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Adsorption of Quaternary Ammonium Compounds on the Surface of Sodium Oxalate: FTIR/ATR Investigation under High-Ionic-Strength, Highly Alkaline Conditions

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Using a recently developed method for the *in situ* investigation of the surface of sodium oxalate—a Bayer process solid—in highly alkaline, high-ionic-strength, aqueous media, “dose-response” curves for a series of alkyltrimethylammonium bromides on the surface of sodium oxalate have been obtained. These curves show the extent of adsorption increasing with alkyl chain length until the point is reached where the alkyl chain of the adsorbed compound adopts a coil-like orientation at the oxalate surface, thereby reducing the amount adsorbed compared with those for the shorter chain homologues. These shorter chain compounds are adsorbed to the oxalate surface in a predominantly perpendicular manner, while the longer chain compound may adopt a more tilted surface orientation. Results obtained for a synthetic oxalate stabilizer formulation suggest that the compound is adsorbed in a manner analogous to that of the shorter chain compounds. Decreased adsorption observed at higher initial concentrations is due to the formation of large cylindrical or lamellar micelles, which exhibit increased stability relative to that of the adsorbed form. The formation of these large micellar aggregates is a result of the high ionic strength of the adsorption matrix. We believe this to be the first instance in which FTIR/ATR has been used to obtain both qualitative and quantitative information as to the nature of the interfacial layer of dispersed particulate matter.

Introduction

Recently,¹ we have reported the development of a new Fourier transform infrared (FTIR) attenuated total reflection (ATR) technique for the investigation of the surface of sodium oxalate (a Bayer process solid) in high-ionic-strength, highly alkaline, aqueous media. Using this method, we were able to detect a series of adsorbed alkyltrimethylammonium compounds on the surface of sodium oxalate, with results suggesting adsorption in the form of hemimicelles. Furthermore, we are now able to demonstrate the acquisition of “dose-response” curves for a series of such compounds on the surface of sodium oxalate under the aforementioned extreme conditions. It is envisaged that this new technique will, combined with a recently developed analytical method for the analysis of quaternary ammonium (QA) compounds in Bayer liquor,² contribute significantly toward the furthering of understanding of the Bayer chemistry of these (and other) types of surface active compounds.

The Bayer process, developed and patented by Karl Josef Bayer in 1888, is used to refine bauxite ore to smelting grade alumina. Quaternary ammonium compounds (QAs) have the potential for use as surface-active agents in this process. In particular they seem suited to the role of sodium oxalate stabilizer.^{3–5} Unfortunately, due mainly to the complex nature of Bayer liquor, there is presently

a lack of fundamental understanding of the surface chemistry of these (and other) types of compounds under Bayer and Bayer-like conditions. Such an understanding (of processes occurring at the solid/aqueous interface under such extreme conditions) would be of great scientific and industrial significance.

Surfactants are among the most versatile and widely used products of the chemical industry.⁶ QAs are a widely used and commercially available cationic surfactant and are of interest to researchers for many reasons. Their cationic nature combined with their dual hydrophilic/hydrophobic properties makes them ideally suited for use as surface modifiers and surface-active agents and has made them useful in areas as diverse as hair and fabric conditioning^{7,8} and weed control,^{9,10} while it is the cationic charged center of QAs¹¹ that makes them significant in many biological systems. The potential applications of this family of compounds in industrial processes are also quickly being realized.^{12–14} Interest in cationic (and anionic) adsorption phenomena has resulted in a large number of investigations, with the subject thoroughly reviewed a number of years ago.¹⁵ The adsorbent of choice for the investigation of cationic adsorption has traditionally been negatively charged silica;^{16,17} however, other

