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The chameleon effect in zwitterionic micelles: Binding of anions and cations and use as nanoparticle stabilizing agents

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ABSTRACT

Zwitterionic surfactants are relatively overlooked and some of their properties resemble those of ionic and non-ionic surfactants, but others are unique. There is unimpeachable evidence that aqueous solutions of zwitterionic micelles interact specifically with anions, forming "anionoid" micelles, which concentrate cations in the surfaces. Thus, unlike ionic micelles, both the cation and anion of the electrolyte solution can be concentrated at zwitterionic interfaces. This unique effect, known as the "Chameleon Effect", can be used to catalyze a variety of simple reactions, as the attraction of ions to the micelle brings the reactants together. Furthermore, zwitterionic surfactants stabilize metallic nanoparticles and the magnetically stirred two-phase system could be reused 3 more times in the hydrogenation of cyclohexene (Pd:cyclohexene ratio of 1:18300), with very little loss in activity, and an average turn-over frequency of 1000 h^{-1}.

1. Introduction

Prior to the 1960s, a number of methods for synthesizing zwitterionic surfactants were developed, but studies of their micellar properties were few compared to ionic and non-ionic micelles. Nevertheless, zwitterionic micelles display interesting behaviors that encompass properties characteristic of both charged and uncharged micelles. Early investigations, carried out by Nakagawa [1–5] and Herrmann [6], concluded that their tendency to aggregate lies between that of ionic and non-ionic surfactants. In addition, varying the different parts of the surfactant molecule, Fig. 1, may affect critical micelle concentration, *cmc*, aggregation number, N_{agg}, and micellar molecular weight, *MMW*. For example, increasing the size of the heteroatom in the positively charged moiety of the headgroup decreases the *cmc*, as does changing the negatively charged group in the following order: $COO^- > SO_3^- > OSO_3^-$, probably due to differences in solvation of these groups.

Later studies revealed that the number of methylenes in the linker between the charges, *m*, also affects the *cmc* [7]. Up to three methylenes, the *cmc* increases, as the repulsive dipole–dipole interactions between neighboring headgroups also increases. However, after 3 methylenes, increasing the number of atoms linking the positive and negative charge decreases the *cmc* as the increasing hydrophobicity of the molecule dominates the repulsive interactions. Furthermore, when the length of the linker exceeds 10 carbons, the aggregation number of the micelle decreases [8], because looping permits the linker to become part of the hydrophobic core of the micelle (Fig. 2), making the headgroup bulkier and increasing their cross sectional area. Although all the headgroups are shown parallel in Fig. 2, most probably they are not aligned and other possible conformations are discussed below.

Headgroup orientation is an important consideration when attempting to understand the properties of zwitterionic micelles. Three conceivable conformations may be adopted (structures A, B and C in Fig. 3). The extents to which these conformations are present in the micelle and in monomeric surfactant were investigated for carboxybetaines and sulfobetaines [9]. Studies of pK_a values, molecular dynamics and UV/Vis spectroscopy of carboxybetaine and sulfobetaine micelles are consistent with the actual conformations of the molecules as something between structures A and B. The authors propose that solvation of the negatively charged group by polar solvent is probably more favorable than interaction with the ammonium group and that the dipole moment is greatest when the headgroup is fully extended and most stabilized by the polar medium. Finally, the greater steric bulk of structure B probably prevents the headgroups from existing solely in this conformation. The interactions between the headgroups and polar solvent are important to the structure of the surfactant in solution, thus conformation B becomes more stable with the decrease of solvent polarity. The C conformation involves the least interaction with solvent and is less favored.

Despite the fact that zwitterionic micelles do not have a formal charge, the presence of both positively and negatively charged groups in the same molecule leads to a large dipole moment in the headgroup. Hence, the behavior of zwitterionic surfactants sometimes resembles that of ionic surfactants. For instance, varying the salt content in solution alters their properties, not as much as in the case of ionic micelles, but considerably more than for non-ionic micelles. Although the salt concentration does not have a big effect on the *cmc* or *MMW*, added

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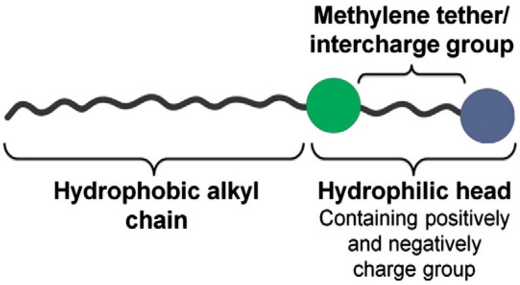

Fig. 1. Cartoon representation of a zwitterionic surfactant molecule.

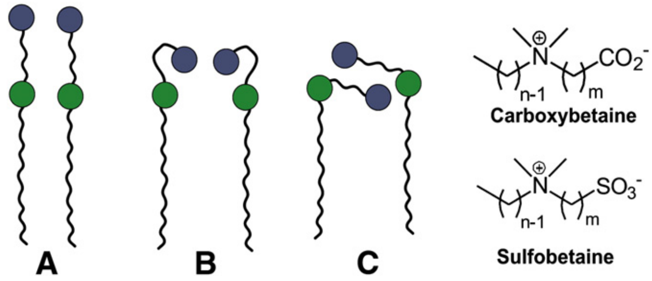

Fig. 3. Possible conformations of zwitterionic surfactant headgroups in micelles.

salt increases the Krafft temperature of ionic surfactants, but lowers it for zwitterionic surfactants.

