composition.
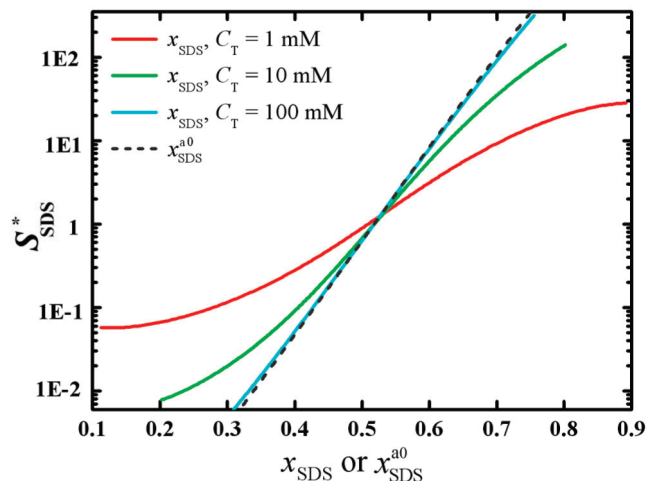
Figure 7. Predicted curves of the selectivity S_{SDS} versus the surfactant compositions in bulk solution (x_{SDS}) or in aggregates (x_{SDS}^{a0}) in SDS/DEAB/β-CD mixed systems.

As for the interaction parameter β, it measures the net energy difference between the mixed and unmixed systems within the regular solution theory. For a binary surfactant mixed system, (1) negative β reveals that the two surfactants are more aggregatable when they are mixed than on their own, that is, they form mixed aggregates in a synergistic way, (2) positive β reveals that the two surfactant are less aggregatable when they are mixed than on their own, that is, they form mixed aggregates in a antagonistic way, (3) zero β reveals that the two surfactant form mixed aggregates in an ideal way, and (4) the magnitude of β reflects the degree of synergism or antagonism. Cationic/anionic surfactant systems are generally of negative β values less than −10 because the aggregation of the mixture is greatly synergized by the strong electrostatic attractions between oppositely charged surfactant head groups. Other binary surfactant systems like cationic/cationic, anionic/anionic, and ionic/nonionic ones are of β values between 0 and −5 due to the lack of significant aggregation synergism. As clearly shown in Table 2, all of the cationic/anionic surfactant systems have highly negative β values and exhibit conspicuously high selectivity ($S_1 \approx 10^3$ or 10^{-3}) for $x_1^{a0} = 0.3$ or 0.7, whereas a cationic/cationic system with $\beta = 0$ displays no appreciable selectivity ($S_1 \approx 1$). For different cationic/anionic surfactant mixtures, a larger absolute value of β corresponds to a higher selectivity value. The above results reveal that β is the leading parameter in eq 18 and that the electrostatic attractions between cationic and anionic surfactants are of the greatest importance to the initial selectivity.

Conclusion

In this work, we systematically investigated the cationic surfactant/anionic surfactant/β-CD ternary aqueous systems. A

Host−Guest versus Biased Aggregation

J. Phys. Chem. B, Vol. 114, No. 6, 2010 **2173**

thermodynamic model was developed to describe the systems, the validity of which was verified by surface tension, PGSE-NMR, and ITC measurements. It is found that these systems are dominated by the interplay between the host−guest and aggregation equilibria. The aggregation equilibrium in nonstoichiometric cationic/anionic surfactant systems is inherently biased, in which the aggregates tend to deplete the excess part of the major surfactant to reach electroneutrality. The bias will force the added β-CD to selectively accept the major surfactant even if the binding constants of β-CD to the two surfactants are similar. The apparent host−guest selectivity is of considerably high value and of an "abnormal" origin, that is, in contrast to "normal" selectivity governed by the difference in binding constants, the present "abnormal" selectivity arises from the strong electrostatic attractions between cationic and anionic surfactants. Since the binding constants between β-CD and surfactants are generally high, the selective binding will efficiently remove the major surfactant (a part of its excess) from the aggregates to β-CD cavities. This behavior leaves the aggregate composition approaching the electroneutral mixing stoichiometry and thus amplifies the bias of the aggregation equilibrium. The approaching of electroneutrality causes the aggregates to be transformed into less-curved ones, as we observed in a recent work.[14] Furthermore, β-CD is defined as a stoichiometry booster for the whole class of cationic/anionic surfactant systems, which provides an additional dimension to directly tune aggregate compositions. Because the aggregate composition is a central parameter of the cationic/anionic surfactant systems, which can profoundly affect the systems at both microscopical and macroscopical levels, the stoichiometry booster, β-CD, is envisioned to be a promising and powerful additive to control this kind of system.