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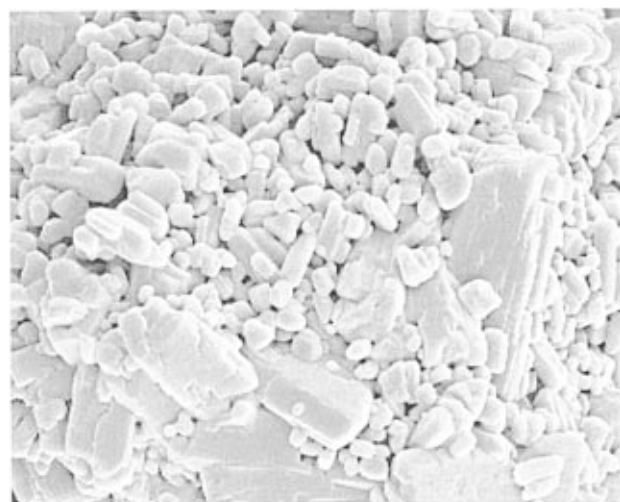
solids have also been investigated.^{18,19} More recently,^{20–24} silica has remained the adsorbent of choice (other solids have again been investigated^{25–27}) with alkylpyridinium,^{20,21,25,26} alkylammonium,^{21,22,24,27} and arylammonium²³ cationic surfactants the subjects of a number of studies. These studies have involved adsorption of the aforementioned compounds under relatively mild conditions (pH 6–9; 0.001–0.1 M [Na⁺, K⁺]), which, unfortunately, bare little resemblance to those conditions encountered in Bayer systems (pH > 14; $\approx 6\text{--}7$ M [Na⁺]^{1,2}). For this reason, we have endeavored to investigate the adsorption of a series of QAs onto the surface of sodium oxalate under highly alkaline (pH 12–13), high-ionic-strength (5 M [Na⁺]) conditions.

Sodium oxalate is a relatively low-surface-area, water-soluble solid whose surface chemistry can be probed *in situ* using FTIR/ATR.¹ Using FTIR/ATR we present, for the first time, dose-response curves for a series of alkyltrimethylammonium bromides adsorbed on the surface of sodium oxalate from high-ionic-strength, highly alkaline, aqueous media. We also present results for the adsorption of a synthetic oxalate stabilizer formulation containing predominantly methylbis(2-hydroxyethyl)-oleylammonium chloride (developed by Alcoa of Australia Ltd and Nalco Chemical Company) on the surface of sodium oxalate. Using a (validated) one-point calibration involving the direct comparison of aqueous QA peaks with adsorbed QA peaks, we obtain nominal oxalate surface QA concentrations for each of the QAs on sodium oxalate at each initial aqueous QA concentration. We believe this to be the first instance in which FTIR/ATR has been used to obtain both qualitative and quantitative information as to the nature of the interfacial layer of dispersed particulate matter.

Experimental Section

Quaternary Ammonium Compounds. Dodecyltrimethylammonium bromide (C12), tetradecyltrimethylammonium bromide (C14), and hexadecyltrimethylammonium bromide (C16; $\approx 99\%$, Sigma-Aldrich Pty Ltd, Castle Hill, NSW, Australia) were obtained commercially and used as received. The critical micelle concentrations (cmc's) of these three compounds in water are approximately 1.5×10^{-2} , 3.5×10^{-3} , and 9.2×10^{-4} M, respectively.²⁸ The methylbis(2-hydroxyethyl)oleylammonium chloride formulation (N138) was obtained from Nalco Chemical Company (Kwinana, WA, Australia) and was used as received (its cmc was not determined, as the formulation was known to be impure). All other reagents used were of analytical reagent (AR) grade, and ultrapure MilliQ water was used in all instances.

Sodium Oxalate. The sodium oxalate used in this study was a high-surface-area (HSA) oxalate prepared from acicular (needle like) sodium oxalate provided by Alcoa of Australia and was found to have a BET surface area of 3.3 ± 0.4 m²/g. The



20μm

Figure 1. SEM of AR grade sodium oxalate.

production of this HSA oxalate has been described elsewhere.¹ Surface area measurements were performed using a Micromeritics ASAP 2000 surface area analyzer, using nitrogen gas adsorption. Scanning electron micrographs (SEMs) of AR, acicular, and HSA oxalate samples were provided by Alcoa of Australia.

Adsorption Experiments. All adsorption experiments were carried out as described previously.¹ Briefly, adsorption matrix (5 M NaCl saturated with respect to oxalate; 10 mL) was added to HSA oxalate (0.1000 ± 0.0005 g), followed by base (10 M NaOH; 80 μ L) and Bayer humate fraction (10 μ L). The HSA oxalate seed was allowed to condition for 1 h at 35 $^{\circ}$ C, prior to addition of the appropriate QA, with the experiment halted 24 h after QA addition. QAs were dosed at 0, 3, 5, 7, 10, 20, and 50 ppm. All additions were made by means of an appropriate digital pipet/micropipet.

