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Surfactant aggregates (solloids) adsorbed on silica as stationary chromatographic phases: structures and properties

Martin G. Bakker*, Todd A. Morris[1], Gregory L. Turner[2], Ed Granger

Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, USA

Abstract

The structure and physical properties of solloids (surfactant aggregates adsorbed on surfaces) adsorbed on particles are of general interest. The relationship between solloid structure and properties of hexadecyltrimethylammonium bromide (HTAB), cetylpyridinium chloride (CPC) and cetylpyridinium salicylate (CPS) adsorbed on silica particles was studied by electron paramagnetic resonance (EPR) spectroscopy using the spin-probes peroxylaminedisulfonate (PADS) and 4-[*N*,*N*-dimethyl-*N*-(*n*-hexadecyl)ammonium]-2,2,6,6-tetramethylpiperidinyl-*N*-oxy bromide (HTAB*). Using HTAB* incorporated in HTAB, CPC and CPC solloids and comparing the results to those in micelles, it was determined that for silica around pH 4 the solloids are very similar in properties to the micelles. This is consistent with a linear solvation–energy relationship (LSER) analysis of solute equilibration data which indicates that at pH 5 HTAB solloids have similar properties to HTAB micelles. The PADS spin-probe appears to be more sensitive to changes in the properties of the double layer, and substantial differences were observed between HTAB, CPC and CPS and as a function of HTAB concentration for HTAB solloids on silica.

Keywords: Surfactant aggregates; Solloids

1. Introduction

The need for environmentally benign solvents is driving the development of a number of novel solvent systems including ionic liquids and supercritical fluids. However, for the foreseeable future, water is likely to be the most cost effective environmentally benign solvent system. Unfortunately, by itself water is not a suitable medium for reactions and separations involving hydrophobic molecules with poor water solubility. One method of addressing this is by formation of hydrophobic domains within the aqueous phase, e.g., by addition of surfactants which self assemble to form micelles. If the aqueous solution containing the micelles is then passed over a stationary phase to which the micelles or solutes bind a reaction mixture can be separated based on differences in partitioning of the various components of the mixture between the aqueous phase, stationary phase, and the micellar phase(s). This is the basis for (ad)micellar chromatographies [1–6]. Surfactant adsorption also impacts micellar electrophoresis [also known as micellar electrokinetic capillary chromatography, (MEKC and MECC)], where the use of quartz capillaries makes the use of cationic surfactants problematical [7]. The application of surfactants to chromatographic separations continues to receive considerable attention based on both current

*Corresponding author.

E-mail address: bakker@bama.ua.edu (M.G. Bakker)

[1]NSF-REU participant.

[2]Current address: Alabama Department of Forensics, University of Montevello, AL, USA.

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applications, and perceived potential. One aspect of surfactant based separations that has been relatively unexplored, is the structure of the surfactant aggregates that form on the surface of various supports and how this affects solubilization in such aggregates. This is despite the clear evidence that there exist a range of aggregate forms [8–13], and that the structure and physicochemical properties of such aggregates varies with surfactant coverage [14], pH [15], surface characteristics [9] and counterion. Thus the potential exists to tune the properties of these media in many dimensions to optimize a separation for a particular application. In fact it is possible to use changes in pH to completely strip the surfactant off the surface [4]. However the number of variables also complicates the optimization of any particular separation. There is therefore a need to understand the relationships between the nature of the surface, surfactant and counterions, the aggregate structure and the properties of the surfactant aggregates.

Adsorption of surfactants on oxide surfaces has other, wider implications. Biological membranes are made up of surfactants, which can bind to particle surfaces. Such systems can give insight on membrane mimetic chemistry, amplification of biomolecular recognition and for the design of biosensors [16]. The binding of cells to silica surfaces plays a part in silicosis [17] and possibly lung cancer induced by crystalline silica [18]. Surfactant aggregates in solution are also used to template the formation of mesoporous phases [19,20], and so the interaction of the surfactant with the growing mesoporous material has many aspects in common with adsorption on particles.

In this report we (1) summarize the types of surfactant aggregates postulated and the spectroscopic and other studies that provide insight into aggregate structure. Present preliminary results of recent electron paramagnetic resonance (EPR) spectroscopy studies of, (2) hexadecyl-trimethylammoniun bromide (HTAB) aggregates binding on silica particles, (3) binding of counterions to HTAB aggregates on silica particles, (4) binding of salicylate counterions to cetylpyridinium aggregates, and (5) present preliminary linear solvation–energy relationship (LSER) correlations of solute binding to HTAB aggregates on silica particles.

The starting point of any discussion of surfactant adsorption on oxide surfaces must be the adsorption isotherm, since this is the most accessible and common method for studying surfactant adsorption. Fig. 1 shows schematically the typical adsorption isotherm observed for adsorption of an ionic surfactant on an oppositely charged metal oxide surface. Typically four regions are distinguished, based on changes in slope [21]. The actual behavior of the surfactant in each of the four regions is however, less well established. In region I the surfactants appear to adsorb as individual molecules, and are usually shown as lying flat on the surface. In region IV the solution concentration of the surfactant exceeds the critical micelle concentration (CMC) and the complete coverage of the surface with bilayers (or possibly multilayers) is to be expected. It is clear that the transition between regions I and II represents the formation of surfactant aggregates, but the structure of such aggregates is a matter of controversy [8–12,22–24]. Kunjappu and Somasundaran have suggested that adsorbed surfactant aggregates be given the collective name of ‘‘solloids’’, which suggestion will be followed hence forth. Fig. 2 summarizes most of the aggregate structures suggested. They range in size from one or two individual surfactant molecules through small aggregates to monolayers and bilayers. There are also a variety of surfactant orientations to the surface. The nature of the oxide surface can

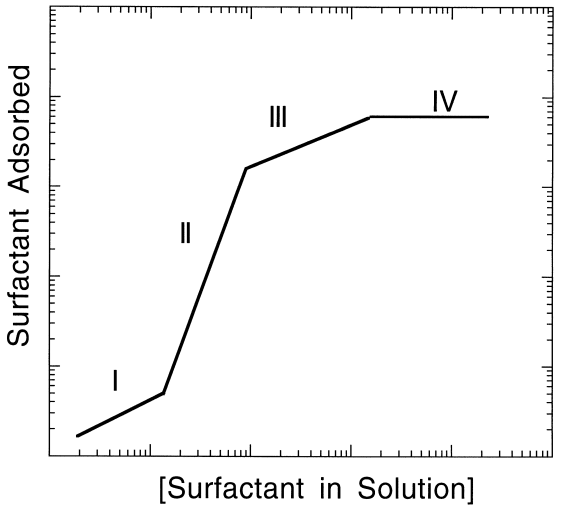

Fig. 1. Prototypical adsorption isotherm for adsorption of charged surfactant on oppositely charged surface.