Nomenclature

C	concentration
C_i	concentration of surfactant **i** in bulk solution
C_i^a, C_i^c, and C_i^m	concentrations of surfactant **i** in aggregated, complexed, and monomeric states, respectively
$C_{\beta\text{-CD}}$	concentration of β-CD in bulk solution
$C_{\beta\text{-CD}}^f$	concentration of free (uncomplexed) β-CD
CAC	critical aggregation concentration of a surfactant mixture
CMC_i	critical micelle concentration of surfactant **i**
D	diffusion coefficient
D^a	diffusion coefficient of aggregates
D_i^{obs}	observed diffusion coefficient of surfactant **i**
D_i^c and D_i^m	diffusion coefficients of surfactant **i** in complexed and monomeric states, respectively
$\Delta H_i^{a\rightarrow m}$, $\Delta H_i^{a\rightarrow c}$, and $\Delta H_i^{m\rightarrow c}$	enthalpy changes in the transfer of surfactant **i** from aggregated to monomeric, from aggregated to complexed, and from monomeric to complexed states, respectively
S_i and Si^*	apparent and initial selectivity of β-CD to surfactant **i**
K_i^b	binding constant of β-CD to surfactant **i**
Q, $Q^{dilution}$, and Q^{obs}	dilution-corrected heat, dilution heat, and observed heat, respectively
$Q_i^{m\rightarrow c}$ and $Q_i^{a\rightarrow c}$	heats due to the transfers of **i** from water and the aggregates to β-CD cavities, respectively
R	gas constant
T	absolute temperature
β	interaction parameter in mixed aggregates
γ	surface tension
γ^{CAC}	surface tension at CAC
Γ	Gibbes adsorption amount
Γ^∞	the maximum of Gibbs adsorption amount
μ_i^a	chemical potential of surfactant **i** in mixed aggregates
$\mu_i^{a\Theta}$ and $\mu_i^{m\Theta}$	standard chemical potential of surfactant **i** in its own pure micelles and in monomeric states, respectively
x_i	molar fraction of surfactant **i** in bulk solution
x_i^a	molar fraction of surfactant **i** mixed aggregates
x_i^{a0}	molar fraction of surfactant **i** mixed aggregates without β-CD addition

Supporting Information Available: Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495. (b) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021.

(2) (a) Hayashi, N.; Kuruma, K.; Mazaki, Y.; Imakubo, T.; Kobayashi, K. *J. Am. Chem. Soc.* **1998**, *120*, 3799. (b) Otto, S.; Osifchin, M.; Regen, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 7276. (c) Svoboda, J.; Konig, B. *Chem. Rev.* **2006**, *106*, 5413.

(3) Trend, J. E.; Kipke, C. A.; Rossmann, M.; Yafuso, M.; Patil, S. L. U.S. Patent 5,474,743, 1993.

(4) For reviews, see: (a) Hao, J.; Hoffmann, H. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 279. (b) Tondre, C.; Caillet, C. *Adv. Colloid Interface Sci.* **2001**, *93*, 115. Note that a similar term "catanionic surfactant" refers to a compound that is usually formed by an equimolar chemical reaction of a basic and an acidic surfactant. For example, see: (c) Consola, S.; Blanzat, M.; Perez, E.; Garrigues, J. C.; Bordat, P.; Rico-Lattes, I. *Chem.−Eur. J.* **2007**, *13*, 3039. (d) Rico-Lattes, I.; Blanzat, M.; Franceschi-Messant, S.; Perez, E.; Lattes, A. *C. R. Chim.* **2005**, *8*, 807.

