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Interfacial ion exchange between monovalent and divalent anions in cationic micelles, revised in the light of correlation analysis[†]

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ABSTRACT: The pH changes of an aqueous carbonate buffer solution (9×10^{-3} M Na_2CO_3, 10^{-3} M $NaHCO_3$, pH_o 10.79), induced by addition of cetyltrimethylammonium chloride (CTA^+Cl^-) in concentrations varying from 10^{-3} to 10^{-1} M, are employed to determine the concentration of dianionic base in the water pseudophase. The pH decreases markedly up to -0.6 pH units at 0.1 M CTA^+. The pH profile is analysed in terms of the pseudophase ion-exchange model from which the equations for mono-/divalent anion exchanges are derived. The fit of the pH data to these equations is satisfactory only when a [CTA^+] dependence of β (the degree of counterion binding) is considered: $\beta = 0.5 + 2[CTA^+]$. The resulting exchange constant, $K_{ex}^{Cl/CO_3} = (6.75 \pm 0.22) \times 10^{-2}$, is markedly larger than that measured previously at only one surfactant concentration without taking into account the β variation. This surfactant concentration dependence of β is discussed in terms of recent results on salt effects on the composition of micellar interfaces, which also show that β depends on the surfactant concentration in the presence or absence of any added salt. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: buffers; cationic micelles; pH metry; micellar solutions; interfacial exchanges; mono- and divalent ions

INTRODUCTION

Much work is presently devoted to pseudophase transfer equilibria or ion exchanges in the interfacial region (or Stern layer) of ionic micellar solutions in the presence of added salts, particularly in the context of micellar catalysis of reactions between a lipophilic substrate and an ionic reagent.[1–3] The kinetic investigation of most reactions, in micellar solutions as well as in bulk solvents, requires control of the ionic strength and/or pH, which is currently obtained by addition of salts and/or buffers in concentrations much larger than those of the reagents and surfactants. Exchanges of the surfactant counterions, X^- in the case of a cationic surfactant, for the ions Y^- added to the aqueous pseudophase can occur in the hydrated interface between this water phase and the micellar hydrophobic core because of the different hydrophilicities of the exchanging anions and also the different abilities to stabilize the positive charge of the cationic surfactant head groups, namely specific ion effects similar to those described in the Hofmeister series.[1,2] However, the salt effects, even on fundamental micellization parameters of current cationic surfactants, such as aggregation number (*N*), critical micelle concentration (cmc) or degree of counterion binding (β), are still not fully understood.[3] The first step to a comprehensive approach to these salt effects in terms of the pseudophase ion-exchange (PIE) model is the measurement of ion-exchange constants or selectivity coefficients, $K_{ex}^{X/Y}$, for the ionic interfaces of micelles, as exemplified in the case of cetyltrimethylammonium chloride (CTACl) by Eqn (1), in which the subscripts 'm' and 'w' refer to the micelle and water pseudophases, respectively.[4]

$$(CTACl)_m + Y^-_w \rightleftharpoons (CTAY)_m + Cl^-_w \qquad (1)$$

According to Eqn (1), the anion exchange provokes a change in the aggregated surfactant from CTACl to CTAY, which exhibits micellization parameters different from those of the precursor surfactant and results in a significant effect on micellar reactivity. A very large set of exchange constants for typical couples of anions have been measured by spectrophotometry using a chromophoric anion.[5] Most of them, particularly those for exchanges

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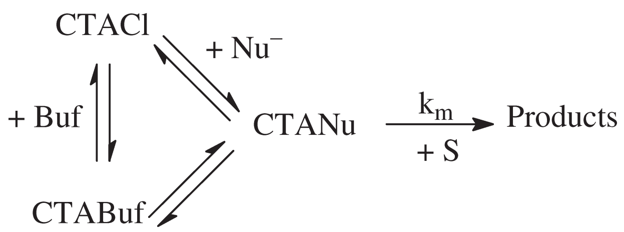

