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Interactions of different counterions with cationic and anionic surfactants

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ABSTRACT

Specific counterion effects on the formation and electrolytic dissociation of micelles have been studied for sodium dodecyl sulfate and hexadecyl-N,N,N-trimethyl ammonium bromide in the presence of different electrolytes. Mass spectrometry has been used to investigate the affinity of counterions to surfactant free monomers in the gas phase. Linear correlations have been found between the parameters determined for micelles in the aqueous phase and the fraction of counterions preferably bound to surfactant free monomers in the gas phase. The work presents a new insight into specific ion effects.

1. Introduction

Ionic surfactants in solution form a wide variety of dynamic aggregates, sometimes called association colloids, including micelles, monolayers, microemulsions, inverse micelles, vesicles, and biological membranes [1–3]. Thermodynamically stable and structurally "simple" aqueous micelles are often used as model systems for the far more complex and metastable biological membranes because their interfaces are structurally similar [4]. So, it is crucial to understand the underlying physical mechanisms of formation of these aggregates.

The influence of different ions of the same valence on the aggregate properties, such as the critical concentration for aggregate formation, aggregate size and shape, aggregate and phase stability, and the binding of ions and molecules, exemplifies the so-called specific ion effects or Hofmeister effects. These effects play a significant role in a wide range of biological and physicochemical phenomena from the electrolyte activities, cloud points of polymers and surfactant solutions to the ion transport across biological membranes and enzyme activities [5]. The ion specificity observed is, in fact, a combination of different subtle effects, such as electrostatics, dispersion forces, thermal motion, fluctuations, hydration, ion size, and interfacial water structure [6]. Therefore, the specific ion effects remain unexplained by the present theories of physical chemistry [5], and we are probably still far away from being able to make exact (general) quantitative predictions [7].

A major difficulty in the study of Hofmeister effects is the fact that many phenomena involve the action of both ions of an electrolyte. One then needs to decouple the effects of anions and cations [8]. There are different techniques for measuring ion binding to micellar interfaces, including: nuclear magnetic resonance (NMR) spectroscopy [9–11], the method based on measuring the ratio of acid-to-base forms of the spectrophotometric indicator pyridine-2-azo-*p*-dimethylaniline, PADA [4], the chemical-trapping method [12], and the method based on measuring the electrophoretic mobility and the so-called zeta potential [13,14]. The above-mentioned methods permit investigation of the binding of either cations or anions to interfaces.

In this study, we use the electrospray ionisation mass spectrometry (ESI–MS) to investigate the ion binding to interfaces. Since its introduction by Yamashita and Fenn in 1984 [15,16], ESI–MS has been widely used in biological research for fast and simultaneous detection of positive and negative ions. The most important advantage of the ESI–MS method is the possibility of recording both cations and anions bound to the interfaces.

This work presents a new and potentially important approach to the question of ion specificity studied by mass spectrometry. Our results have shown new applications and possibilities of mass spectrometry. The ESI–MS technique is cheap, quick, and highly sensitive; it is simple, does not cause fragmentation of the molecules, and gives a spectrum easy to interpret. Our results have shown that ESI–MS can provide information on the composition of the Stern double layer in mixed systems, such as ionic micelles with an added electrolyte, and can be used to study the competition between ions in their binding to the surfactant molecules. In this work the interactions of different counterions with the ionic

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surfactants, i.e. with sodium dodecyl sulfate (SDS) and hexadecyl-N,N,N-trimethyl ammonium bromide, commonly known as cetyltrimethyl ammonium bromide (CTAB), are studied. The differences between cations and anions, and between chaotropic and cosmotropic ions in their interactions with the micelle surfaces have been shown and interpreted. The terms "cosmotropic" and "chaotropic" originate from Greek κοσμος (order) and χαος (disorder) [17]. Consequently, cosmotropic and chaotropic ions are the ions exhibiting water structure making (i.e. ability to make hydrogen bonds) and breaking (i.e. ability to break hydrogen bonds) properties, respectively [18].

2. Experimental

2.1. Materials

The salts used: NaCl, $NaClO_4$, $KClO_4$, $LiClO_4$, $NaNO_3$, NaF, KBr, NaI (P.P.H. Polish Chemical Reagents "POCH" Gliwice, all salts: p.a.), NH_4ClO_4 (Johnson Matthey Alfa Products, 99%), and $Mg(ClO_4)_2$ (Merck, 92%) were twice or three times recrystallized from doubly deionised water. SDS (Merck, purity above 99%) and CTAB (SIGMA, 99%) were used without further purification.

All solutions were prepared with doubly deionised water, whose conductivity was 0.05 $\mu S\ cm^{-1}$.

2.2. Methods

2.2.1. The conductivity measurements

A solution with a given concentration of the salt studied was prepared. The solution was divided into two parts. In one of them a given surfactant was dissolved so that the surfactant concentration in the salt solution was 0.069 M for SDS and 0.008 M for CTAB. The surfactant concentration in the prepared salt solution should be much higher than the critical micelle concentration (*CMC*) of a given surfactant. In this work the surfactant concentrations were about eight times higher than *CMC*. The values of *CMC* for SDS and CTAB determined in this work are equal 7.8×10^{-3} M and 9.2×10^{-4} M, respectively. The solution of the surfactant with the salt was added successively to the surfactant-free salt solution; thus the salt concentration remained constant during the experimental run. The conductivity of the resulting solution was measured successively. The electric conductivities were measured at 25 °C and 1 kHz using a Wayne Kerr B905 automatic precision bridge and a conductometric bell-shaped cell, type OK-0902P.