FTIR Spectroscopic Measurements. Infrared spectra were acquired using a Perkin Elmer System 2000 FTIR spectrometer equipped with deuterated triglycine sulfate (DTGS) and liquid-nitrogen-cooled mercury cadmium telluride (MCT) detectors. Spectra were obtained as described in our earlier publication,¹ with spectral manipulations (based upon the Biber–Stumm protocol²⁹) also performed as previously outlined.¹ Briefly, respective slurry and supernatant spectra were subtracted from each other to yield solid spectra; then subtraction of blank solid from dosed solid resulted in interfacial spectra revealing the adsorbed form of the QA. Dose-response curves were then obtained by plotting nominal oxalate surface QA concentration ([QA]_{surf}; see Results and Discussion) against the initial QA solution concentration ([QA]_{Dose}). Curves presented are the result of four separate acquisitions for the C12, C14, and C16 QAs, while the N138 curve is the result of two separate acquisitions.

Oxalate Morphology. The surface area of the solid under investigation is a major factor in determining the feasibility of FTIR/ATR interfacial studies.¹ In order to obtain meaningful spectroscopic information, we were forced to produce HSA oxalate from acicular oxalate (in turn produced from AR oxalate). In producing this higher surface area sample, BET surface area was seen to increase from 0.5 to 1.3 m²/g and finally 3.3 m²/g¹ for the HSA sample. Recently obtained SEMs of these different oxalates (see Figures 1–3) clearly depict the change in oxalate morphology accompanying this increase. The change in aspect ratio accompanying the transition from AR grade (see Figure 1) to acicular oxalate (see Figure 2) is quite obvious and explains the increased surface area of the acicular form. The SEM of the HSA sample (see Figure 3) is also quite self-explanatory. The attrition of the acicular needles (a result of the grinding, sieving, and ultrasonification process¹) is apparent and, again, explains the further increase in oxalate surface area. It is envisaged that a continued grinding regimen would result in an even greater

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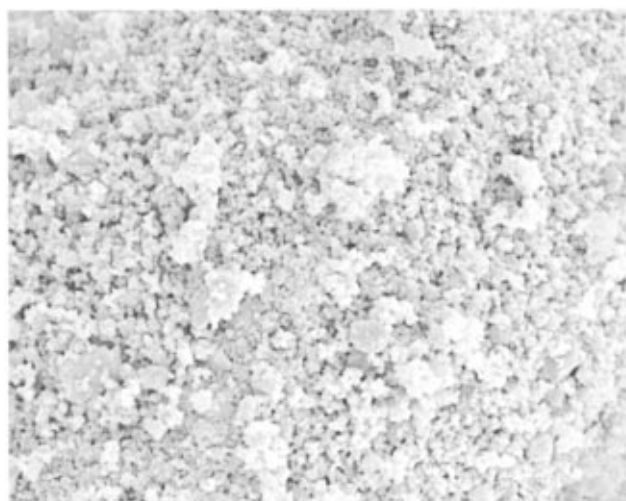
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20 μm

Figure 2. SEM of acicular sodium oxalate.



20 μm

Figure 3. SEM of HSA sodium oxalate.

surface area increase. It must be noted here however that ease of oxalate sample handling decreases noticeably with increased surface area.

Results and Discussion

Quantitative Interfacial Spectroscopy. The main aim of this research program was the development of an *in situ* spectroscopic method for the *qualitative* investigation of the surface of sodium oxalate under high-ionic-strength, highly alkaline conditions. *Quantitative* analysis of the *adsorbed* or *interfacial* layer of the oxalate surface was initially considered unlikely. While quantitative analysis of colloidal and particulate silica^{30,31} and goethite³² has been reported using ATR and Hug and Sulzberger³³ have reported a quantitative, *modified* ATR technique utilizing a *coated* internal reflection element (IRE), other FTIR/ATR interfacial studies involving adsorption onto *solids* in contact with the IRE have, at best, reported