Scheme 1

between monovalent ions, have been confirmed by more sophisticated techniques. Nevertheless, the few constants measured for exchanges between monovalent and divalent anions are probably unreliable, either because the resulting values seem to be dependent on the surfactant concentration or because they were obtained from measurements at one surfactant concentration only.[6] In our work on micellar catalysis of nucleophilic substitutions in buffered CTACl solutions[7] we were faced with these uncertainties in our extension of the PIE model to reactivity in multicomponent micellar systems in which at least three ion exchanges have to be considered, as shown in Scheme 1, where Nu, Buf and S are the anionic nucleophile, an ionic buffer species and a substrate, respectively, with $K_{ex}^{Cl/Nu}$, $K_{ex}^{Cl/Buf}$ and $K_{ex}^{Nu/Buf}$ for the relevant exchange constants.

In the present paper we combine the experimental pHmetry method[1b,2c,7] and a new calculation procedure for obtaining reliable constants for univalent/divalent anion exchanges on the example of chloride exchange for carbonate (CO_3^{2-}), the basic component of the widely used buffer for the weakly basic pH range. The value obtained from data measured over a relatively large range of surfactant concentration ($10^{-3} < [CTACl] < 10^{-1}$ M) is markedly larger than that published previously.[8] Moreover, the statistical approach shows that β changes significantly with the overall surfactant concentration, in sharp contrast to the widely accepted assumption of β independence for this concentration.[1,4]

THEORY

Formalism of mono-/divalent anion exchange

Equation (1) and the derived exchange constant [Eqn (2)] are the currently used equations for obtaining any $K_{ex}^{X/Y}$ but they are valid only when X and Y are two monovalent ions

$$K_{ex}^{X^-/Y^-} = \frac{[X^-]_w[Y^-]_m}{[X^-]_m[Y^-]_w} \qquad (2)$$

For exchanges between mono- and dianions, Eqn (1) is transformed into Eqn (3)

$$2(CTA^+X^-) + Y_w^{2-} \rightleftharpoons 2(CTA^+)Y^{2-} + 2X_w^- \qquad (3)$$

As pointed out earlier,[6,8] the corresponding expression for K_{ex} cannot be obtained by a simple modification of Eqn (2) by considering the stoichiometry only because the relevant concentrations of the micellized ions (denoted, as usual, without square brackets) are those, X_m, in the micellar volume available to the hydrated ions,[3b,c] V_m, and not those in the total solution volume, $[X]_m$ [Eqn (4), where $[D_n]$ is the micellized surfactant concentration]

$$X_m = \frac{[X]_m}{[D_n]V_m} = \beta/V_m \qquad (4)$$

Therefore, the terms in $[D_n]V_m$ that cancelled in Eqn (2) are now included in the expression of exchange constants for dianions [Eqn (5)], so the concentration ratios of the two competing ions are not expected to be constant but dependent on the surfactant concentration.

$$K_{ex}^{X^-/Y^{2-}} = \frac{[X^-]_w^2[Y^{2-}]_m}{[X^-]_m^2[Y^{2-}]_w} \times [D_n]V_m \qquad (5)$$

Applications of Eqns (2) and (5) require evaluation of the concentration of ions involved in the exchanges. Equations (6) and (7) (for mono- and dianions, respectively) and Eqn (8) (expressing the mass balance in the micellar and aqueous pseudophases) are employed to obtain $[X^-]_m$ and $[X^-]_w$

$$[X^-]_m = \beta \times [D_n] - [Y^-]_m \qquad (6)$$

$$[X^-]_m = \beta \times [D_n] - 2[Y^{2-}]_m \qquad (7)$$

$$[X^-]_w = [X^-]_T - [X^-]_m \qquad (8)$$

where $[Y]_m$ and $[Y]_w$ are the experimental data. In these equations that we applied to CTACl, β is the degree of counterion binding (or micelle charge) at the interface and is taken as 0.7, a widely established value for CTACl micelles.[9] The experimental cmc of aqueous CTACl with added buffers or salts is 4×10^{-4} M,[7] and V_m is 0.35 l mol^{-1}, a recently measured value.[3b] Plots of the experimental $[Y^-]_w/[Y^-]_m$ or $[Y^{2-}]_w/([Y^{2-}]_m[D_n]V_m)$ ratios versus calculated $[X^-]_w/[X^-]_m$ ratios, or their square, should be linear with a slope providing the average value of the exchange constant.