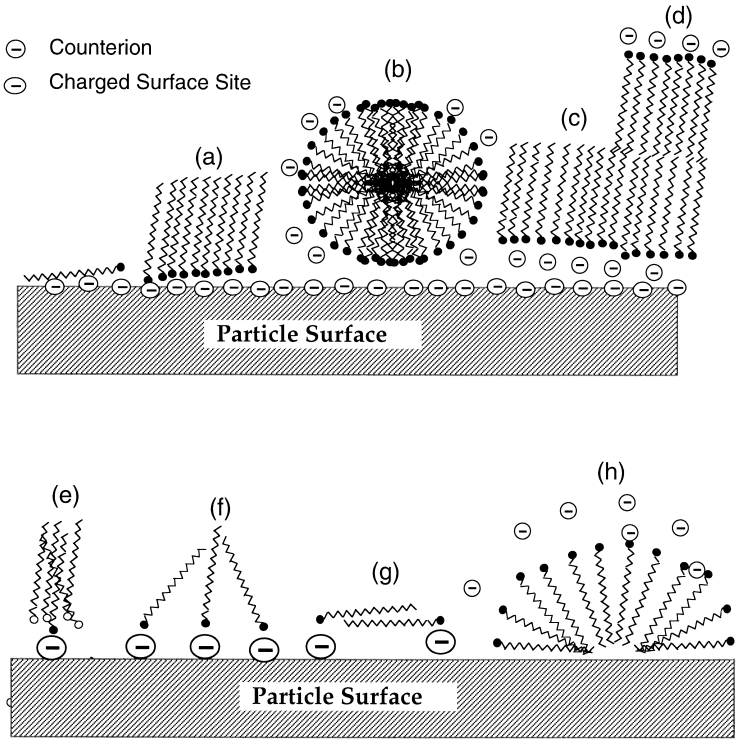

Fig. 2. Suggested surfactant aggregate structures. (a) Hemimicelle [25,26], (b) admicelle [12,92], (c) monolayer [25,26], (d) bilayer [12,92], (e) small aggregate [10,11], (f) charge compensated small aggregate [14], (g) hydrophobic bound small aggregate [15], (h) inverse hemimicelle [15,29].

affect the structure of the surfactant aggregates; directly through the density and distribution of charged sites on the surface, and indirectly through the size and extent of surface pores. The earliest structures suggested were the hemimicelle, monolayer and bilayer, which date back at least as far as the work by Fuerstenau [25] and Somasundaran et al. [26] who postulated such structures to explain the effect of surfactant concentration on the efficiency of forth flotation of silica. Subsequently Harwell and Yeskie have postulated the formation of ''admicelles'' based on model calculations which predict that the formation of such structures is energetically favored over hemimicelle formation [12,23]. At about the same time, Rupprecht and co-workers suggested that the adsorption isotherms of cationic and non-ionic surfactants on silica surfaces could best be explained by postulating the existence of a small number of strongly binding surface sites, and that adsorption of a single surfactant molecule at such a site would serve to catalyze the formation of a small aggregate [8,11,22]. More recently Behrends and Herrmann [14] have postulated the existence of small aggregates of surfactants lying flat on silica surfaces to explain the adsolubilization of anthracene by HTAB. Such aggregates have their headgroups bound to anionic surface sites, which provide charge compensation. For want of a better name we refer to this as a ''charge compensated small aggregate''. The lower limit for the size of such aggregates is two surfactants, which Holzheu et al. [15] have postulated to explain the binding of anthracene and other hydrophobic organic molecules on silica surfaces at low HTAB concentration. A more radical suggestion comes from interpretation of AFM images on silica surfaces by Manne and co-workers [27–29], and Drucker and co-workers [30–33] who postulate that cationic surfactants form inverse hemimicelles,

which at higher concentrations form half-cylinders that stretch in regular order across various hydrophobic and hydrophilic surfaces.

The structures in Fig. 2 are drawn to reflect the presence of counterions. Only in the last decade has it begun to be appreciated that for many oxide surfaces the surface charge density is not sufficient to compensate for the charge of the headgroups and so counterions bind in among the headgroups [34–36]. Recently Favoriti and co-workers [37–39] have reported a series of studies of adsorption of cetylpyridinium on silica with salicylate counterions. From the extent of adsorption and the shape of the isotherm these authors postulate a two-dimensional condensation on the silica surface in which the aromatic pyridinium headgroups and salicylate ions stack across the silica surface. The concentration and presence of counterions are expected to substantially effect the solloid structure both in terms of density and type of structure, in the same way as these factors affect micellar structure and properties. That structure can change is illustrated by an elegant AFM study by Burgess et al. [40] in which the structure of surfactant aggregates on a gold surface changed from a partial inverse hemimicelle form to a bilayer form when the charge density on the surface was raised.

The wealth of suggested structures and the transition between structures with changes in pH, concentration and other variables is extremely interesting from the standpoint of self-organization and self-assembly, and is of more than academic interest. The different structures are expected to have different properties, and indeed there is already clear experimental evidence that different structures have different solvation properties for organic solutes [14]. This difference in solvation properties can be shown quantitatively as we will discuss below.