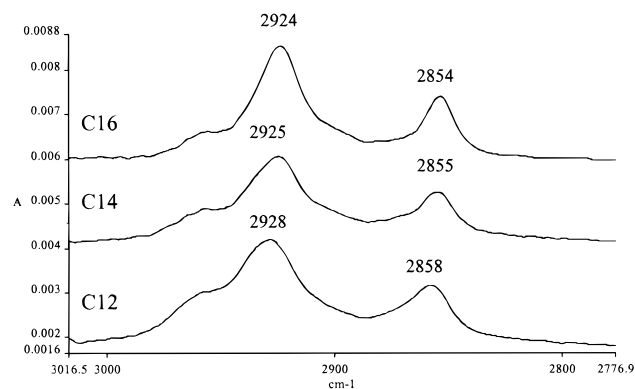


Figure 4. FTIR/ATR spectra of aqueous C12, C14, and C16 QAs at 75% cmc QA concentrations (see Table 1).

Table 1. 75% Cmc Values for C12, C14, and C16 QAs (Cmc for N138 Was Not Determined)

QA	75% cmc (g/L)		75% cmc (M)	
	lit. ²⁸	actual	lit. ²⁸	actual
C12	3.470	3.491	0.011 250	0.011 319
C14	0.883	0.884	0.002 625	0.002 627
C16	0.252	0.254	0.000 690	0.000 697

semiquantitative findings.³⁴ With this and the relatively low surface area of the oxalate adsorbent in mind, this second phase of the study was approached with some trepidation. The preliminary results obtained however were most encouraging and, as outlined in the Introduction, have led to the acquisition of dose-response curves for the series of QAs tested and the determination of nominal oxalate surface QA concentrations.

Determination of Oxalate Surface QA Concentration. In order to quantify the amount of QA adsorbed on the surface of sodium oxalate, the adsorbed QA peak areas were calibrated with respect to the analogous aqueous QA peak areas (asymmetric and symmetric CH₂ stretching vibrations of the methylene chain; occurring at approximately 2925 and 2855 cm⁻¹, respectively^{1,34}). In this manner, *nominal* oxalate QA surface concentrations were obtained. Using a suitable normalization factor to account for between run variations in ATR throughput and detector response, a one-point calibration technique was developed and validated. This technique allowed the acquisition of QA dose-response curves.

The quantitative analysis of aqueous alkyltrimethylammonium bromides by ATR has been demonstrated previously.¹ A tendency toward nonlinearity is observed above the cmc for the C12, C14, and C16 QAs, as expected (N138 was not investigated); however, below the cmc of each QA, a linear correlation between QA peak area and QA concentration is seen. One-point calibrations were thus performed using QA solutions of concentration equal to 75% of the respective QA cmc (see Table 1; N138 calibration was carried out using a 1.57 g/L solution). An ATR spectrum of each 75% cmc QA (75%QA) solution was acquired immediately following the acquisition of the respective slurry and supernatant¹ spectra (see Figure 4). Following this, a spectrum of a 2.0% w/v sodium oxalate solution was acquired, and the area of the $\nu(\text{CO})_{\text{asym}}$ stretch at 1308 cm⁻¹ was determined. The area of this peak was then used to normalize all aqueous and adsorbed QA peak areas, with these normalized areas used for the one-point calibration.

In order to test the validity of this normalization regime, spectra of the 75%QA solutions and the 2.0% w/v oxalate

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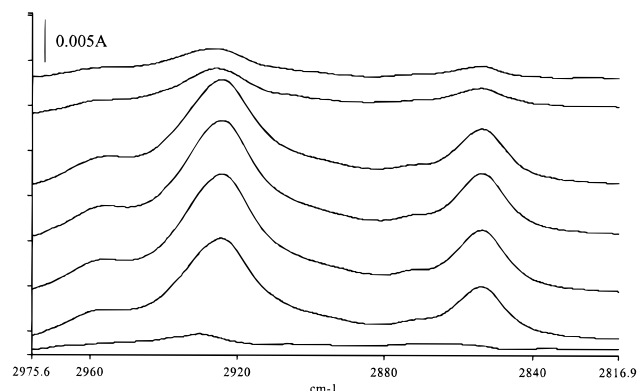


Figure 5. Representative interfacial spectra of the adsorbed C14 QA at 0, 3, 5, 7, 10, 20, and 50 ppm (bottom to top) initial QA concentration.