RESULTS AND DISCUSSION

The $[CO_3^{2-}]_m$ measurements by pHmetry

The concentration of dianionic carbonate ions bound to the micellar interface, $[CO_3^{2-}]_m$, by exchange for the chloride counterion of the surfactant is obtained by pHmetry, which provides [acid]/[base] ratios in the water pseudophase only of buffered micellar solutions. The micellar binding of carbonate decreases its concentration in the aqueous phase, $[CO_3^{2-}]_w$, and therefore decreases the pH of the carbonate buffer solution. In our experiments, we worked with buffer solutions at 10^{-2} M $[Buffer]_{total}$ containing 90% basic $[CO_3^{2-}]_{total}$, i.e. $[CO_3^{2-}]_{total} = 9 \times 10^{-3}$ M. It was expected that the conjugate acid of the buffer, HCO_3^-, would not bind appreciably to the micelle due to a combination of anion/cationic interface electrostatic interactions that are stronger for divalent CO_3^{2-} than for monovalent HCO_3^- and the relative concentration effect, $[CO_3^{2-}]_{total}/[HCO_3^-]_{total} = 9/1$. Our expectation has been verified experimentally, therefore the pH changes (ΔpH) of the aqueous carbonate buffer solution induced by CTACl addition can be attributed reasonably to the change in carbonate concentrations in the water pseudophase only [Eqn (9)].

$$\Delta pH = \Delta(\log[CO_3^{2-}]_w) \tag{9}$$

The concentration of carbonate anions in the micellar pseudophase is then obtained from Eqn (10) describing the buffer material balance, where subscripts 'total', 'w' and 'm' refer to total, aqueous and micellar concentrations, respectively, and 'o' to concentrations in the absence of added surfactant.

$$[CO_3^{2-}]_o = [CO_3^{2-}]_{total} = [CO_3^{2-}]_w + [CO_3^{2-}]_m \tag{10}$$

Carbonate buffer solutions more concentrated than 10^{-2} M were not investigated because, as observed previously,[7a] the corresponding pH changes are almost negligible due to the fraction of micellized carbonate being very small compared with its total concentration in the aqueous pseudophase. In these experiments, the 10^{-3}–10^{-1} M surfactant concentration domain was considered, so that [CTACl] is either smaller or larger than $[Buffer]_{total}$. Therefore, the $[CTACl]/[(CTA)_2CO_3]$ ratios could vary in the range 1–10 at least, as required for reliable exchange constant measurements.

The pH effect of CTACl addition to the carbonate solution (shown in Fig. 1) is quite large, with ΔpH reaching − 0.6 pH units at [CTACl] = 0.1 M. (It is therefore obvious that carbonate buffer is not appropriate for buffering micellar solutions.) From the experimental pH variations, $[CO_3^{2-}]_w$ and $[CO_3^{2-}]_m$ are readily obtained [Eqns (9) and (10)]. The associated values of $[Cl^-]_m$ and $[Cl^-]_w$ are then, calculated using Eqns (7) and (8). The log–log plot of the experimental $([CO_3^{2-}]_w/[CO_3^{2-}]_m) \times [D_n]V_m$ versus calculated $([Cl^-]_w/[Cl^-]_m)^2$ is satisfactorily linear (Fig. 2), particularly for the larger [CTACl]. In the low [CTACl] range (10^{-2} M), the calculated concentration ratios are less accurate because small ΔpHs values, i.e. small $[CO_3^{2-}]_m$, may result in large errors in $[Cl^-]_m/[Cl^-]_w$. According to Eqn (11)