The wealth of postulated structures is unfortunately not matched by a similar abundance of spectroscopic studies to characterize the structure. Such spectroscopic studies are required to reveal solloid structure as adsorption isotherms and similar probes of macroscopic properties are not capable of distinguishing between the postulated alternatives. The majority of spectroscopic studies have used fluorescence probes to determine local polarity and viscosity. Somasundaran and co-workers [41,42] have used this technique to study sodium dodecyl sulfate (SDS) solloids on alumina surfaces, and have used time-resolved fluorescence to determine the average size of such SDS solloids. Other fluorescence studies have been reported by Levitz and co-workers [43–46] on the adsorption of non-ionic surfactants of the Triton-X series onto silica. EPR spectroscopy can also be used to determine both local polarity and local viscosity. In an elegant study using the doxyl stearic acid series of spin probes Somasundaran et al. [47,48] determined that the viscosity was highest close to the SDS headgroups (presumed to be adsorbed on the alumina surface) and decreased monotonically away from the surface. Bakker and co-workers have applied EPR spectroscopy using a spin-labeled analog of HTAB to study adsorption of cationic surfactants onto the surface of silica [9,36,49,50]. This group was able to establish the formation of HTAB solloids and more recently, showed that at low concentration HTAB binds to a relatively small number of strongly binding surface sites. These sites may serve to nucleate the growth of the solloids that form at higher HTAB concentration, or higher pH: a result that will be discussed in more detail below. Fan et al. [51] subsequently applied the same probe to study adsorption of quaternary ammonium surfactants on alumina at high pH. Bakker et al. [50] have also recently reported the use of an anionic spin-probe to study the binding of counterions, which is to date the only report of spectroscopic evidence for binding of counterions to solloids.

Soderlind and Stilbs have reported nuclear magnetic resonance (NMR) studies of adsorption of SDS on alumina [52,53] and HTAB, and dodecyltrimethylammonium bromide (DTAB) on silica [52,54]. On silica they find two surfactant domains which they ascribe to formation of bilayers, this occurs at surface coverages of ca. 20% which is compatible with formation of admicelles. They also report that the motions of both the headgroups and the alkyl chains are slower than in micelles. NMR has also been used to study the structure of phospholipid aggregates on silica particles [52,55], where there is controversy about the nature of these aggregates [16,55,56].

IR spectroscopy, particularly attenuated total internal reflection has also been used to study adsorption of surfactants on oxide surfaces [57–61]. From such

studies it is clear that a variety of aggregate structures exist, however these are reflectance based studies for quantitation is difficult [62] and so the relative amounts of the various solloid types are difficult to determine. If water is not present quantitative transmission IR experiments can be carried out, however there is clear evidence that in drying particles the nature of the solloids changes [9,57].

In many of the studies cited above the relationship between the structure of the surface and the solloid structure is ignored. In most reports the surface is simply assumed to have certain general properties, e.g., a certain zeta potential corresponding to a positively or negatively charged surface. Where the nature of the surface has been explored it is mostly by variation of pH and observation of changes in solloid structure or properties as the average surface charge changes. In many ways this type of approach corresponds to a continuum model, where the surface serves only to generate a double layer. There have been some models developed, most notably those of Rupprecht and Gu, which suggested that the nature of the surface might play a more active role in determining solloid structure. These authors postulated the existence of a low concentration of strongly acid surface sites on silica, which would act to strongly bind individual cationic surfactants. These strongly bound surfactants would then template the formation of small aggregates. There have also been suggestions that silica surfaces might also possess a hydrophobic binding component [15,63]. We have recently found strong evidence for both suggestions [9]. Using EPR spectroscopy applied to a spin-labeled form of HTAB we found evidence that cationic surfactants on silica bind strongly at a small number of charged sites. By comparing the binding of spin-labeled HTAB with HTAB we inferred that the binding site must also include a hydrophobic component. Unknown to us at the time was the extensive chromatographic literature on the nature of silica surfaces. Based on the retention behavior of amines on silica surfaces and other experiments it had been established that there exist a small number of strongly acidic sites on silica [64–66]. From Fourier transform (FT) IR and NMR studies it was inferred that these sites correspond to isolated silanols [67–70]. Chromatographic studies also showed evidence for weak hydrophobic sites on silica at low and neutral pH values [67–70]. These hydrophobic sites were assigned to siloxane groups (Si–O–Si) [71,72]. Available evidence suggests that siloxanes in water should be hydrolyzed to silanol groups, however the rate of this process is much slower at acidic and neutral pH values [73] and so it seems reasonable to postulate that siloxane groups are present under these conditions. What does not appear to previously have been appreciated is that isolated silanols must be surrounded by such siloxane groups, as the surface of silica consists of only these two components (possible trace metal impurities appear to be unimportant [72]). Therefore the strong binding site found in chromatography must have both an electrostatic and a hydrophobic component and so correspond to the strong binding site for cationic surfactants that we have identified.

2. Experimental

2.1. Equipment

EPR spectra were obtained from a hybrid EPR spectrometer consisting of an X-band (approximately 9 GHz) Varian E-109 bridge with IBM ER 073 10 in. magnets and a IBM ER 082 (155/45) power supply (1 in.=2.54 cm). The magnetic field was controlled via a Bruker B-H15 field controller. The samples were placed in a 0.3 mm flat cell and this was placed into a Varian TE102 rectangular microwave cavity. All spectra were collected using 100 kHz modulation frequency. Data were collected using a Macintosh II computer running Labview. EPR spectra were analyzed using least-squares fitting of simulated spectra as described previously [9].

2.2. Chemicals

4-[*N*,*N*-Dimethyl-*N*-(*n*-hexadecyl)ammonium]-2,2,6,6-tetramethylpiperidinyl-*N*-oxy bromide (HTAB*) was prepared following the procedure of Kwan et al. [74]. In the study of salicylate binding to cetylpyridinium the iodide form of HTAB* was used, as purchased from Molecular Probes. Hexadecyltrimethylammonium bromide (HTAB), cetylpyridinium chloride (CPC) and potassium peroxylamine disulfonate (PADS) were purchased from Aldrich, and used

as supplied. The cetylpyridinium salicylate salt was a gift from Professor Claude Treiner of the University of Paris. The silica used was Aerosil 200 from DeGussa Corporation and is a non-porous, fumed silica with surface area of 200 m^2/g and average particle size of 12 nm.