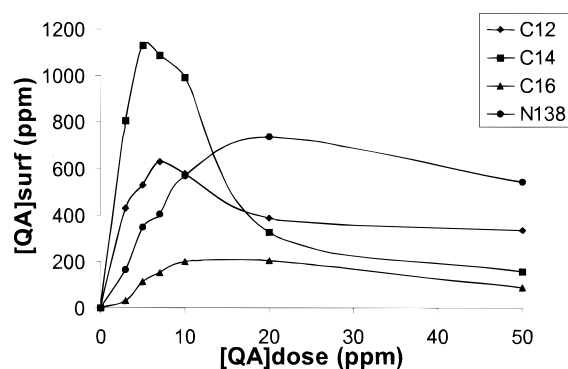


Figure 6. Dose-response curves for C12, C14, C16 and N138 QAs.

solution were acquired on three occasions over three separate days, with the ATR cell realigned and the MCT detector refilled with liquid nitrogen between each acquisition. Peak areas of the ~ 2855 and ~ 2925 cm^{-1} C12, C14, and C16 QA methylene vibrations were then determined and normalized with respect to the 1308 cm^{-1} carboxyl stretch of the oxalate solution. The normalized QA peak areas were found to have an average relative standard deviation of 4.8%, and the normalization technique was deemed valid.

Dose-Response Curves. Representative interfacial spectra of the adsorbed C14 QA at different initial QA concentrations can be seen in Figure 5. The average dose-response curves for the four QAs tested (Figure 6) show the trend of increasing oxalate surface QA concentration with increasing initial aqueous QA concentration or dose. The three alkyltrimethylammonium bromides exhibit adsorption maxima in the QA dose range 5–10 ppm, while the N138 compound shows a maximum at 20 ppm. It is also apparent that, for the alkyltrimethylammonium compounds, the amount adsorbed follows the trend $\text{C14} > \text{C12} > \text{C16}$ until the dose rate exceeds 20 ppm. Thereafter, the amount of the three QAs adsorbed decreases to a minimum, occurring at the highest dose rate used (50 ppm). Similarly, the amount of N138 adsorbed shows a minimum at the same dose rate.

The trend described above is contradictory to that which we previously predicted.¹ Initially, it was hypothesized that QA adsorption would occur in the order $\text{C16} > \text{C14} > \text{C12}$. This prediction was based upon semiquantitative calculations made using aqueous QA solutions which were above (C16) and below (C12, C14) cmc concentrations. Interpretations for the C12 and C14 compounds were thus valid; however, those for the C16 compound were invalid. By calibrating with a solution that was of a concentration substantially greater than the C16 cmc and well outside

the linear portion of the calibration curve, the concentration of the adsorbed species was overestimated.

Effect of Increasing Alkyl Chain Length on Adsorption. It is generally accepted that an increase in the chain length of the hydrophobic group of a surfactant increases the efficiency of adsorption. This is because the free energy decrease associated with both the removal of the hydrophobic chain from contact with the water and the tendency to aggregate or adsorb via dispersion forces increases with an increase in the length of the chain.⁶ The effect of increasing chain length on the adsorption of cationic surfactants from aqueous solution is thus well documented. On negatively charged surfaces, increasing the alkyl chain length of the adsorbate has been shown to increase the amount adsorbed.¹⁵ Alkylammonium acetates³⁵ and alkanesulfonates¹⁷ on quartz and alkyltrimethylammonium¹⁸ ions on polystyrene latex particles provide excellent examples of this phenomenon. However, the mild pH and low-ionic-strength conditions (pH 6–9; 0.001 – 0.1 M $[\text{Na}^+, \text{K}^+]$) used in these and other similar studies must be taken into account when interpreting results obtained in highly alkaline, high-ionic-strength media. It was from such studies that our initial hypothesis¹ was formulated.