$$\log\frac{[CO_3^{2-}]_w}{[CO_3^{2-}]_m \times [D_n]V_m} = -\log K_{ex}^{Cl^-/CO_3^{2-}} + 2\log\frac{[Cl^-]_w}{[Cl^-]_m} \tag{11}$$

the intercept is obtained with reasonable precision (0.04 ± 0.004). However, these results cannot be considered a reliable K_{ex}^{Cl/CO_3} measurement because the slope of the log–log plot (Fig. 2) is markedly larger than 2.0, which is expected from Eqn (11).

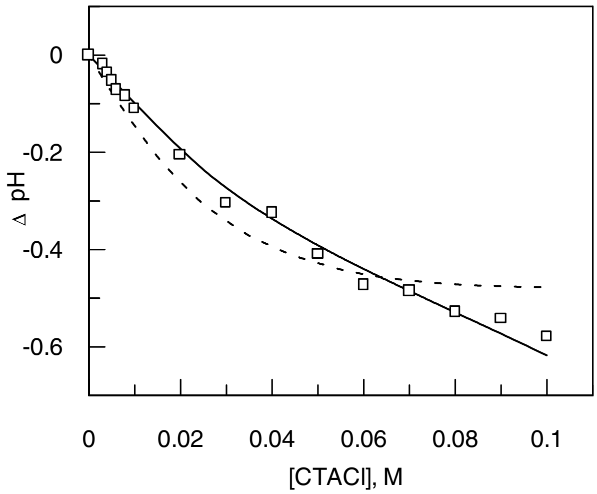

Figure 1. The pH decrease of the aqueous carbonate solution (9×10^{-3} M Na_2CO_3 and 1×10^{-3} M $NaHCO_3$) by addition of CTACl: (□) experimental data, (---) calculated pH profile at constant β [Eqn (11)]; (—) calculated pH profile at variable β ($\beta = 0.5 + 2\,[CTA^+]$)

Further evidence for the inconsistency of this trivial ion-exchange analysis is illustrated in Fig. 1, where the pH data are compared with the pH profile calculated by employing for K_{ex} the value of the intercept of the above-mentioned log–log plot. The concentrations of the micellized base at every [CTACl], $[CO_3^{2-}]_m$, for the divalent base are calculated from Eqn (12), which is cubic instead of the usual quadratic for monovalent ions.[4,10] Equation (12) with $x = [CO_3^{2-}]_m$, $a = \beta \times [D_n]$; $b = [CO_3^{2-}]_o$; $c = [CTACl]$ and $d = V_m[D_n]$, expresses the mass balance at the ionic interface by assuming a constant β value

$$\begin{aligned} x^3\left(4 + 4\frac{K_{ex}}{d}\right) + x^2\left(4c + 4a - 4a\frac{K_{ex}}{d}\right) \\ + x\left(c^2 - 2ac + a^2 + 4ab\frac{K_{ex}}{d} + a^2\frac{K_{ex}}{d}\right) \\ - a^2b\frac{K_{ex}}{d} = 0 \end{aligned} \tag{12}$$

As seen in Fig. 1 (dotted line), a leveling of the pH change at large surfactant concentrations is expected,

