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The Interactions of Surfactant Viologens with Cyclodextrins

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Abstract. *N*-ethyl-*N'*-hexadecyl-4,4'-bipyridinium bromide ($C_{16}VBr_2$) and *N*-ethyl-*N'*-octadecyl-4,4'-bipyridinium bromide ($C_{18}VBr_2$) were used as electroactive probes to assess the interactions between surfactants and cyclodextrins. Cyclic voltammetry, visible spectroscopy, fluorescence spectroscopy and surface tension techniques were used to detect the formation of complexes between the surfactant viologen probes and α- and β-cyclodextrins. The voltammetric results suggest the formation of inclusion compounds in which the hydrophobic tail of the surfactant viologens penetrate the cyclodextrin cavity. The dimerization of the viologen cation radicals is essentially suppressed by the presence of α-cyclodextrin (ACD) while no effects are observed in the presence of β-cyclodextrin (BCD). The observed results are best explained by the relative solubility in aqueous media of each of the inclusion complexes in the several accessible viologen oxidation states.

Key words. Cyclodextrin, viologens, surfactant, voltammetry.

1. Introduction

Cyclodextrins [1–3] are glucopyranose cyclic oligomers having a characteristic toroidal shape. These compounds are soluble in aqueous media because of the hydrophilic nature of the outer surface of the torus. The inner surface is more hydrophobic and thus hydrated cyclodextrins represent a high energy state that can readily accept guest hydrophobic molecules in place of the inner water molecules [1]. Indeed, as expected for inclusion complexes, the better the fit of the guest molecule in the inner cavity of the cyclodextrin the more stable the host–guest complex will be [1–3]. β-Cyclodextrin (BCD, 7 glucopyranose units) forms complexes with many organic molecules because its cavity is perfectly suited to include substituted phenyl rings and many other commonly found groups. α-Cyclodextrin (ACD, 6 glucopyranose units) does not form so many complexes because of its smaller cavity diameter. However, the examination of CPK models reveals that ACD is well suited to bind compounds having long, linear alkyl chains such as surfactants.

Scattered reports are available in the chemical literature concerning the interactions of surfactants and cyclodextrins. For instance, Ise and coworkers [4] have reported on the interaction of colloidal electrolytes and cyclodextrins. They observed that the apparent critical micelle concentrations (cmc) of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTABr) increase upon the addition of ACD and BCD. They concluded that the cyclodextrins form 1 : 1 complexes with the surfactants. More recently Satake *et al.* [5] determined the association constants of ACD with several ionic surfactants. For 1-alkanesulfonate

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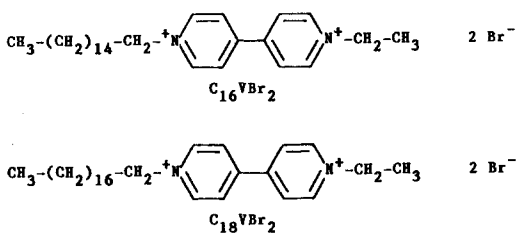
ions with 5–12 (n) carbon atoms in the alkyl chain, the association constant was found to increase regularly with n and become abruptly constant at $n = 10$. The association constants with sodium 1-dodecanesulfonate, dodecylammonium chloride, dodecyltrimethylammonium chloride, and 1-dodecylpyridinium chloride were all similar in magnitude.

Thomas and coworkers [6] have investigated the formation of cyclodextrin-surfactant-aromatic fluorophore ternary complexes. Quite recently, Kusumoto *et al.* [7] have also reported on the interaction of pyrene with BCD in aqueous surfactant solutions. Yasuda *et al.* [8] have studied the interactions between several rather hydrophobic viologens and BCD aiming at the development of a practical electrochromic display system. Willner and Eichen [9] have found that a complex between octylviologen and BCD acts efficiently as a photoelectron collector on the surface of CdS and TiO_2 colloidal particles. It is then clear that (1) the interactions between surfactants and cyclodextrins are rather unexplored, and (2) the use of surfactant viologens for this purpose appears as very appropriate not only because of the electroactivity imparted by the viologen group (which enables the use of electrochemical techniques for the characterization of the interactions) but also because the properties of previously known viologen-cyclodextrin complexes appended an additional interest to the study.

