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Effect of electrolyte species on the adsorption of a cationic surfactant to silica: The common intersection point

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ABSTRACT

Adsorption isotherms for cetyltrimethylammonium bromide (CTAB) on silica have been measured using optical reflectometry (OR) in the presence of 1 mM and 10 mM NaBr, KBr and CsBr in order to elucidate the role of specific adsorption of the electrolyte to silica. In this regard the surface excess at concentrations up to the common intersection point (CIP) is most revealing as Koopal and co-workers have demonstrated that in the presence of an indifferent electrolyte the CIP corresponds to the isoelectric point and the charge compensation point. CsBr exhibited a CIP at 0.035 mM considerably higher than the CIP for NaBr and KBr (0.025 mM), indicating specific adsorption of Cs^+ ions to silica.

1. Introduction

In a series of papers published in the early to mid-1990s, Koopal and co-workers investigated the adsorption of ionic surfactants to solids and found that at a particular concentration of surfactant, the surface excess was not influenced by the salt concentration [1–5]. At surfactant concentrations below this point an increase in electrolyte concentration reduced surfactant surface excess and at concentrations above this point an increase in electrolyte concentration led to an increase in surfactant surface excess. Therefore a family of adsorption curves for a particular surfactant in the presence of different ionic strengths of an electrolyte would intersect at this point – they called this the common intersection point (CIP). In particular two papers examined the effect of added electrolyte on cationic surfactant adsorption at the silica–aqueous solution interface [4,5]. The authors identified a design flaw in many previously conducted surfactant solution depletion experiments: the ionisation of surface groups increases as surfactant adsorbs, leading to an increase in the solution hydrogen ion concentration. As a result the solution pH decreases along the concentration axis of adsorption isotherms determined using solution depletion, unless pH is carefully controlled. Furthermore, for a given surfactant concentration, the magnitude of the pH change depends on the surface area of the silica particles and volume of the surfactant solution. As these parameters vary from experiment to experiment and study to study, and most papers reported only the initial pH, this meant that quantitative comparison of data between studies was impossible. Goulob et al. [4,5] overcame this problem via the addition of acid or base as the surfactant equilibrated with the substrate to a constant pH value (typically 7 or 9). With this improvement, the effect of added electrolyte on substrate surface charge and surfactant adsorption could be commented upon with certainty [5].

For low salt concentrations (1 mM), it was found that surface charge increased as soon as adsorption was detected. This indicates that surfactant adsorption to surface charged sites increases the acidity of nearby hydroxyl groups, inducing ionisation of the silica surface. Experiments revealed that at low concentrations an adsorbing surfactant creates more than one charged site. As the surfactant concentration is increased and the surface charge compensation point (CCP) is approached, the number of surfactants adsorbing and the number of charged sites created was approximately equal. Above the CCP the surface charge remained constant as the surfactant surface excess increased. That is, no further increase in surface charge took place.

In high salt concentration solutions (100 mM) the situation is somewhat different, as the surface charge prior to introduction of the surfactant is much greater. Consequently, the increase in surface charge as surfactant adsorbs is markedly less. Surfactants must compete with electrolyte cations for adsorption sites resulting in a reduction in adsorption at lower surfactant concentrations in comparison to the 1 mM salt systems. However, as electrostatic repulsions between surfactant headgroups are screened when

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electrolyte concentration is high, once adsorption commences the isotherm increases steeply and at high surfactant concentration the equilibrium surface excess above the CIP is greater in the high salt case.

This difference in behaviour for low and high electrolyte concentrations means that isotherms determined at different salt concentration must cross each other at the CIP. The position of the CIP was accurately determined for a variety of systems [5] in which the pH was carefully controlled (as described above). At the CIP, added electrolyte has no effect on surface excess so, in the absence of specific interactions between the surface and the surfactant, the CIP designates the substrate isoelectric point (IEP). This was confirmed by electrophoretic mobility experiments [5]. In fact, not only did the CIP correspond to the IEP, but also the CCP. Therefore, the CIP represents the point where the electrostatic contribution to the adsorption process changes from attractive to repulsive, and where the orientation of adsorbing surfactants changes from predominantly 'heads towards the substrate' to 'heads towards solution', such that bilayered aggregates begin to form.

Whilst these studies clearly defined the role of surface charge in determining the features of adsorption isotherms, the mechanism of surfactant adsorption remained open to question. In the early part of this decade a series of papers examining the adsorption kinetics of cationic surfactants to silica [6–9] using optical reflectometry (OR) were published. This instrument was based on a design developed at Wageningen University [10] employing stagnant point flow hydrodynamics [11]. Prior to this work, the fast kinetics associated with surfactant adsorption at the solid–aqueous interface prevented accurate investigation of adsorption kinetics, which led to the mechanism of surfactant adsorption being inferred from thermodynamic data. The use of OR with well defined hydrodynamics allowed the adsorption mechanism to be discerned [12]. In these experiments there is a continual flow of solution over the low surface area silica wafer substrate. Therefore, desorption of surface ions does not influence the ambient pH as per depletion experiments. The key findings were that above the critical micelle concentration (CMC) surfactant adsorption was more efficient, indicating direct adsorption of micelles to the surface [6,7,12], and the identification of a concentration range, the slow adsorption region (SAR), where surfactant adsorption requires many hours to reach equilibrium [6–8,12].