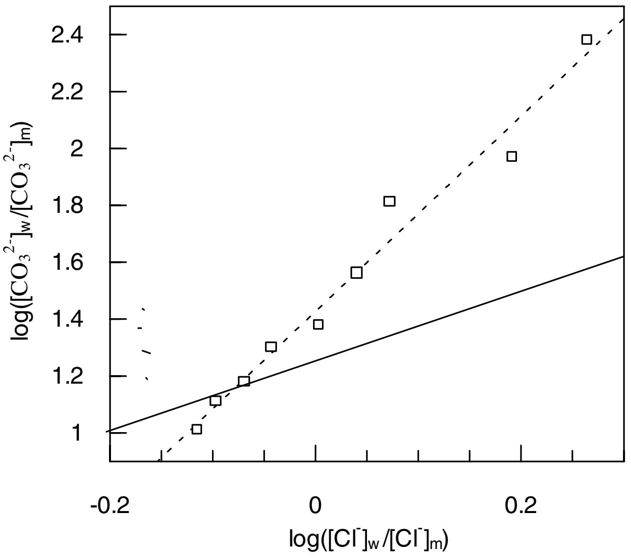

Figure 2. Log–log plot of the data: Eqns (7)–(10). The dashed line represents the linear regression whereas the full line shows the theoretical slope of +2, according to Eqn (11). The parameters of the linear regression of the data (□), $y = a + bx$, are: $r = 0.988$, $a = 1.43 \pm 0.025$ and $b = 3.43 \pm 0.20$

whereas in the experimental profile an almost linear pH decrease is observed. It is worth noting that this leveling cannot be attributed to a concomitant micellization of the buffer conjugate acid because this would decrease ΔpH, whereas the ΔpH values are larger than those expected from calculated K_{ex}. The differences in the shapes of the calculated and experimental profiles are very clear evidence for the inadequacy of Eqn (11) and the derived calculations, which are too simple to describe the ion exchanges involved in the surfactant addition to aqueous carbonate. The main drawback of these calculations is related to the evaluation of micellized $[Cl^-]_m$ by Eqn (7), which assumes a constant β equal to that of CTACl in the absence of added buffer. Therefore, we consider the effect of a β dependence on the surfactant concentration on the calculated pH profile and on the K_{ex} value.

Dependence of *β* on the surfactant concentration and chloride–carbonate exchange constant

A change in β as a function of increasing [CTACl] is likely because of buffer-induced changes in the properties of the micellar interfaces.[3b] At very small $[D_n]$, carbonate dianion ($[CO_3^{2-}]_{total} = 9 \times 10^{-3}$ M) is in excess compared with the surfactant ($[D_n] = 10^{-3}$–10^{-2} M), which is, at least partly, present as $(CTA)_2CO_3$. The latter has its own $\beta_{carbonate}$ value, which is most likely different from that of CTACl. At larger $[D_n]$, the predominant surfactant becomes progressively CTACl itself with β_{Cl}, the value we used in previous calculations. Consequently, the β value employed in $[Cl]_m$ estimations by Eqn (7) should be treated as a $[D_n]$-dependent parameter. The pH data of Fig. 1 were therefore analyzed in terms of a continuous β variation with $[D_n]$, as described by Eqn (13).

$$\beta = a + b[\text{CTACl}] \qquad (13)$$

An initial value of 0.4 for a [$\beta_{carbonate}$ in Eqn (13)] is chosen because $\beta_{carbonate}$ is necessarily smaller than β_{Cl} due to the differences in the steric requirements and hydration of divalent carbonate and monovalent chloride. This value and its dependence on $[D_n]$ was then optimized. The best fit of the experimental pH profile (Fig. 1, full line) was obtained when $a = 0.5$ and $b = 2$. The reliability of the results was finally confirmed by the agreement between the observed and expected values of the slope of the log–log plot of the ratios of calculated micellized and aqueous anion concentrations [Eqn (11)]. As shown in Fig. 1, this analysis works fairly well: the experimental pH profile is reproduced satisfactorily and the slope of the log–log plot of 2.0 is consistent with that of the ion-exchange equation. The intercept of this plot provides the following exchange constant: $K_{ex}^{Cl/CO_3} = (6.75 \pm 0.22) \times 10^{-2}$. This value is markedly different from those previously published[5,8] of 0.47 or 7.65×10^{-3}.