3. Results and discussion

3.1. Studies of HTAB solloids

EPR spectroscopy can give information about the polarity, viscosity and concentration a spin-probe experiences. The most popular spin-labels used are nitroxyl radicals which incorporate the >N–O (nitroxide) group. In this work we have used two spin-probes that contain this group. The first is 4-[*N*,*N*-dimethyl-*N*-(*n*-hexadecyl)ammonium]-2,2,6,6-tetramethylpiperidinyl-*N*-oxy bromide (HTAB*, **1**). This spin-probe can best be thought of as the cationic surfactant HTAB with one methyl group replaced by a six-membered ring containing the nitroxide group. The other spin-probe is potassium peroxylamine disulfonate, which is the nitroxide radical with two sulfonates groups attached. For both spin-probes the EPR spectrum consists of three lines which correspond to the nitrogen hyperfine interaction with the unpaired electron. The relative widths and heights of the three lines give quantitative information about the rate of rotation of the spin-probe about the molecular axes. When the spin-probe is incorporated within a surfactant aggregate the local viscosity changes from that of water and this is observed as a change in the relative heights and widths of the three peaks. This is illustrated in Fig. 3, which shows EPR spectra from HTAB* in aqueous solution, in HTAB micelles, and incorporated into HTAB solloids on silica. In aqueous solution (Fig. 3a) the linewidths of the three peaks in the EPR spectrum are very similar indicating that rotation is relatively rapid. In micelles (Fig. 3b) rotation is an order of magnitude slower and not completely isotropic, this is also the case in solloids. Fig. 4 shows the rotational correlation times calculated for HTAB* in HTAB solloids at pH 7 for various HTAB concentrations. Two rotational correlation times τ_b, and τ_c are shown, and correspond to rotation about different molecular axes. Above 10^{-3}

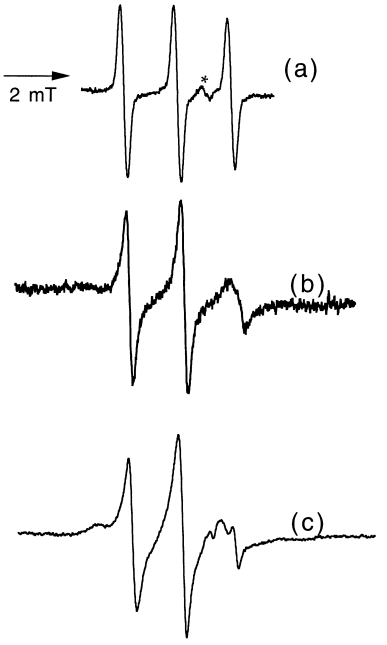

Fig. 3. EPR spectra from HTAB* (a) 10^{-4} *M* in solution, (b) 10^{-4} *M* in HTAB micelles ([HTAB] 10^{-2} *M*), (c) in HTAB solloids on silica, $4\cdot10^{-3}$ *M* HTAB, 1% (w/w) silica.

M [HTAB] the two rotational correlation times are constant and comparable with the values in micelles $\tau_b=2.1\cdot10^{-9}$ s and $\tau_c=1.1\cdot10^{-9}$ s found previously [36]. This indicates that some rotational anisotropy exists, which is consistent with formation of surfac-

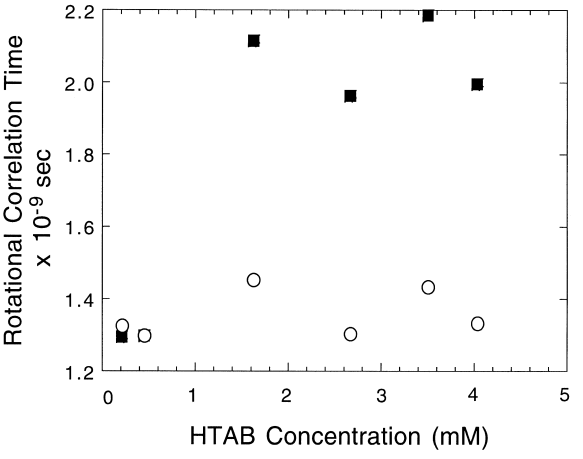

Fig. 4. Rotational correlation times for HTAB* adsorbed on 1% (w/w) silica as a function of total surfactant concentration, (■) τ_b, (○) τ_c.

tant aggregates. That the values are similar to those for micelles indicates that unlike SDS solloids on alumina [47], adsorption on the surface does not prevent relatively free lateral motion. Below 10^{-3} *M* [HTAB] the rotational correlation times appear to be higher than for HTAB* in solution, but less than those for HTAB* in micelles. It is not yet clear if this reflects the structure of the solloids present or if this is an artifact of the fitting procedure used.