In this work we report the interactions of ACD and BCD with the following two surfactant viologens:



2. Experimental

The surfactant viologen bromides, $C_{16}VBr_2$ and $C_{18}VBr_2$, were synthesized as reported elsewhere [10]. ACD and BCD were obtained from Fluka or Aldrich and used without further purification. No difference in behavior was detected with cyclodextrins purchased from different suppliers. Pyrene (Sigma) was recrystallized from ethanol. All solutions were freshly prepared with distilled water that had been further purified by passage through a pressurized, four-cartridge Barnstead Nanopure system.

The equipment for the electrochemical experiments has been already described. [11]. Absorption spectra were measured with a Hewlett Packard 8452A spectrophotometer. Steady-state emission spectra were recorded with an Aminco Bowman spectrophotofluorimeter. Surface tension measurements were performed on a Fisher Model 20 tensiometer using the du Nuoy method with platinum-iridium rings.

A two-compartment cell was used to obtain the cyclic voltammograms. All solutions were thoroughly deoxygenated by purging with purified nitrogen. A nitrogen blanket was maintained above the solution during the electrochemical experiments. Glassy carbon and platinum working electrodes (Bioanalytical Systems, Indiana) were regularly polished following standard procedures prior to use. All potentials were measured against the sodium chloride saturated calomel electrode (SSCE).

Samples of the viologen cation radicals were prepared by controlled potential electrolysis of solutions containing adequate concentrations of the parent dications. These electrolyses were directly performed in a spectrophotometer cuvette in which a glass strip covered with SnO_2 (transmittance 80%, Delta Technologies) was affixed to one of the optical windows so that the conductive surface faced the solution in the cuvette, thus allowing its use as the working electrode. The auxiliary and reference electrodes were situated out of the optical pathway of the spectrophotometer. This arrangement allowed the recording of the visible spectra for the reduced viologen species either in deposited films at the electrode surface or in solution.

3. Results and Discussion

Several asymmetric viologens with surfactant properties have been previously reported in the chemical literature. For instance, Gratzel and coworkers have published the synthesis and aggregation properties of a series of asymmetric, amphiphilic viologens [12]. We have already reported the synthesis and aggregation properties of $C_{16}V^{2+}$ and $C_{18}V^{2+}$ [10]. Both of these viologen derivatives form micelles and show well defined cmc values in pure water (2.8 and 1 mM, respectively). It was of interest to this work to obtain cmc values in aqueous 50 mM NaCl solutions since this is the medium commonly used for cyclic voltammetry experiments. Figure 1 shows the surface tension of 50 mM NaCl aqueous solutions containing variable concentrations of $C_{16}V^{2+}$. The shape of the plot is characteristic of micelle formation with an apparent cmc slightly below 0.4 mM. Under the same experimental conditions the cmc of $C_{18}V^{2+}$ was determined to be 0.03 mM.

The association of the surfactant viologen with the cyclodextrins was initially assessed by using the emission spectral characteristics of pyrene. To this end, a saturated solution of pyrene in 50 mM NaCl was prepared by stirring several pyrene crystals in the solution for about 12 h, followed by filtration to remove undissolved pyrene crystals. According to reported accounts [13], the final pyrene concentration in this saturated solution is about 5×10^{-7} M. Enough $C_{16}VBr_2$ was then added to this solution to make the concentration of the surfactant viologen dication 1.0 mM. The characteristic emission spectrum of pyrene was barely observable under these conditions (excitation wavelength: 332 nm). This is probably the result of effective quenching of the excited state pyrene molecules by the viologen acceptors. If one accepts the current view of solubilization of hydrophobic molecules by ionic surfactant micelles, the pyrene molecules must reside near the Stern layer in very close proximity to the polar viologen groups. This spatial proximity would explain satisfactorily the highly efficient level of quenching observed. Addition of ACD to this solution appears to diminish the efficiency of the quenching process. In the