Salt effects on the composition of the micellar interface

The early published, large value of 0.47 for the carbonate–chloride exchange constant[5] is very probably wrong. It has been obtained by using the equation that is valid for monoanion exchanges [Eqn (2)], because the equation relevant to mono-/divalent anions [Eqn (5)] is not mentioned. Later on, the formalism appropriate for exchanges between anions of different valencies was developed[6] and finally applied[8] to carbonate–hydroxide anion exchange from which carbonate–halide exchange constants were derived. The constants were obtained from kinetic salt effects on the OH^--dehydrochorination of polyhalogenated pesticides in CTAOH micelles. The resulting K_{ex}^{Cl/CO_3} value of 7.65×10^{-3} is about ten times smaller than that reported here. The discrepancy between the two values cannot arise from differences in the experimental methods because it has been shown that spectrophotometry, fluorimetry, ultrafiltration, kinetics and pHmetry provide closely similar values for monoanion exchange constants.[1–3] The reason for the observed discrepancy may be traced to the differences in the experimental conditions.

Our pHmetric measurements are carried out at a constant added buffer (salt) concentration of 10^{-2} M with variable surfactant concentrations ($10^{-3} < [CTA^+] < 10^{-1}$ M), i.e. under the conditions of interest in reactivity studies that require constant ionic strength and/or pH. With this procedure, a statistical analysis of the $[CTA^+]$ effect on K is possible, averaging the measurement uncertainties in the small surfactant concentration range and underscoring that the β constant assumption can be irrelevant. In contrast, the above-mentioned kinetic experiments involved a constant surfactant concentration (close to 10^{-2} M) and variable added salt concentrations (from 5×10^{-3} to 4×10^{-2} M). Now, recent chemical trapping experiments on the effect of adding salts with ions common to CTABr or CTACl show[3b] that the micellized concentration of X [X_m as defined in Eqn (4)] is not independent of surfactant and salt concentrations as required by Eqn (4), and in contrast the experimental X_m values increase with added [X_w] in agreement with Eqn (14).

$$X_m = \beta/V_m + [X_w] \qquad (14)$$

Experimentally it was observed that the X_m increase is larger in the small salt concentration range (up to 0.1 M), i.e. when [X_w] is negligible compared with β/V_m. In other words, and in disagreement with the general assumption,[1,4,11] β and/or V_m depend on the added salt concentration mainly when the latter is small. Therefore, measurements of exchange constants with variable salt concentration can be unreliable when this β (or V_m) variation is not considered. In previous experiments for K_{ex}^{Cl/CO_3} estimation the β value was taken as 0.7 at all salt concentrations, whereas the initially used surfactant was CTAOH whose counterion (OH^-) is a very readily exchangeable, hydrophilic anion at a concentration smaller than that of the added salt. Under these experimental conditions the real surfactant is probably CTAY (for a salt with a Y anion), whose β value is necessarily different from those[11] of CTAOH and CTACl. Moreover, the reliability of the final calculation could not be checked by applying Eqn (11). Therefore, the resulting K_{ex}^{Cl/CO_3} value is markedly doubtful.

Our results are not suspicious because they are obtained at constant [buffer] (≡[salt]). Nevertheless, according to the recent results[3b] mentioned above, β and/or V_m are also dependent on the surfactant concentration, which in our experiments varies significantly from 10^{-3} to 10^{-1} M. The β dependence that we adopt in our calculations [Eqn (11)] takes this fact into account, in addition to the obvious change in the actual surfactant as the [Cl^-]/[CO_3^{2-}] ratio increases. Until now we have focused on a β increase with increasing surfactant concentration, although in Eqn (4) the same effect could also arise from a V_m decrease. In the present work we used $0.35\,l\,mol^{-1}$, the V_m value measured for CTACl at 0.1 M added Cl^-. But, because we work at a ten times smaller salt concentration, the actual V_m can be larger as a result of the known salt-induced contraction of the electrical double layer, leading to a decrease in the interfacial volume.[2d,3b] This possible V_m decrease with buffer (salt) addition,[12,3b] associated with the above-discussed β increase, is probably also taken into account by Eqn (11) empirically. If in Eqn (5) we had used a larger V_m value, we would have obtained a larger K_{ex}^{Cl/CO_3} value, i.e. a still larger discrepancy with the previously published value for this constant. Finally, whatever the salt effect on β or V_m, the most convincing evidence for the reliability of our estimation is the agreement between the experimental results and Eqn (11).