In this article the effect of electrolyte species on the CIP for CTAB adsorption to silica is examined. Previously we were unable to study this region of the isotherm because the surface excess values were close to the detection limit of the OR used. Here we present data obtained using a new OR that has been modified such that resolution is improved by an order of magnitude. This allows us to detect the cetyltrimethylammonium bromide (CTAB) CIP for 1 mM and 10 mM NaBr, KBr and CsBr. A more complete description of the instrument modifications will be presented in a future article.

2. Materials and methods

CTAB (purity greater than 99%) was obtained from Aldrich, recrystallised twice from acetone and freeze-dried prior to use. KBr, NaBr and CsBr (Analytical Grade, 99.9+%) were obtained from Aldrich and were used as received. All water used was filtered, distilled and passed through a Millipore Gradient filtration unit before use. The surface tension of the water was measured regularly by the pendant drop technique (KSV) and found to be >73 mN m^{-1}.

Silicon wafers with a well defined 319 nm oxide layer were used in all the studies (Silicon Valley Microelectronics, CA). Surfaces with low hydroxyl group density are obtained upon baking due to condensation reactions at the silica surface that result in the formation of siloxane bonds [13]. The remaining hydroxyl groups are isolated and therefore less likely to participate in hydrogen bonded stabilisation of hydronium ions at the surface [13]. In solution, these hydroxyl groups are therefore more acidic and the silica surface will be more highly charged. Silica of this type is known as pyrogenic. Pyrogenic silica will slowly rehydroxylate when immersed in water resulting in hydroxylated silica. In this work, the initially pyrogenic silica was cleaned with Piranha solution (H_2O_2 80%, w/w; 20%, w/w HNO_3) for <30 s, rinsed with water, soaked in 10% (w/w) NaOH for <30 s and stored in water until use. This process ensured that the silica surface was fully hydroxylated without altering the thickness of the oxide layer. Immediately before use the surfaces were rinsed with water and distilled ethanol before being dried under a dry nitrogen stream. We often employ an RF water plasma to clean surfaces before surface studies however here it was found that this treatment led to drift in the baseline suggesting that the silica substrate was slowly dissolving in water after plasma treatment. Therefore plasma treatment was not employed. The thickness of the oxide layer present on the silicon wafer was determined ellipsometrically to be 319 ± 2 nm (Beaglehole instruments). The refractive indices of water, silica and silicon used were 1.333, 1.46 and 3.80, respectively.

The OR technique used follows that used by Dijt et al. [10]. Briefly, OR relies upon the changes in the reflective properties of a substrate that occur upon adsorption. In a typical reflectometry experiment the cell initially contains only solvent (in this case water or the relevant salt solution) whilst a stable baseline is recorded. Surfactant is then passed into the cell via a two-way valve and upon adsorption the ratio of the intensities of the two perpendicular polarisations of the laser beam is altered. An optical model and sensitivity parameter are used to convert changes in the intensity ratio into surface excess via the sensitivity parameter. The sensitivity parameter A_s was determined to be $-0.024\,\mathrm{m^2\,mg^{-1}}$ from a four layer optical model, using a dn/dC value for the surfactant of $0.149\,\mathrm{cm^3\,g^{-1}}$. The reflectometer is entirely contained in an incubator, in a temperature controlled room allowing the temperature to be accurately maintained at 23 ± 0.1 °C.

3. Results and discussion

Typical data for the adsorption of CTAB in the presence of electrolyte are presented in Fig. 1. The systems shown are 0.025 mM CTAB in 10 mM NaBr and 0.05 mM CTAB in 10 mM NaBr. The general form of the adsorption data was consistent for all other surfactant and electrolyte concentrations and for variation in salt species,

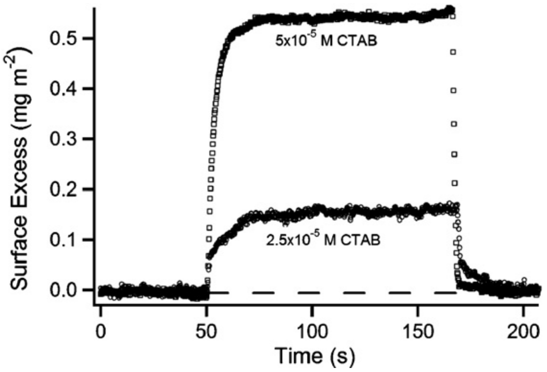

Fig. 1. Typical optical reflectometry data for the adsorption of CTAB at the silica–solution interface in the presence of 10 mM NaBr. The systems presented are 0.025 mM CTAB in 10 mM NaBr (open circles) and 0.05 mM CTAB in 10 mM NaBr (open squares). A stable baseline is first recorded using 10 mM NaBr then the surfactant solution is passed into the cell at ~50 s leading to surfactant adsorption. The plateau level of adsorption is maintained whilst the surfactant solution is flowing into the cell. Upon re-introduction of 10 mM NaBr the surfactant rapidly desorbs from the substrate.