Another feature that zwitterionic micelles share with ionic micelles is that both interact with ions from solution, normally with a greater affinity for anions [10–12]. This property is independent of the charge order in the headgroup [13,14], for example micelles of both sulfobetaine (SB*m*-*n*, *n* = alkyl chain length, *m* = methylene tether group length) and *n*-hexadecylphosphorylcholine (HPC), shown in Fig. 4, incorporate anions. However, reversal of the charges affects catalytic activity and N_{agg} [15].

Zwitterionic micelles bind ions selectively and this property has been treated theoretically [16]. The affinity for different anions follows the Hofmeister series: “softer”, less hydrophilic anions, such as $C1O_4^-$, are adsorbed more strongly than “harder”, hydrophilic anions, such as $C1^-$ [17]. This ion specificity was demonstrated for cationic and zwitterionic surfactants [18,19].

Thus zwitterionic micelles, like cationic micelles, catalyze bimolecular reactions containing an anionic reactant [20]. Micellar effects upon bimolecular organic reactions are explained by means of hydrophobic and electrostatic interactions. Hydrophobic reactants are more soluble in the non-polar cores of micelles and are readily incorporated in micelles. Polar or charged groups on reactants orient themselves in the polar interfacial region and the degree of association will depend upon the structure and charge of both the surfactant and the reactants. In this sense, micelles act as micro-reactors that concentrate reactants and speed the overall reaction rate. These considerations are useful guides for predicting micellar catalysis, but also for explaining reaction inhibition, as discussed below. Nucleophilic bimolecular reactions in micellar systems are often treated quantitatively and can be interpreted by using the Pseudophase Ion Exchange (PIE) model. The PIE model treats the totality of the micelles and the aqueous solution as separate phases and describes the observed rate of reaction in terms of distribution of the reactants and differential reactivity in each pseudophase [20].

The addition of electrolytes into micellar solutions may have a significant impact on the reaction rates, far more than expected in homogeneous solution. For example, the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (Fig. 5) is catalyzed by zwitterionic micelles in the presence of hydrophilic anions, but becomes slower when more hydrophobic anions are added to the reaction mixture [21], because the hydrophobic anions bind to the zwitterionic micelles and displace the substrate.

The following sections explore the special aspects of ion binding effects on the properties of zwitterionic micelles and conclude with future applications.

2. Zwitterionic sulfobetaine surfactants: the chameleon effect

One of the most studied groups of zwitterionics surfactants is sulfobetaines, Figs. 3 and 4. These surfactants are also prepared with different size alkyl groups on nitrogen, where R = Et, Pr or Bu, in addition to R = Me.

Sulfobetaine micelles preferentially incorporate anions, despite the absence of net headgroup charge. As discussed in the introduction, ion binding follows the Hofmeister series and the lower charge density anion, $C1O_4^-$ displaces more hydrophilic anions, e.g. OH^-, Br^- and $C1^-$ from the micelle. This correlation was demonstrated by a variety of techniques including ion selective electrodes (ISE), NMR, capillary electrophoresis, ion conductance and kinetics [22–25].

ISE and capillary electrophoresis show the influence of anion concentration. The partitioning of anions between water and sulfobetaine micelles fits a Langmuir isotherm, and this binding is illustrated with the perchlorate, Eq. (1),

$$([\mathrm{ClO}_4^-]_M/[\mathrm{SB3}-n]) = \frac{\theta_{\max}\mathrm{K_L}[\mathrm{ClO}_4^-]_{\mathrm{total}}}{1+\mathrm{K_L}[\mathrm{ClO}_4^-]_{\mathrm{total}}} \tag{1}$$

where SB3-*n* is the surfactant, $\theta_{\max}$ is the maximum occupancy of head groups by ClO_4^- and $\mathrm{K_L}$, M^{-1}, is the Langmuir association constant. ISE reveals that binding of ClO_4^- to sulfobetaine micelles displays saturation behavior, with a maximum occupancy of headgroups by ClO_4^-, $\theta_{\max}$, of roughly 0.2, which is much lower than the values observed in cationic micelles.

The zeta potential, ξ, measured by capillary electrophoresis in the presence of anions shows the influence of different anions on the mobility or zeta potential of the micelle, Fig. 6, and provides an

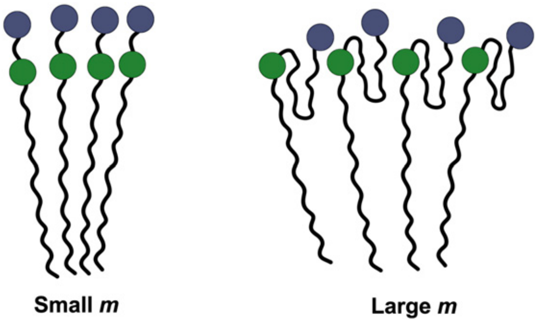

Fig. 2. Conformations of zwitterionic surfactants headgroups with short and long linkers.

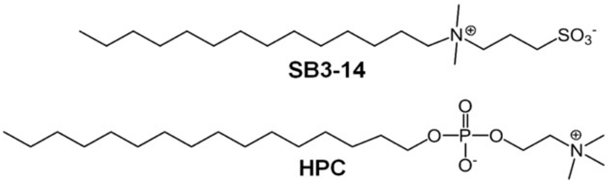

Fig. 4. Zwitterionic surfactant molecules, SB3-14 and HPC, with opposite headgroup charge order.