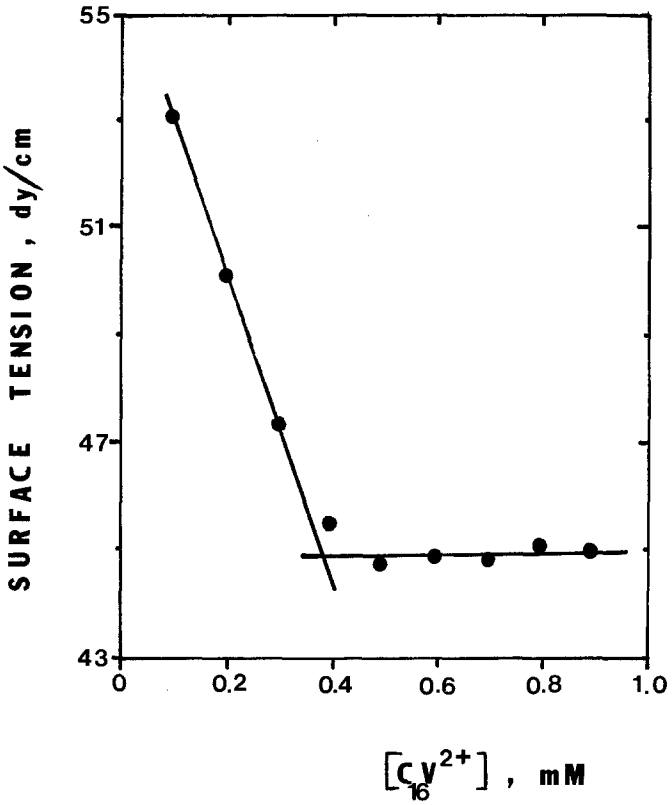


Fig. 1. Concentration dependence of the surface tension of an aqueous solution containing 50 mM NaCl and variable concentrations of $C_{16}VBr_2$.

presence of 1 mM ACD, the emission intensity increases substantially. This cyclodextrin-induced increase in the observed fluorescence intensity quickly levels off at ACD concentrations above 3 mM. It has been previously established that the ACD cavity is too small to form host–guest complexes with pyrene [7]. Thus, these results can only be explained by the formation of a rather stable complex between the surfactant viologen and ACD. The cyclodextrin host associates with the surfactant viologen molecules, causing the concentration of free viologen to decrease below the cmc (in effect destroying the micelles) and releasing the pyrene molecules to the bulk solution where the quenching process proceeds more slowly at diffusion-controlled rates. The slower quenching rate explains the observed increase in the fluorescence intensity. In agreement with this interpretation, the relative intensities of the vibronic bands in the fluorescence spectrum of pyrene after the addition of ACD correspond to those expected for an isotropic aqueous solution [13], thus supporting the disruption of the micellar aggregates by the cyclodextrin host.

The complexation of the surfactant viologens by the cyclodextrins was also clearly demonstrated with surface tension data. Figure 2 shows the surface tension of 50 mM NaCl aqueous solutions also containing 1.0 mM $C_{16}VBr_2$ as a function of the concentration of added ACD. In the absence of ACD, the surface tension is

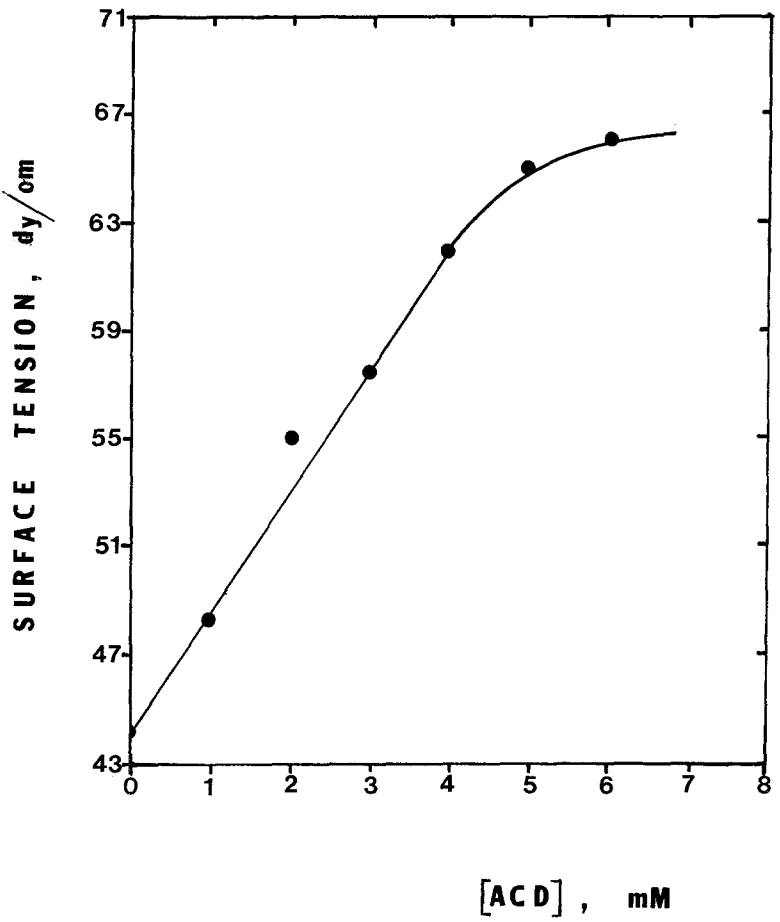
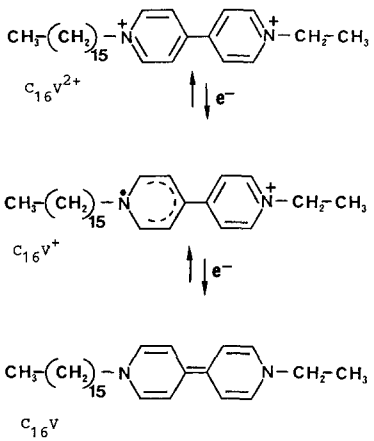


