NOVA

University of Newcastle Research Online

nova.newcastle.edu.au

Howard SC, Atkin R, Craig VSJ, 'Effect of electrolyte species on the adsorption of a cationic surfactant to silica: The common intersection point'. Originally published in Colloids and Surfaces A: Physicochemical and Engineering Aspects, 347 109-113 (2009)

Available from: <http://dx.doi.org/10.1016/j.colsurfa.2009.01.014>

Accessed from: <http://hdl.handle.net/1959.13/916775>

Effect of Electrolyte Species on the Adsorption of a Cationic Surfactant to Silica: The Common Intersection Point

Shaun Christopher Howard,¹ Rob Atkin² and Vincent Stuart James Craig^{1,*}

1. Department of Applied Mathematics

Research School of Physical Sciences and Engineering

Australian National University

Canberra, ACT 0200, Australia

2. Centre for Organic Electronics

Chemistry Building

The University of Newcastle

Callaghan, NSW 2308, Australia

* Corresponding Author.

Telephone: +61 2 6125 3359

Facsimile: +61 2 6125 0732

e-mail: Vince.Craig@anu.edu.au

Abstract.

Adsorption isotherms for 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 coworkers 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 0.35 mM considerably higher than the CIP for NaBr and KBr (0.25 mM), indicating specific adsorption of Cs^+ ions to silica.

Introduction.

In a series of papers published in the early to mid-1990's, 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 the surface excess of surfactant 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 the adsorption of cationic surfactants 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 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 systems⁵ 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 charge compensation point (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 'heads towards the substrate' to 'heads towards solution', such that bilayered aggregates begin to form.

While 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 silica⁶⁻⁹ using optical reflectometry (OR) were published. This instrument was based on a design developed at Wageningen University¹⁰ 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 cetyltrimethyl ammonium 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.

Materials and Methods.

Cetyltrimethylammonium Bromide (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 $>73 \text{ mNm}^{-1}$.

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.¹⁰ Briefly, OR relies upon the changes in the reflective properties of a substrate that occur upon adsorption of the species of interest. In order to convert changes in optical properties to surface excess

an optical model is required and the sensitivity parameter is used to convert changes in the polarisation of reflected light to a measure of surface excess. The sensitivity parameter A_s was determined to be $-0.024 \text{ m}^2 \text{ mg}^{-1}$ from a four layer optical model, using a dn/dC value for the surfactant of $0.149 \text{ cm}^3 \text{ g}^{-1}$. In a typical reflectometry experiment the cell initially contains only solvent (in this case water or the relevant salt solution) while a stable baseline is recorded. Surfactant is then passed into the cell via a two-way valve and the change in the ratio of the two perpendicular polarisations of the laser beam recorded; which is proportional to the surface excess. The reflectometer is entirely contained in an incubator, in a temperature controlled room allowing the temperature to be accurately maintained at $23^\circ\text{C} \pm 0.1^\circ \text{C}$.

Results and Discussion.

Typical data for the adsorption of CTAB in the presence of electrolyte are presented in Figure 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, although at some concentrations slow adsorption was observed as previously reported.^{6,7} Before the introduction of surfactant, a baseline was first recorded using the solvent; in this case, a 10 mM NaBr solution. Surfactant was then passed into the cell at 50 s resulting in a rapid increase in the surface excess. The equilibrium surface excess remained constant whilst surfactant solution was flowing into the cell. Upon solvent being passed into the cell, desorption was rapid and complete. Note the consistency of the baseline and in the signal obtained at equilibrium, which suggests that the instrumental error gives an uncertainty in the surface excess of the order of 0.02 mg m^{-2} , a 10 times improvement over previous

data. It is this increase in resolution that allows us to examine sub-CIP surfactant concentrations using OR, heretofore impossible.⁸

Figure 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 (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.

CTAB adsorption isotherms for 1 mM and 10 mM NaBr and 1 mM and 10 mM KBr are presented in Figures 2 and 3. These isotherms are determined by conducting several wash on / wash off experiments like those shown in Figure 1 at different surfactant concentrations in the presence of the appropriate salt solution.