3.2. Counterion binding to HTAB aggregates

There have been no reported spectroscopic studies of binding of counterion binding to solloids, apart from indirect evidence for binding of ferricyanide anions to HTAB solloids on silica [36]. Following the reports by Favoriti and co-workers [37–39] of unusual behavior of pyridinium salicylate salts we initiated a series of spectroscopic studies of the binding counterions to solloids using EPR. For studying binding to cationic solloids the spin-probe peroxylamine disulfonate (**2**, PADS) was used as it is relatively small and gives sharp EPR spectra. When this spin-probe binds to micelles a decrease in rotational mobility is observed [50] as changes in relative width of the three lines in the EPR spectrum. In the presence of HTAB solloids adsorbed on silica, substantial changes in the EPR spectrum result. This can be seen in Fig. 5 which shows the EPR spectra and rotational correlation times of PADS with 1% (w/w) silica particles as the HTAB concentration is varied. Below the hemimicelle concentration (HMC) the form of the EPR spectra is similar to those of PADS in aqueous solution, and the rotational correlation times are low. Once HTAB solloids start to form the EPR spectrum changes markedly and the rotational correlation times increase steadily, rising to $\tau_b = 2.3 \cdot 10^{-10}$ s and $\tau_c = 9 \cdot 10^{-10}$ s. In comparison the rotational correlation times of PADS bound to HTAB micelles are $\tau_b = 3.42 \cdot 10^{-11}$ s and $\tau_c = 2.4 \cdot 10^{-10}$ s, and in solution the rotational correlation time is [75] $3 \cdot 10^{-12}$ s. In calculating these values the assumption has been made that there is no substantial change in *g* values or hyperfine tensor when PADS binds to micelles or solloids. Noteworthy are the order of magnitude difference between the two rotational correlation times, which indicates a substantial difference in rotation about the different molecular axes, and the large increases in rotational correlation time between solution, micelles, and solloids. It seems likely that this reflects the charge distribution in PADS, which would be expected to favor motions

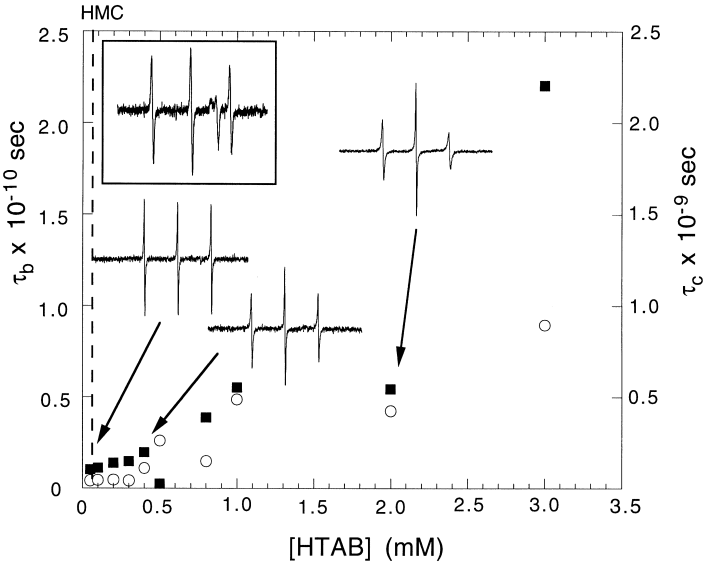

Fig. 5. Rotational correlation times for PADS binding to HTAB on 1% (w/w) silica as a function of total surfactant concentration, (■) τ_b, (○) τ_c. Representative EPR spectra at indicated HTAB concentrations, inset is PADS in the presence of HTAB micelles.

that keep both sulfonate groups near the HTAB headgroups. From the EPR spectra it is not possible to determine if PADS is bound in the double layer between HTAB headgroups and silica surface, or to the top layer of a double layer structure. In very recent work using high frequency EPR we have seen evidence suggesting that PADS is bound at the HTAB–silica double layer [76]. This in turn would suggest that the lower rotational correlation times observed for PADS bound to HTAB solloids reflects the lower mobility within the double layer between silica surface and HTAB headgroups.

3.3. Studies of salicylate counterions binding to cetylpyridinium aggregates

PADS is bound to cetylpyridinium chloride micelles, with rotational correlation times of $\tau_b = 2 \cdot 10^{-11}$ s and $\tau_c = 6 \cdot 10^{-11}$ s, which are much smaller and more isotropic than those observed for HTAB micelles and solloids. When bound to CPS micelles much larger changes in rotational correlation times are observed. The EPR spectra show the very clearly the presence of two different species with different g values, hyperfine coupling constant, and rotational correlation times. Preliminary analysis of the spectra gives values of $\tau_b = 4 \cdot 10^{-12}$ s and $\tau_c = 7 \cdot 10^{-10}$ s for the major (80%) species and $\tau_b = 3 \cdot 10^{-12}$ s, $\tau_c = 10^{-11}$ s for the minor species. High frequency (W-band) studies confirm the presence of two species with different g values and rotational correlation times for PADS bound to CP) [76]. A difference in the nitrogen hyperfine coupling constant is also found, consistent with the major component being PADS in a less polar environment. That is incorporated in the double layer among the salicylate ions.

The spin-probe HTAB* has also been used to study the effect on cetylpyridinium aggregation of replacing chloride with salicylate. Fig. 6 shows the experimental and simulated EPR spectra for CPC and CPS at concentrations ca. $3 \cdot 10^{-2}$ M in the presence and absence of 2% (w/w) silica. In the absence of silica the rotational correlation times for HTAB* are $\tau_b = 8.5 \cdot 10^{-10}$ s and $\tau_c = 1.4 \cdot 10^{-9}$ when incorporated in CPC micelles, and $\tau_b = 1.2 \cdot 10^{-9}$ s and $\tau_c = 2.7 \cdot 10^{-9}$ s when incorporated in CPS micelles. The presence of the salicylate ions within the double layer at the micelle surface therefore acts to cause a significant increase in rotational correlation times. At comparable surfactant concentrations in the presence of silica the rotational correlation times are $\tau_b = 6.7 \cdot 10^{-10}$ s and $\tau_c = 1.5 \cdot 10^{-9}$ s for CPC solloids and $\tau_b = 1.2 \cdot 10^{-9}$ s and $\tau_c = 2.9 \cdot 10^{-9}$ s for CPS solloids. For both counterions any increase in rotational correlation time is small. This is similar to the result for HTAB above, where micelles and solloids appear to have very similar mobilities.