(5) (a) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley & Sons: New York, 1989. (b) Yu, Z. J.; Zhao, G. X. *J. Colloid Interface Sci.* **1989**, *130*, 414.

(6) (a) Kaler, E. W.; Murthy, A. K.; Rodriguez, B. E.; Zasadzinski, J. A. N. *Science* **1989**, *245*, 1371. (b) Kaler, E. W.; Herrington, K. L.; Murthy, A. K.; Zasadzinski, J. A. N. *J. Phys. Chem.* **1992**, *96*, 6698.

(7) For icosahedra, see: (a) Dubios, M.; Deme, B.; Gulik-Krzywicki, T.; Dedieu, J.-C.; Vautrin, C.; Desert, S.; Perez, Emile.; Zemb, T. *Nature* **2001**, *411*, 672. For flat nanodiscs, see: (b) Zemb, T.; Dubios, M.; Deme, B.; Gulik-Krzywicki, T. *Science* **1999**, *283*, 816. For onion structures, see: (c) Song, A. X.; Dong, S. L.; Jia, X. F.; Hao, J. C.; Liu, W. M.; Liu, T. B. *Angew. Chem., Int. Ed.* **2005**, *44*, 4018. For polyhedra, see: (d) Gonzalez-Perez, A.; Schmutz, M.; Waton, G.; Romero, M. J.; Krafft, M. P. *J. Am. Chem. Soc.* **2007**, *129*, 756. For tubelike structures, see: (e) Lu, T.; Han, F.; Li, Z. C.; Huang, J. B.; Fu, H. L. *Langmuir* **2006**, *22*, 2045. (f) Yan, Y.; Xiong, W.; Li, X. X.; Lu, T.; Huang, J. B.; Li, Z. C.; Fu, H. L. *J. Phys. Chem. B* **2007**, *111*, 2225. For hollow cones, see: (g) Douliez, J.-P. *J. Am. Chem. Soc.* **2005**, *127*, 15694.

(8) (a) Yin, H. Q.; Zhou, Z. K.; Huang, J. B.; Zheng, R.; Zhang, Y. Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 2188. (b) Renoncourt, A.; Vlachy, N.; Bauduin, P.; Drechsler, M.; Touraud, D.; Verbavatz, J. M.; Dubois, M.; Kunz, W.; Ninham, B. W. *Langmuir* **2007**, *23*, 2376. (c) Jiang, L. X.; Wang, K.; Deng, M. L.; Wang, Y. L.; Huang, J. B. *Langmuir* **2008**, *24*, 4600. (d) Jiang, L. X.; Wang, K.; Ke, F. Y.; Liang, D. H.; Huang, J. B. *Soft Matter* **2009**, *5*, 599.

(9) (a) Rubingh, D. N. *Solution Chemistry of Surfactants*; Plenum Press: New York, 1979. (b) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984. (c) Herrington, K. L.; Kaler, E. W.; Miller, D. D.; Zasadzinski, J. A.; Chiruvolu, S. *J. Phys. Chem.* **1993**, *97*, 13792. (d) Rodenas, E.; Valiente, M.; Villafruela, M. S. *J. Phys. Chem. B* **1999**, *103*, 4549. (e) Nagarajan, R.; Ruckenstein, E. *J. Colloid Interface Sci.* **1979**, *71*, 580. Yuet, P. K.; Blankschtein, D. *Langmuir* **1996**, *12*, 3802.

(10) (a) Rosen, M. J.; Hua, X. Y. *J. Colloid Interface Sci.* **1982**, *86*, 164. (b) Goralczyk, D. *J. Colloid Interface Sci.* **1991**, *159*, 361. (c) Rosen, M. J.; Hua, X. Y. *J. Am. Oil Chem. Soc.* **1982**, *59*, 582.

(11) (a) Saenger, W.; Muller-Fahrnow, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 393. (b) Junquera, E.; Tardajos, G.; Aicart, E. *Langmuir* **1993**, *9*, 1213. (c) Mwakibete, H.; Cristantino, R.; Bloor, D. M.; Wyn-Jones, E.;

2174 *J. Phys. Chem. B, Vol. 114, No. 6, 2010*

Jiang et al.