Plotting the data on a log-log scale accentuates the features of the isotherms at low surfactant concentrations. This often allows isotherms to be divided into 4 regions based on the change in the gradient of lines of best fit to each region. The slopes change as the mode in which the surfactant is adsorbed varies. At low surfactant concentrations (region I) monomers are electrostatically adsorbed to the substrate in isolation, with headgroups in contact with the surface. In region II the surface excess rapidly increases. Adsorption involves strong lateral interactions between adsorbed

monomers to form hydrophobic patches on the surface called hemimicelles. Surface excess increases in region III are due to surfactant adsorption with headgroups facing into solution - onto the hemimicelles formed in region II, without any increase in the number of surface aggregates. In region IV, the plateau region, the surface is saturated with adsorbed aggregates and the surface excess does not change as the solution surfactant concentration is increased.

It is not clear from Figures 2 and 3 where the first region ends and the second region begins. Corresponding results were obtained previously using cetylpyridinium chloride,⁴ and attributed to the strength of the hydrophobic attraction between monomers preventing the adsorption of isolated monomers to charged sites. In previous work four regions were most evident for dodecylpyridinium chloride, which has a shorter chain length.⁴

Figure 2 Adsorption isotherms for CTAB in the presence of 1 mM NaBr (filled red circles) and 10 mM NaBr (open black circles). The dashed black vertical line indicates the cmc for the 10 mM salt system and the dashed red vertical line indicates the cmc for the 1mM salt system. The CIP occurs at 0.025 mM and is indicated by a blue vertical arrow.

Figure 3 Adsorption isotherms for CTAB in the presence of 1 mM KBr (filled red diamonds) and 10 mM KBr (open black diamonds). The CIP occurs at 0.025 mM and is indicated by a vertical blue arrow.

Figure 4 Adsorption isotherms for CTAB in the presence of 10 mM CsBr (open black squares) and 1 mM CsBr (filled red squares) indicating the position of the CIP. The CIP occurs at 0.035 mM and is marked with a vertical blue arrow.

CTAB adsorption isotherms determined at different salt concentrations allow the CIP to be identified. In figure 2 the influence of 1 and 10 mM NaBr on the adsorption of CTAB is shown. The isotherms cross over at a CTAB concentration of 0.025 mM, defining the CIP for this system. Similarly the CIP has been determined in the presence of KBr and CsBr as shown in figures 3 and 4 respectively. When KBr is used as the electrolyte the CIP is the same as that found with NaBr at 0.025 mM, whereas in the presence of CsBr the CIP occurs at a significantly higher concentration, 0.035 mM. Koopal and co-workers have previously shown in silica systems with KCl as the electrolyte that the CIP corresponds to the isoelectric point and the charge compensation point, demonstrating that the specific adsorption of potassium ions is weak or absent. As the CIP for the sodium and potassium salts are equivalent within error we can say that the sodium ion does not exhibit specific adsorption. However, the CIP in the presence of CsBr is shifted to significantly higher concentrations.

This difference may be rationalised on the basis of the relative ‘hardness’ of the salt cation and the effect this has on its affinity for the substrate. Small, hard ions have a high affinity for water and therefore will not interact as strongly with the surface in comparison to larger cations which interact with water relatively weakly. This effect is frequently explained in terms of the Hofmeister Series and the polarity of the ions, though a detailed explanation is yet to be fully provided.¹³ Whilst originally Hofmeister effects were thought to originate from influence of ions on bulk water structure in the framework of structure making or structure breaking ions, it is

now more widely believed that these effects are manifest at interfaces.¹⁴ The relative affinity of the ions for the substrate may be related to the strength of the van der Waals interaction acting between the ions and the surface and may include additional effects due to the polarisability of the ion in turn influencing the local water structure. Using this rationalisation the hard Na^+ and K^+ ions do not interact as strongly with the silica substrate as the soft Cs^+ ion. The conclusion being that Cs^+ ions specifically adsorb at the surface and in doing so compete with the surfactant ions for the surface charge sites. However this is not supported by the data. At a salt concentration of 10 mM the isotherms barely differ for each salt type (Figure 5). It is at the lower electrolyte concentration of 1 mM where differences in the isotherms are evident (see Figure 6). Here it can be seen that at very low concentrations the surface excess is greater in KBr than it is in NaBr or CsBr and this fits the above explanation. However at CTAB concentrations above 10^{-5} M the order is reversed and the surface excess increases on going from KBr to NaBr to CsBr. The slopes of the isotherms differ considerably below this concentration. This corresponds to the II region of the isotherm where lateral interactions between the hydrocarbon chains are taking place in addition to adsorption of surfactant headgroups to charged surface sites.