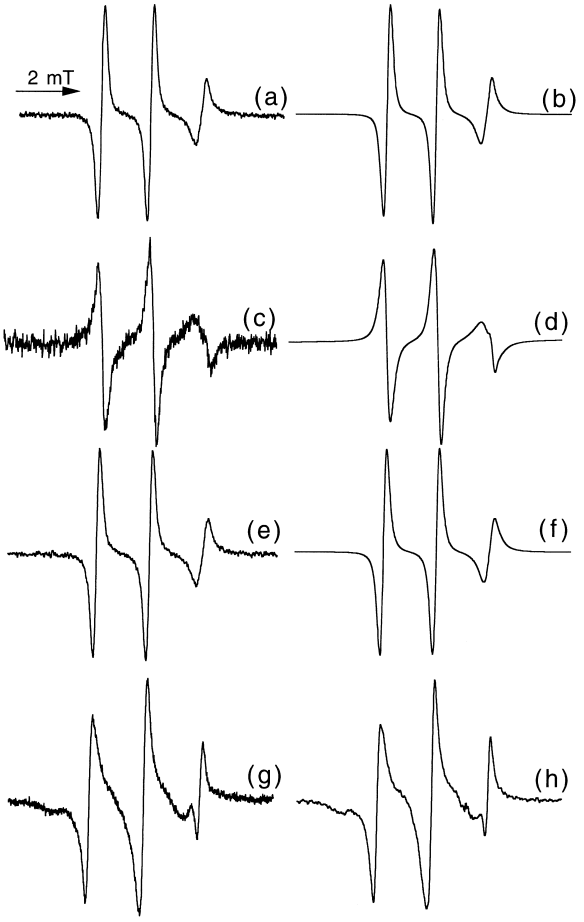

Fig. 6. EPR spectra of HTAB* (a) in 0.1 M CPC micelles, (b) simulated, (c) in 0.1 M CPS micelles, (d) simulated, (e) with $4 \cdot 10^{-2}$ M CPC and 2% (w/w) silica, (f) simulated, (g) with $3.2 \cdot 10^{-2}$ M CPS and 2% (w/w) silica, (h) simulated.

It is also of interest to consider how the HTAB* probe partitions between the various environments. For CPC micelles the ratio of HTAB* bound to the micelle to that in solution is 35:1, whereas for CPS micelles the ratio is 26:1. Since the surfactant

concentration is the same for both (0.1 *M*) this is clear evidence for stronger inclusion in CPS micelles than in CPC micelles. In the presence of silica, the presence of the strong binding site provides a third environment for HTAB*. For CPS on silica, HTAB* bound to surface sites was found to be the major species; accounting for 55% of the HTAB*, 40% was in solloids and 5% in solution, giving an solloid:solution ratio of 8:1. For CPC on silica no more than ca. 20% of the HTAB* was bound to the surface 75% was incorporated in CPC solloids and 2% was in solution, giving an solloid:solution ratio of 40:1. The smaller fraction of HTAB* on the surface in the presence of CPC compared to CPS, suggests that the cetyl pyridinium cation competes more aggressively for the surface sites in the presence of chloride than for salicylate. This is consistent with a larger fraction of the salicylate ions binding than of the chloride ions. This would give better charge compensation and so lower the electrochemical potential of the solloids relative to that of the surface site. For CPC micelles and solloids the ratio of HTAB* in aggregates vs. solution is not significantly different, again suggesting that the micelles and solloids are not significantly different in their properties in this concentration range. For CPS the difference is more significant suggesting that CPS solloids are significantly better at solubilizing HTAB* than CPS micelles.

Based on the EPR evidence presented above we do not see changes in the behavior of the HTAB* spin-probe that would suggest the type of aromatic stacking that Treiner and co-workers have suggested. However, indications are that PADS is much more sensitive to changes in the double layer, and so we are currently carrying out a study of adsorption of CPS and CPC on silica using this spin-probe.

3.4. Linear solvation–energy relationship analysis of adsolubilization in HTAB on silica

There is already qualitative evidence that as solloid structure changes adsolubilization properties change [77]. In a soon to be published work Holzheu and co-workers provide the data to demonstrate this in a more quantitative manner [15,78]. These workers report chromatographic retention data for 26 solutes for a stationary phase of HTAB adsorbed on silica. Two different HTAB concentrations and pH values are reported. This data provides the basis for a LSER type analysis, such as is summarized in Eq. (1)

$$\log K = c + nR_2 + mV_i/100 + s\pi^* + b\beta_m + a\alpha_m \quad (1)$$

where K is an equilibrium constant, $V_i/100$, is the molecular volume, R_2 is excess molar refraction, π^* describes the dipolarity–polarizability, β_m describes the hydrogen bond basicity, and α_m describes the hydrogen bond acidity [79]. These parameters are collectively referred to as solvatochromic parameters as they were first determined from changes in the peak positions of adsorption and emission peaks [80]. For such an analysis to be used to quantitatively describe the properties of a solvent it is necessary to have appropriate solvatochromic parameters for each solute. The parameter set developed by Kamlet and co-workers [80–82] and extended by Abraham and co-workers [79,83,84] is perhaps the best known and has provided the basis for successfully correlating a wide range of properties. Unfortunately, the solvatochromic parameters have been determined for only 18 of the 26 solutes studied. Since there are seven variable parameters this means that there are only 11 degrees of freedom, or described another way: there are only 2.5 observations per variable which falls well short of the 5:1 ratio recommended by Abraham [84]. An alternative approach is to estimate the necessary solvatochromic parameters, by a method such as that given by Hickey and Passino–Reader [85] (H&PR). In this case all 26 solutes can be used, as described below. A third alternative is to use quantum chemistry to calculate comparable parameters as advocated by Famini and co-workers [86–88] among others. We are currently exploring this last option with some success. In order to provide a basis for comparison between the different approaches, and to allow comparison between solloid properties and micelle properties we are also investigating the work of Quina et al. on solubilization in micelles [89].