2.2.2. The ESI–MS and MS/MS measurements

Electrospray mass spectra were recorded on a ZQ single-quadrupole mass spectrometer (Waters & Micromass, Manchester, UK) equipped with an electrospray interface and probe. The solution studied was infused continuously at the flow rate of 40 $\mu L\ min^{-1}$. Nitrogen was used as both the nebulizing (80 $L\ min^{-1}$) and the desolvation gas (300 $L\ h^{-1}$). The source temperature was 120 °C. The electrospray capillary voltage was set to 3000 V and the extractor was set to 4 V. The ESI–MS experiments were performed at a constant cone voltage (V_C) of 30 V. Mass spectra were collected from m/z 200 to 900 in the positive and negative ion mode and the data were acquired in the multi channel analysis mode. The 10 scans were summed to obtain representative spectra. The ESI mass spectra were reproducible with a fluctuation of the peak intensities of ±5%. Further analysis was performed of the averaged mass spectra obtained from three consecutive experiments.

The MS/MS measurements were carried out on the Q-TOF mass spectrometer (Waters, USA & Micromass, UK) with electrospray ion source.

3. Results and discussion

3.1. Effect of the electrolytes on the micellization parameters of anionic and cationic surfactants

The critical micelle concentration (*CMC*) and the degree of electrolytic micelle dissociation (α) were studied. Both parameters were obtained from the plots of conductivity versus surfactant concentration. The value of the surfactant *CMC* in the presence of a given salt was determined from the intersection point of the lines above and below the corresponding breakpoint, as described earlier [19]. According to Refs. [20–22], the values of α were obtained from the ratio of the slopes of the lines above and below *CMC*. The values of *CMC* and α determined for both surfactants in the presence of different electrolytes are given in Table 1. The both variable values determined in this work and those reported in the literature are collected in Table 2. As follows from Table 2, the literature data are in accordance with our results.

3.1.1. SDS

The influence of $NaClO_4$, $KClO_4$, $LiClO_4$, NH_4ClO_4, and $Mg(ClO_4)_2$ on the micellization parameters of SDS was investigated. The SDS micelle surface is charged negatively (due to the sulfate head groups of the surfactant monomers) so that its properties are mainly affected by the salt cations [27,28]. As follows from the data in Table 1, the decrease in *CMC* and α for SDS is the greatest in the presence of Mg^{2+} ions, while in the presence of Li^+ ions this decrease is the smallest. The series of cations ordered according to their effect on the *CMC* and α values for the SDS surfactant follows the "reverse" Hofmeister sequence $Li^+ < Na^+ < NH_4^+ < K^+$.

Fig. 1 shows a good correlation between the degree of electrolytic micelle dissociation and the ion hydration radius (r_{hydr}). For ions of the same charge, their size is one of the most fundamental properties. It defines not only the excluded volume interactions in solution and at interfaces, but it also determines the strength of the electric field of an ion, and also – to a certain extent – its polarizability [8].

As shown in Fig. 1, the smaller the hydrated cation derived from an electrolyte added (i.e. the lower the r_{hydr} value), the lower the α value for SDS micelles (relative to the α value for SDS micelles in the absence of any electrolyte), i.e. the more negative the $\Delta\alpha$ value

Table 1
Values of the critical micelle concentration (*CMC*), the degree of electrolytic micelle dissociation (α), and the intensity quotients (calculated from the intensities, *I*, of mass peaks) reflecting the fraction of the counterions bound to the surfactant monomers, for SDS and CTAB solutions in the presence of the salts added. The *CMC* and α values were determined from the conductivity measurements carried out at 25 °C.

Electrolyte	*CMC* (M)	$\alpha \pm 0.01$	Peak intensity quotients
For SDS[a]	$\pm 5 \times 10^{-5}$		$I_X/(I_X + I_{Na})$[c]
None	7.8×10^{-3}	0.42	–
$LiClO_4$	5.6×10^{-3}	0.50	0.18
$NaClO_4$	4.3×10^{-3}[e]	0.45[e]	–
NH_4ClO_4	3.5×10^{-3}[e]	0.28[e]	0.18
$KClO_4$	1.8×10^{-3}	0.22	0.67
$Mg(ClO_4)_2$	1.1×10^{-3}[e]	0.155[e]	0.82
For CTAB[b]	$\pm 1 \times 10^{-5}$		$I_Y/(I_Y + I_{Br})$[d]
None	9.2×10^{-4}	0.350	–
NaF	8.1×10^{-4}	0.351	0.075
NaCl	6.5×10^{-4}	0.367	0.15
KBr	4.1×10^{-4}	0.470	–
$NaNO_3$	3.5×10^{-4}	0.442	0.325
NaI	Precipitation		

[a] In the presence of 0.015 M electrolyte.
[b] In the presence of 0.002 M electrolyte.
[c] X is Li, NH_4, K, or Mg.
[d] Y is Cl, NO_3, or F.
[e] Data from Ref. [27].