CONCLUSIONS

The statistical analysis of the pH change of an aqueous carbonate solution by addition of CTACl at various concentrations shows that the β value of the micelles, i.e. the fraction of counterions bound to the surfactant head groups within the interfacial region (micelle charge), depends on the surfactant concentration at a given added salt concentration. This β dependence could not be observed in previous work at constant surfactant concentration on the determination of mono-/divalent ion exchange constants, and in particular of K_{ex}^{Cl/CO_3}. Our more reliable value of $K_{ex}^{Cl/CO_3} = 6.7 \times 10^{-2}$ is about ten times larger than that previously published, probably because this β change was not taken into account. It has to be underlined that our working conditions (constant buffer or salt concentration and variable surfactant concentration) are those currently used in investigations of micellar effects on reaction rates. The observed β dependence strengthens the recent, extremely important results[3b] of the chemical trapping method for the determination of the interfacial composition of micelles in the absence or presence of common-ion salts. It was clearly shown that, in contrast with the current but nowadays wrong assumption of the PIE model,[1,4] β increases with the surfactant concentration.[2,3b,11] Even in the absence of any added salt, this increase is quite significant. The β dependence that was recognized previously[11] for strongly hydrophilic anions (OH^-, F^- or AcO^-) occurs whatever the counterion. Moreover, the increase in the interfacial counterion concentration [Eqn (14)] is accompanied by a decrease in the concentration of interfacial water. Altogether these results, associated with our finding on the buffer effects on micelles, have a bearing on our current view[2,3] of the 'Stern region' of surfactant aggregates. With the pseudophase model, the idea of an undefined but separate region of a micelle between the micellar core and the water pseudophase has been extremely useful for roughly understanding many of the micellar properties.[1,4] Nevertheless, it is now obvious that the nature of the totality of the water pseudophase influences strongly the way in which the charged surfactant head groups, assembled at the interface, are stabilized by interactions with their counterions, their solvating water and any additive (salts and buffers in particular) within this water pseudophase.

More work is in progress to extend our results on buffered micellar solutions with the view to understanding better how the composition of this interfacial region is influenced by the addition of buffering salts.

EXPERIMENTAL

Materials

Sodium carbonate and bicarbonate (Aldrich) were of the highest grade available. Cetyltrimethylammonium chloride (CTACl), 25 wt.% solution in water, was from Aldrich and used without further purification. Buffer solutions were prepared with CO_2-free distilled water. Freshly prepared solutions were used in all experiments.

pH Determinations

The pH data were measured under argon at $25 \pm 0.1\,^{\circ}C$ with a Radiometer pH M 84 research pH-meter, equipped with a Metrohm glass electrode (ref. 6.0219.100) with a sleeve diaphragm and a double junction to the Ag/AgCl ([KCl] = 3 M) inner reference. This electrode, specific for pH measurements in surfactant solutions, prevents clogging of the diaphragm. The glass electrode was standardized by using standard pH 7.0 and 10.0 buffers (Sigma). The electrode standardization was checked after each series of runs and found not to be affected by the surfactant solutions studied.