Table 1 summarizes the values of the LSER parameters for adsolubilization in HTAB solloids on silica at pH 5 and pH 8 at two different HTAB concentrations. That at pH 5 is at an HTAB con-

Table 1
Summary of solvent parameters using solute parameters from Abraham and co-workers [79,84,90,91]

	pH 5			pH 8, Regions I&II			pH 8, Region III			Micelle[a]		
	Value	S.E.[b]	P[c]	Value	S.E.	P	Value	S.E.	P	Value	S.E.	F
Intercept	−0.910	0.222	$1.4\cdot10^{-3}$	−1.624	0.571	$1.5\cdot10^{-3}$	−1.778	0.818	0.05	−0.759		
$V_i/100$	5.66	0.44	$2.4\cdot10^{-8}$	6.673	1.093	$5.3\cdot10^{-5}$	7.445	1.529	$3.9\cdot10^{-4}$	3.57	0.22	273
R_2	0.618	0.146	$1.1\cdot10^{-3}$	0.031	0.297	0.91	0.017	0.671	0.98	0.766	0.18	17.7
π^*	−0.684	0.130	$2.0\cdot10^{-4}$	−0.104	0.249	0.68	−0.235	0.529	0.66	−0.32	0.20	2.7
β_m	−2.02	0.21	$6.2\cdot10^{-7}$	−2.090	0.437	$4.5\cdot10^{-4}$	−2.794	0.755	$3.0\cdot10^{-3}$	−3.78	0.26	218.2
α_m	0.790	0.110	$1.1\cdot10^{-5}$	1.403	0.227	$4.6\cdot10^{-5}$	1.964	0.372	$1.9\cdot10^{-4}$	1.023	0.19	29.2
R	0.986		$F=84.8$	0.944		$F=19.7$	0.901		$F=10.5$	0.986		$F=273$

[a] From Quina et al. [89].
[b] Standard error.
[c] The P statistic gives the probability of randomly obtaining this degree of correlation for the particular parameter.

centration corresponding to region III of the adsorption isotherm, the pH 8 data corresponds to regions I&II, and to region III. The last column is that for HTAB micelles. The correlations are between 0.986 and 0.90 which are considered excellent, and certainly comparable to the value of 0.986 reported by Quina et al. [89]. The overall F statistics range from 85 down to 10.5 which indicates that in all cases these are good models to describe the retention times. However the F statistic is much lower than that reported by Quina et al., presumably because the number of observations is much lower. The LSER analyses using the H&PR estimated solvatochromic parameters are summarized in Table 2. The correlations are not as good as those found using the Abraham parameters, and despite the larger number of observations used, the F statistic is generally lower. The two sets of analyses can also be compared in terms of the degree of correlation, this is shown in Figs. 7 and 8, which compare the experimental and calculated retention times on a log scale. The scatter for the LSER using Abraham's parameters is noticeably smaller and does not appear to have any particular trend. The LSER using the H&PR parameters shows a larger scatter, particularly at long retention times and, in the case of the micelle data, does show systematic deviations.

It is of interest to compare the values of the various parameters between the different solloids and the micelle. With the sole exception of the Abraham fit to HTAB micelles, the dominant component is the molecular volume. This is consistent with removing generally hydrophobic solutes from water into a non-aqueous phase. The hydrogen bond basicity and acidity (β_m and α_m) are important for all four systems using both sets of parameters, with negative values for the hydrogen bond basicity and positive values for the hydrogen bond acidity. At low pH

Table 2
LSER values fitted to solute adsorption in HTAB solloids on silica and in micelles using estimated solvatochromic parameters

	pH 5			pH 8, Regions I&II			pH 8, Region III			Micelle		
	Value	S.E.[a]	P[b]	Value	S.E.	P	Value	S.E.	P	Value	S.E.	P
Intercept	−0.620	0.434	0.179	−0.242	0.417	0.57	−0.627	0.484	0.21	−0.656	0.259	$1.4\cdot10^{-2}$
$V_i/100$	5.00	0.706	$9.6\cdot10^{-7}$	4.16	0.659	$3.7\cdot10^{-6}$	4.84	0.785	$5.0\cdot10^{-6}$	4.70	0.478	$4.2\cdot10^{-13}$
π^*	0.295	0.200	0.16	0.256	0.183	0.18	0.506	0.231	$4.1\cdot10^{-2}$	0.533	0.230	$9.2\cdot10^{-3}$
β_m	−2.63	0.440	$9.7\cdot10^{-6}$	−1.90	0.388	$8.8\cdot10^{-5}$	−2.845	0.485	$9.7\cdot10^{-6}$	−2.76	0.470	$3.8\cdot10^{-7}$
α_m	0.921	0.235	$9.3\cdot10^{-4}$	1.30	0.208	$4.1\cdot10^{-6}$	1.851	0.258	$6.1\cdot10^{-7}$	0.105	0.455	0.74
R/F	0.86		$F=14.2$	0.86		$F=14.4$	0.87		$F=16.6$	0.86		$F=40.7$

[a] Standard error.
[b] The P statistic is the probability of randomly obtaining this degree of correlation for the individual.