Fig. 2. Effect of ACD additions on the surface tension of a solution containing 50 mM NaCl and 1.0 mM $C_{16}VBr_2$.

44 dyne/cm. However, the addition of ACD causes a quick increase of the surface tension. When the ACD concentration is increased to the 4–5 mM level, the surface tension reaches values characteristic of surfactant-free solutions. Similar observations were made with 1.0 mM solutions of $C_{18}V^{2+}$. Since ACD does not have any surface activity [14], the increase in the surface tension values is attributable to the formation of a surfactant-cyclodextrin complex. Hence, as the concentration of the cyclodextrin increases, the concentration of free viologen in solution decreases. In turn, this diminishes the concentration of surfactant viologen ions at the air-solution interface, thus increasing the surface tension of the solution. Therefore, the addition of cyclodextrin has the overall effect of removing surfactant viologen ions from the air-solution boundary via complexation of the free viologen in the solution.

The redox behavior of the surfactant viologens is represented in Scheme I, exemplified by $C_{16}V^{2+}$. As any viologen, these surfactants can be reduced in two consecutive monoelectronic steps to yield, first, a cation radical, and, second, an



Scheme I.

uncharged, hydrophobic species. Both reductions are chemically reversible. However, the voltammetric behavior of these surfactants is highly complicated by precipitation of the two reduced forms, $C_{16}V^+$ and $C_{16}V$, at the electrode surface. These precipitation reactions have been previously reported with other hydrophobic viologens, like the commercially available heptylviologen [14], and form the basis for the proposed use of viologens as active components in electrochromic systems.

In contrast to this, the first reduction of $C_{16}V^{2+}$ in the presence of a ten-fold excess of ACD is free of these precipitation effects as shown in the voltammogram of Figure 3. The potential separation between the reduction and the oxidation peaks is about 60 mV for moderate scan rates, and a plot of reduction peak current vs the square root of scan rate was found to be linear in the range 20–400 mV/s. Both of these pieces of evidence clearly indicate that the first reduction is a reversible, diffusion-controlled electrochemical process which was assigned to the reduction of the ACD–$C_{16}V^{2+}$ complex, that is

$$\text{ACD–}C_{16}V^{2+} + e \rightleftharpoons \text{ACD–}C_{16}V^{2+}, \qquad E^{0'} = -0.66 \text{ V}.$$

The half-wave potential, as obtained from the average of the reduction and oxidation peak potentials, is very close to that reported for the more hydrophilic methylviologen (-0.69 V vs the same SSCE reference electrode) [15]. This probably reveals that the electroactive 4,4′-bipyridinium moiety is essentially unaffected by the complexation, arguing in favor of an inclusion complex between the lipophilic tail of the surfactant and the cyclodextrin host.