Figure 5 Isotherms for CTAB in the presence of 10 mM salts: NaBr (open red circles), CsBr (open blue squares), and KBr (open black diamonds). The dashed line represents the approximate cmc for the 10 mM salt systems.

Figure 6 Partial isotherms for CTAB in the presence of 1 mM salts: CsBr (open blue squares), NaBr (open red circles) and KBr (closed black diamonds).

Goloub and Koopal.⁴ have shown that at low surface coverages, surfactant chains lie flat on silica surfaces due to favourable interactions with hydrophobic patches. The suggestion here is that the adsorption of Cs⁺ ions reduces the hydrophobicity of the interface and prevents the surfactant chains from lying flat and thereby promotes lateral hydrophobic interactions between surfactant chains, the result being an increase in surface excess. An increase in ion adsorption (and the associated counter-ions) will also more effectively shield the electrostatic repulsion between neighbouring head-groups. The surface excess must be sensitive to these effects at these electrolyte concentrations whereas at higher salt concentrations no specific ion effects are seen.

The adsorption kinetics for each of the CTAB – salt systems were determined. Within error limits the electrolyte species had no effect on adsorption rate.

Conclusions.

Adsorption isotherms for CTAB in the presence of NaBr, KBr and CsBr at concentrations of 1 mM and 10 mM have been determined in order to examine whether ion specific effects influence the CIP concentration. The CIP for CsBr occurs at higher concentrations than for KBr and NaBr, indicating that Cs⁺ ions specifically adsorb to the silica surface. Interestingly, this is manifest as an increase in the surface excess in the presence of CsBr in comparison to NaBr and KBr in 1 mM salt but not in 10mM salt. This is interpreted as arising from an increase in lateral hydrophobic interactions between surfactant ions due to the specific adsorption of Cs⁺ ions.

Acknowledgments

RA wishes to acknowledge his meetings with Luuk Koopal while visiting Wageningen University during his PhD. These meeting were immensely valuable and contributed to the success of my project. RA also wishes to acknowledge the University of Newcastle for provision of a research fellowship. VSJC gratefully acknowledges financial support from the Australian Research Council and the International Fine Particle Research Institute. SCH gratefully acknowledges financial support from the Smartprint CRC. We also thank Dr Erica Wanless who generously donated the silicon oxide substrates with controlled oxide layer thickness.

References.

- (1) Bohmer, M. R.; Koopal, L. K. *Langmuir* **1992**, *8*, 2660.
- (2) Bohmer, M. R.; Koopal, L. K. *Langmuir* **1992**, *8*, 1594.
- (3) Bohmer, M. R.; Koopal, L. K. *Langmuir* **1992**, *8*, 2649.
- (4) Goloub, T. P.; Koopal, L. K. *Langmuir* **1997**, *13*, 673.
- (5) Goloub, T. P.; Koopal, L. K.; Bijsterbosch, B. H.; Sidorova, M. P. *Langmuir* **1996**, *12*, 3188.
- (6) Atkin, R., Craig, V.S.J., Biggs, S. *Langmuir* **2000**, *16*, 9374.
- (7) Atkin, R., Craig, V.S.J., Biggs, S. *Langmuir* **2001**, *17*, 6155.
- (8) Atkin, R., Craig, V.S.J., Wanless, E.J., Biggs, S. *J. Colloid and Interface Science* **2003**, *266*, 236.
- (9) Atkin, R.; Craig, V. S. J.; Hartley, P. G.; Wanless, E. J.; Biggs, S. *Langmuir* **2003**, *19*, 4222.
- (10) Dijt, J. C.; Cohen Stuart, M. A.; Hofman, J. E.; Fleer, G. J. *Colloids and Surfaces* **1990**, *51*, 141.
- (11) Dabros, T.; van de Ven, T. G. M. *Colloid Polym. Sci.* **1983**, *261*, 694.
- (12) Atkin, R.; Craig, V. S. J.; Wanless, E. J.; Biggs, S. *Advances in Colloid and Interface Science* **2003**, *103*, 219.
- (13) Iler, R. K. *The Chemistry of Silica*; Wiley-Interscience Publishers: New York, 1979.