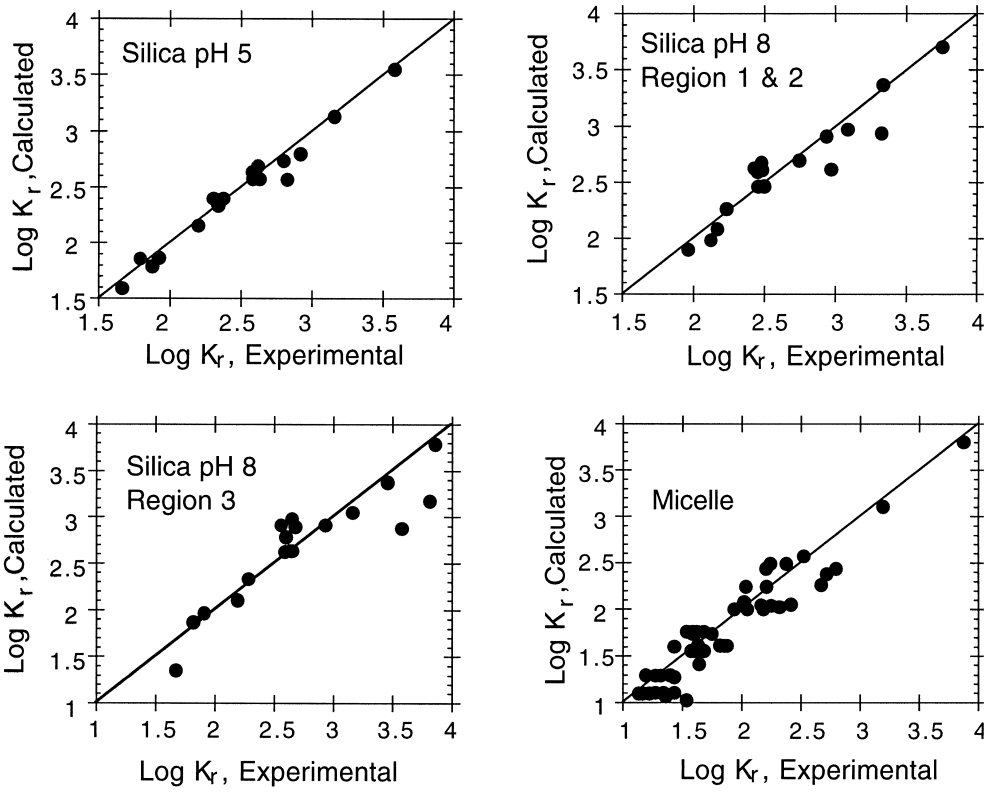

Fig. 7. Correlation plots for LSER analyses using Abraham's solvatochromic parameters.

using the Abraham LSER, the R_2 and π^* terms are important with the polarizability having a negative value, but at higher pH and in micelles neither term is particularly significant. Using the H&PR parameters the polarization is significant only at high pH and HTAB concentrations and in micelles. Comparing pH 5 (region III) and pH 8, region III both analyses suggest that at higher pH hydrogen bond acidity becomes more important, and that hydrogen bond acidity becomes a large negative factor. A similar trend is observed for comparisons between the two sets at pH 8. From EPR studies of the effect of pH on HTAB aggregation we determined that as pH rose the degree of surfactant aggregation at given concentration increased. Interestingly enough the two best fits: those at pH 5 and for HTAB micelles using the Abraham parameters also show the strongest similarity between the fitted parameters. This is consistent with our expectation of the nature of the HTAB solloids at low pH, i.e., a low surface charge density, which should give counterion binding similar to that in HTAB micelles and so predicts properties similar to HTAB micelles.

4. Conclusions

The structure and properties of hexadecyltrimethylammonium and cetylpyridinium solloids on silica surfaces has been investigated using EPR spin-probes. The HTAB probe is sensitive to changes occurring among the headgroups, and the results suggest that at low pH the properties of the HTAB, CPC and CPS solloids are not greatly different from those of the corresponding micelles. Although some differences were noted. This is in agreement with LSER analysis of equilibrium constant data which suggests that the properties of the solloids at pH 5 are most similar to those of the micelles. Using the small anionic PADS spin-probe much larger changes

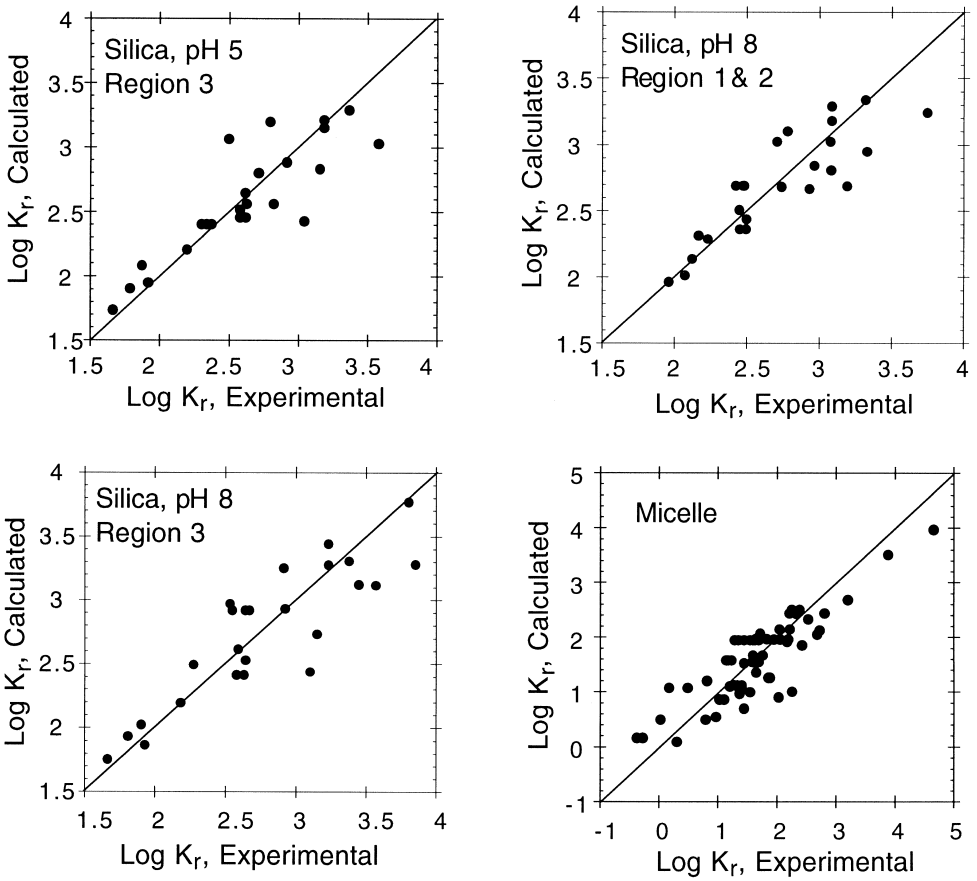

Fig. 8. Correlation plots for LSER analyses using Hickey–Passino-Reader solvatochromic parameters.

were found in the properties of the double layer between HTAB, CPC and CPS micelles. Large changes were also found as a function of HTAB concentration on silica surfaces indicating substantial changes in the physical properties in the silica–HTAB double layer.

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