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REFERENCES

1. (a) Bunton CA, Nome F, Quina FH, Romsted LS. *Acc. Chem. Res.* 1991; **24**: 357–364; (b) Zana R. In *Cationic Surfactants, Physical Chemistry*, Rubingh DN, Holland PM (eds). Marcel Dekker: New York, 1991; 41–85; (c) Bunton CA, Yao J, Romsted LS. *Curr. Opin. Colloid Interface Sci*. 1997; **2**: 622–628; (d) Romsted LS. In *Reactions and Synthesis in Surfactant Systems*, Texter J (ed). Marcel Dekker: New York, 2001; 265–294.
2. (a) Underwood AL, Anacker EW. *J. Colloid Interface Sci*. 1987; **117**: 242–250; (b) Morgan JD, Napper DH, Warr GG. *J. Phys. Chem.* 1995; **99**: 9458–9465; (c) Toullec J, Couderc S. *Langmuir* 1997; **13**: 1918–1924; (d) Romsted LS. In *Surfactant Science Series: Adsorption and Aggregation of Surfactants in Solution*, Vol. 109, Mittal KL, Shah DO (eds). Marcel Dekker: New York, 2003; 149–170; (e) Kunz W, Lo Nostro P, Ninham BW. *Curr. Opin. Colloid Interface Sci.* 2004; **9**: 1–18.
3. (a) Gallion L, Lelievre J, Gaboriaud R. *J. Colloid Interface Sci.* 1999; **213**, 287–297; (b) Soldi S, Keiper J, Romsted LS, Cuccovia IM, Chaimovich H. *Langmuir* 2000; **16**: 59–71; (c) Tada EB, Novaki LP, El Seoud OA. *Langmuir* 2001; **17**: 652–658; (d) Tada EB, Ouarti N, Silva PL, Blagoeva IB, El Seoud OA, Ruasse MF. *Langmuir* 2003; **19**: 10666–10672; (e) Buurma NJ, Serena P, Blandamer MJ, Engberts JBFN. *J. Org. Chem.* 2004; **69**; 3899–3906.
4. (a) Bunton CA, Savelli G. *Adv. Phys. Org. Chem.* 1986; **22**; 213–309; (b) Khan MN, Ismail E. *J. Chem. Soc. Perkin 2* 2001; 1346–1350.
5. (a) Bartet D, Gamboa C, Sepulveda L. *J. Phys. Chem.* 1980; **84**: 272–275; (b) Gamboa C, Sepulveda L, Soto R. *J. Phys. Chem.* 1981; **85**: 1429–1434.
6. Lissi EA, Abuin EB, Sepulveda L, Quina, FH. *J. Phys. Chem.* 1984; **88**: 81–85.
7. (a) Ouarti N, Marques A, Blagoeva IB, Ruasse MF. *Langmuir* 2000; **16**: 2157–2163; (b) Blagoeva IB, Toteva MM, Ouarti N, Ruasse MF. *J. Org. Chem.* 2001; **66**: 2123–2130; (c) Ouarti N, Blagoeva IB, El Seoud OA, Ruasse MF. *J. Phys. Org. Chem.* 2001; **14**: 823–831.
8. Nascimento MG, Miranda SAF, Nome F. *J. Phys. Chem*. 1986; **90**: 3366–3368.
9. Bacaloglu R, Bunton CA, Ortega F. *J. Phys. Chem.* 1989; **93**: 1497–1502.
10. (a) Quina FH, Chaimovich H. *J. Phys. Chem.* 1979; **83**: 1844–1850; (b) Romsted LS. *J. Phys. Chem*. 1985; **89**: 5107–5113; (c) Kawamuro MK, Chaimovich H, Abuin EB, Lissi EA, Cuccovia IM. *J. Phys. Chem*. 1991; **95**: 1458–1463.
11. Bunton CA, Frankson J, Romsted LS. *J. Am. Chem. Soc.* 1979; **101**: 1253–1259; Stadler E, Zanette D, Rezende MC, Nome F. *J. Phys. Chem*. 1984; **88**: 1892–1896; Neves MFS, Quina F, Moretti MT, Nome F. *J. Phys. Chem.* 1989; **93**: 1502–1505.
12. Perrin CL, Chen JH, Ohta BL. *J. Am. Chem. Soc*. 1999; **121**: 2448–2455; Mancini G, Schiavo C, Cerichelli G. *Langmuir* 1996; **12**: 3567–3573.