Holzwarth, J. F. *Langmuir* **1995**, *11*, 57. (d) Dorrego, A. B.; Garcia-Rio, L.; Herves, P.; Leis, J. R.; Mejuto, J. C.; Perez-Juste, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2945. (e) Dharmawardana, U. R.; Christian, S. D.; Tucker, E. E.; Taylor, R. W.; Scamehorn, J. F. *Langmuir* **1993**, *9*, 2258.

(12) (a) Cabaleiro-Lago, C.; García-Ro, L.; Hervs, P.; Prez-Juste, J. *J. Phys. Chem. B* **2009**, *113*, 6749. (b) Haller, J.; Kaatze, U. *J. Phys. Chem. B* **2009**, *113*, 1940. (c) Nilsson, M.; Valente, A. J. M.; Olofsson, G.; Sderman, O.; Bonini, M. *J. Phys. Chem. B* **2008**, *112*, 11310. (d) Mehta, S. K.; Bhasin, K. K.; Dham, S.; Singla, M. L. *J. Colloid Interface Sci.* **2008**, *321*, 442.

(13) Xing, H.; Lin, S. S.; Yan, P.; Xiao, J. X.; Chen, Y. M. *J. Phys. Chem. B* **2007**, *111*, 8089.

(14) Jiang, L. X.; Deng, M. L.; Wang, Y. L.; Liang, D. H.; Yan, Y.; Huang, J. B. *J. Phys. Chem. B* **2009**, *113*, 7498.

(15) Myers, D. *Surfaces, Interfaces, and Colloids*, 2nd ed.; Wiley: New York, 1999.

(16) Misselyn-Bauduin, A. M.; Thibaut, A.; Grandjean, J.; Broze, G.; Jerome, R. *Langmuir* **2000**, *16*, 4430.

(17) (a) Yunus, W. M. Z.; Taylor, J.; Bloor, D. M.; Hall, D. G.; Wyn-Jones, E. *J. Phys. Chem.* **1992**, *96*, 8979. (b) Park, J. W.; Song, H. J. *J. Phys. Chem.* **1989**, *93*, 6454.

(18) (a) Pettersson, E.; Topgaard, D.; Stilbs, P.; Söderman, O. *Langmuir* **2004**, *20*, 1138. (b) Otto, W. H.; Britten, D. J.; Larive, C. K. *J. Colloid Interface Sci.* **2003**, *261*, 508.

(19) (a) Stejskal, J. E.; Tanner, J. E. *J. Chem. Phys.* **1965**, *40*, 345. (b) Stilbs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1.

(20) Actually, the Le Chatelier principle also predicts that β-CD will form more complexes with the surfactant at a higher concentration. According to this principle, one might intuitively expect the difference to be similar to the difference in concentrations of the two surfactants. In the present case (SDS/DEAB 15/5 mM), it was found that the selectivity of β-CD to SDS over that to DEAB is ~100:1, much larger than the ratio of concentrations of SDS and DEAB, 3:1. Therefore, the interplay between the host−guest and biased aggregation equilibria is within the frame of the Le Chatelier principle, yet they are not exactly the same. In addition, the present thermodynamic model can predict the exact value of the selectivity, whereas the Le Chatelier principle cannot.

(21) Recently, it has been established that β-CD can form aggregates with diameters ~200 nm above 3 mM by itself; see: (a) Bonini, M.; Rossi, S.; Karlsson, G.; Almgren, M.; Nostro, P. L.; Baglioni, P. *Langmuir* **2006**, *22*, 1478. (b) Rossi, S.; Bonini, M.; Nostro, P. L.; Baglioni, P. *Langmuir* **2007**, *23*, 10959, and references thereinHowever, in the present case of SDS/DEAB/β-CD solutions, most of β-CD will form complexes with SDS or DEAB, and the complexes will not aggregate, as evidenced by the diffusion coefficient of the complexes (measured by PGSE-NMR).

(22) Rubingh, D. N.; Holland, P. M. *Cationic Surfactants: Physical Chemistry*; M. Dekker: New York, 1991.