The effectiveness of adsorption may increase, decrease, or show no change with an increase in the length of the hydrophobic group, depending upon the orientation of the adsorbate at the adsorbent/solution interface. If the arrangement is predominantly perpendicular but not close packed, or if it is somewhat tilted away from the perpendicular, there may be some increase in effectiveness of adsorption with an increase in the length of the hydrophobic group. If, however, the orientation of the adsorbate is more parallel to the interface, then the effectiveness of adsorption may decrease with an increase in chain length.⁶

Evidence exists which suggests that, when the number of carbon atoms in a straight chain hydrophobic group reaches 16, the cmc no longer decreases as rapidly with increasing chain length and that, when the number of carbon atoms reaches 18, the cmc may remain substantially unchanged with a further increase in chain length. This has been attributed to the *coiling* of these long chains in water.³⁶ Also, for anionic and cationic surfactants, the presence of electrolyte is known to cause cmc depression, due mainly to the decrease in thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the added electrolyte and the consequent decreased electrical repulsion between them in the micelle.⁶

Thus, considering the results obtained and the conditions under which they were obtained, we propose that the C12 and C14 QAs adsorb to the oxalate surface in a predominantly perpendicular manner, as originally postulated, with the amount adsorbed increasing with increasing alkyl chain length. The C16 QA, on the other hand, adopts a coil-like structure at the oxalate surface (a consequence of the high ionic strength of the system and the resultant cmc depression), this explaining the reduced adsorption of the C16 QA as compared to the those of the C12 and C14 compounds. The coiled C16 compound may also adopt a more tilted surface orientation (compared to those of the C12 and C14 compounds); however, this requires further investigation. The amount of N138 (see Experimental Section) compound detected on the oxalate surface suggests that the compound is

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adsorbed in a manner analogous to that of the C12 and C14 QAs. Investigation of a (pure) homologous series of such compounds is necessary however before definite conclusions as to the nature of the interaction can be drawn. Unfortunately, use of such homologues would require synthesis and purification of said compounds.

The decreased adsorption observed at higher QA concentrations for the four compounds tested may also be explained by the high ionic strength of the adsorption matrix. The effect of cmc depression by added electrolyte⁶ has already been mentioned, and preliminary results obtained in Bayer liquor² also suggest that the cmc's of these types of compounds are two orders of magnitude less than those reported in water. It may thus be postulated that, under such conditions, the QAs may be present as micellar aggregates at concentrations as low as 20–50 ppm. Given the fact that high salt content has been shown to dramatically increase the aggregation numbers of ionic surfactants containing a single long alkyl chain,³⁷ it may also be postulated that these compounds form relatively large cylindrical or lamellar micelles³⁷ with increased stability. So, given the choice between adsorption at the oxalate surface or continued micellar existence, the latter option may prove the most desirable and result in reduced adsorption at higher initial QA concentrations.

Conclusion

Using FTIR/ATR we have obtained, for the first time, dose-response curves for a series of alkyltrimethylammonium bromides adsorbed on the surface of sodium oxalate from high-ionic-strength, highly alkaline, aqueous media. Results were also obtained for the adsorption of a synthetic oxalate stabilizer formulation containing predominantly methylbis(2-hydroxyethyl)oleylammonium chloride on the surface of sodium oxalate. Using a one-

point calibration involving the direct comparison of aqueous QA peaks with adsorbed QA peaks, we also obtain nominal oxalate *surface* QA concentrations for each of the QAs on sodium oxalate at each initial aqueous QA concentration. To the best of our knowledge this is the first instance in which FTIR/ATR has been used to obtain both qualitative and *quantitative* information as to the nature of the *interfacial* layer of *dispersed particulate matter*.

Spectroscopic results suggest adsorption in the order C14 > C12 > C16, with the N138 formulation falling between the C12 and C16 compounds. Results also suggest that the C12 and C14 QAs adsorb to the oxalate surface in a predominantly perpendicular manner, with the amount adsorbed increasing with increasing alkyl chain length, while the C16 compound adopts a coil-like structure at the oxalate surface and, as a result, adsorbs to a lesser extent. Decreased adsorption observed at higher QA concentrations is explained by the formation of large cylindrical or lamellar micelles exhibiting increased stability relative to that of the adsorbed form of the QA. The formation of these large micellar aggregates is a result of the high ionic strength of the adsorption matrix.

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