In the presence of a ten-fold excess of ACD, if the negative potential scan is extended to -1.0 V vs SSCE (using glassy carbon electrodes), a second reduction wave is observed. However, its shape is strongly distorted by precipitation processes indicating that the electrogenerated species (ACD–$C_{16}V$) is no longer soluble in the electrolysis medium. The first reduction couple of $C_{16}V^{2+}$ in the presence of ACD at concentration levels below 10 mM is also distorted by precipitation of the residual uncomplexed $C_{16}V^{2+}$. It is thus necessary to add an excess of cyclodextrin to the surfactant solution in order to decrease substantially the concentration of free

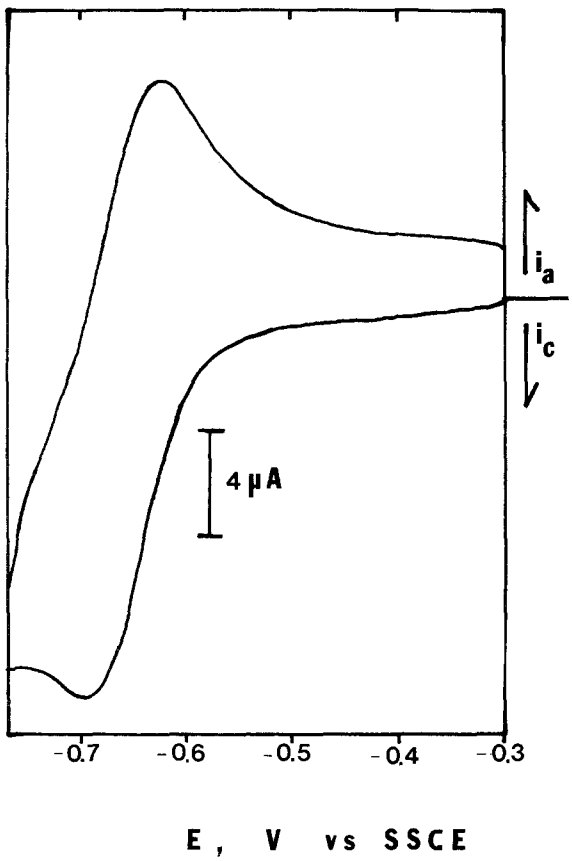


Fig. 3. Cyclic voltammogram on Pt of 1.0 mM $C_{16}VBr_2$ also containing 50 mM NaCl and 10 mM ACD. Scan rate = 20 mV/s.

surfactant viologen and allow a clean observation of the ACD–$C_{16}V^{2+}$/ACD–$C_{16}V^{+}$ couple.

The voltammetric behavior of $C_{18}V^{2+}$ in the presence of a ten-fold excess of ACD is close to that observed for the shorter chain analog. However, at slow scan rates a small desorption spike can be seen in the oxidative scan probably as a reflection of the greater hydrophobic character of this surfactant. Nonetheless, the voltammetric response at scan rates faster than 100 mV/s is essentially diffusion-controlled.

A ten-fold excess of BCD also changes the voltammetric behavior of either $C_{16}V^{2+}$ or $C_{18}V^{2+}$. However, the first reduction couple does not exhibit reversible behavior at the scan rates surveyed (up to 1000 mV/s). In both cases, the reduction current appears to be kinetically controlled, perhaps by the dissociation of the BCD complexes, but quantitative analysis of the voltammetric data is hindered by precipitation of the reduced products at the electrode surface.

An important aspect of the aqueous chemistry of viologen cation radicals is their tendency to dimerize [16, 17]. The extent of the dimerization reaction can be easily estimated by visible spectrophotometry of the cation radical solutions. Figure 4 shows the visible spectrum recorded after reduction of a 1mM solution of $C_{16}V^{2+}$

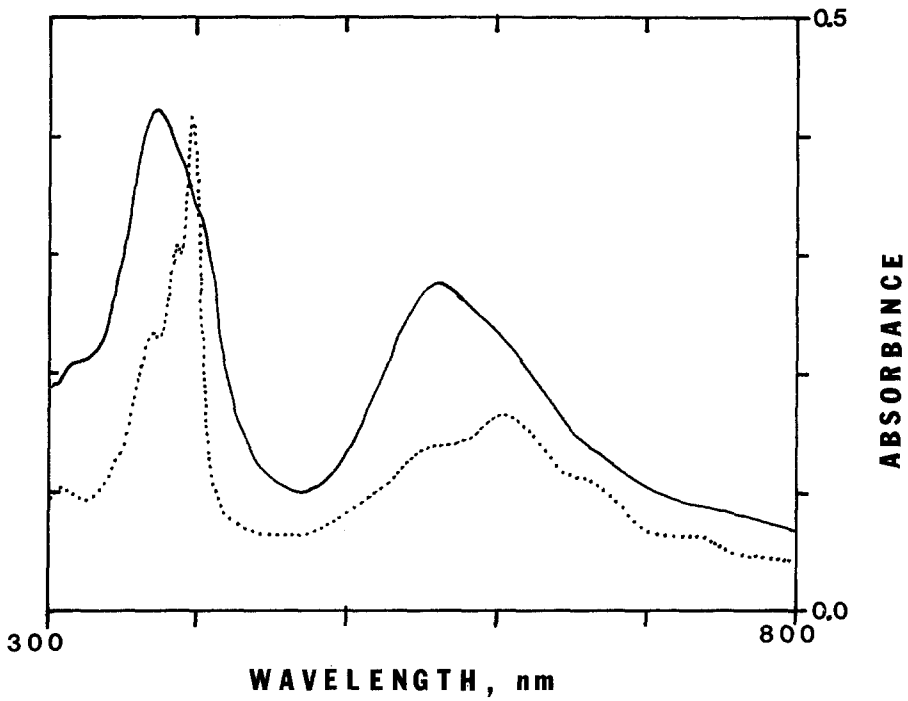


Fig. 4. Absorption spectra of reduced surfactant viologens. (——) 1.0 mM $C_{16}V^+$ in 50 mM NaCl (this spectrum corresponds to the film deposited on the electrode surface). (· · · · ·) 1.0 mM $C_{16}V^+$ + 10 mM ACD in 50 mM NaCl (this spectrum corresponds to an homogeneous solution of the cation radical species).

in the presence of 10 mM ACD (dotted line). The spectrum is characteristic of the monomeric cation radical [16, 17] and does not show any hints of dimer absorption. This is a solution spectrum since the purple color of the cation radical was observed to spread through the solution. In contrast to this, the reduction of $C_{16}V^{2+}$ in the absence of ACD yielded an insoluble purple film on the optically transparent electrode whose visible spectrum is also given in Figure 4 (continuous line). This spectrum shows all the absorptions characteristic of the dimer, and only hints of those corresponding to the monomer. The insoluble blue film is then mostly composed of dimeric $C_{16}V^+$. Interestingly, this behavior was exactly reproduced by the same surfactant viologen in the presence of a ten-fold excess of BCD. Reduction of $C_{18}V^{2+}$ followed an identical pattern, that is, soluble monomeric $C_{18}V^+$ in the presence of a ten-fold excess of ACD, and dimeric deposits in the presence of BCD or in the absence of cyclodextrin hosts. In summary, only ACD appears to be capable of preventing the extensive dimerization and precipitation of these surfactant cation radicals.

Evans and coworkers have published an interesting study of the electrochemical behavior of a ferrocene-carboxylic acid derivative in the presence of BCD [18] and a summary of general guidelines on the electrochemical methodology that can be used to assess the complexation of redox-active molecules by cyclodextrin hosts [19]. However, the amphiphilic character of the surfactant viologens used in this work prevented us from applying most of these methods because the voltammetric

parameters (reduction potentials and diffusion coefficients) of the surfactant viologens in the absence (or at low levels) of cyclodextrins were not accessible due to the precipitation processes observed upon reduction. Therefore, the obtention of complexation equilibrium constants from purely voltammetric data is impossible. We have reported elsewhere [10] the determination of these association constants by a conductometric technique. The results indicate only small differences among the several cyclodextrin-surfactant viologen complexes, with the ACD complexes showing slightly larger association constants. Thus, the thermodynamic parameters of complexation do not appear to be the crucial factors to explain the observed differences in voltammetric and cation radical dimerization behavior. With the experimental information available at this point, it seems adequate to interpret these differences as the result of varying solubilities in the aqueous medium. In this way, the ACD–$C_{16}V^{2+}$ complex is slightly more soluble than the ACD–$C_{18}V^{2+}$ complex because of the slightly shorter alkyl chain of the surfactant. Moreover, BCD complexes must show less solubility as a reflection of the lower aqueous solubility of BCD as compared to ACD. These arguments can explain all the dimerization results and the electrochemical data for ACD complexes but do not explain fully the voltammetric data for BCD complexes where some kinetic effects were clearly detected.

Our research with these systems is still underway in an attempt to better define the thermodynamic and kinetic parameters that determine the behavior of these complexes. We are also currently looking at similar host systems that could be used to control the chemistry of rather reactive species, such as the viologen cation radicals.

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