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Surface activity and redox behavior of nonionic surfactants containing an anthraquinone group as the redox-active site

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Abstract Two new nonionic surfactants, α-anthraquinonyloxyhexyl-ω-hydroxy-*oligo*(ethylene oxide) (ACPEG) and α-anthraquinonyl-ω-hydroxy-*oligo*(ethylene oxide) (APEG), were synthesized. The fundamental interfacial behavior of these surfactants at the air/water interface has been investigated by means of surface tensiometry to provide an insight into the relationship between the structure of the hydrophobic moiety and the surfactant properties, with specific emphasis on the anthraquinone linkage. Aggregation numbers of the surfactants have been determined from static light scattering measurements. At a constant hydration of the ethylene oxide chain, the increase in the hydrophobic chain length in ACPEG raises its hydrophobic interaction and results in enhanced aggregation and significant variation in the interfacial and micellization properties compared to APEG. The electrochemical behavior of the surfactants has also been studied in 0.16 M NaCl aqueous solutions and in 0.1 M tetrabutylammonium perchlorate acetonitrile solutions at the interface of a glassy carbon electrode. A difference in the extent of aggregation has a pronounced effect on the cyclic voltammetric behavior of the surfactants in aqueous solution. In organic media, on the other hand, the redox process depends only on the molecular geometry of the monomeric species. A comparison of the electrochemical responses in the two phases has been made to explain the distinctive features of the redox properties of the surfactants.

Key words Surfactant · Anthraquinone · Surface activity · Aggregation · Redox activity

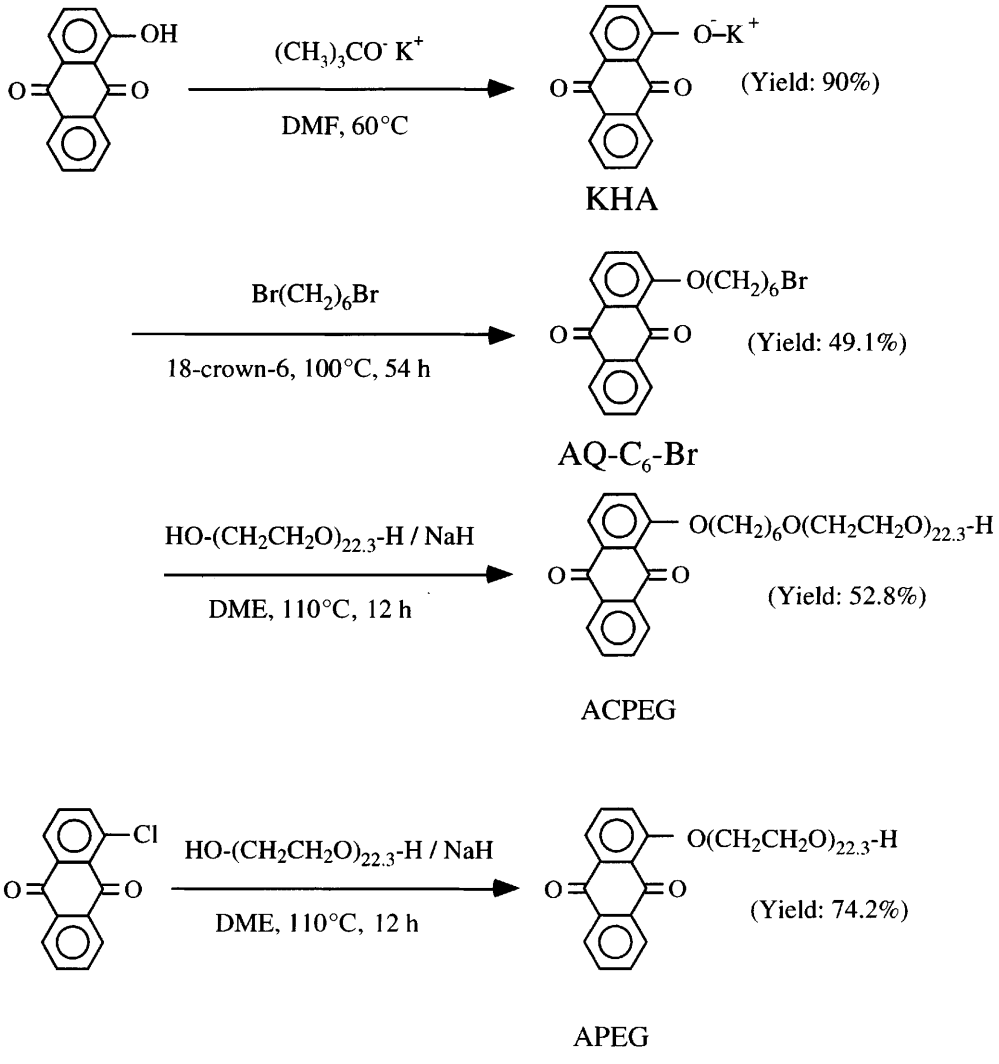
Introduction

The study of the electrochemistry of anthraquinone and its derivatives has a long history possibly due to the complex behavior of these compounds and their numerous applications. Most of the studies have so far dealt with the behavior in organic phases due to the low solubility of anthraquinone in aqueous media. Polarographic studies of anthraquinone have been reported and quantitative methods have been developed in aprotic solvents: *N*,*N*-dimethylformamide (DMF) [1], acetonitrile [2, 3] and $CHCl_3$ [4]. Echegoyen and coworkers [5, 6] have studied intensively the electrochemical switching in anthraquinone-substituted carbon-pivot lariat ethers and podands in the organic phase. The mechanism of electron-transfer mediation to molecular oxygen by anthraquinone has also been reported [7]. Revenga et al. [8] have studied the redox behavior of anthraquinone in DMF and/or its water mixtures by means of direct-current polarography and differential-pulse polarography and have proposed a reduction mechanism in aqueous media. The redox behavior of certain hydroxy and sulfonic acid derivatives of anthraquinone in aqueous solutions has also been studied in detail using polarography [9–13], potentiometry [14, 15], coulometry [13], spectrophotometry [15] and

cyclic voltammetry [16, 17]. The kinetics of the reduction of anthraquinone and sodium anthraquinone-2-sulfonic acid has also been reported [18, 19].

Despite numerous studies on the electrochemistry of anthraquinone and its derivatives, solution behaviors of redox-active amphiphiles linked with an anthraquinone group have still not been unveiled. There are no reports on the electrochemical properties of such amphiphiles. Most of the studies have been concerned with surfactants containing a ferrocenyl group as the electroactive site [20–38]. Also most of the efforts have been directed towards the study of the electrochemical behavior. The surface activity of redox-active surfactants has attracted negligible attention although it has significant importance as for other conventional surfactants. Gallardo and coworkers [30–33] have recently reported the principles for active control of interfacial properties of ferrocenyl surfactants at the surface of water. They have demonstrated that control of the oxidation state of the redox-active group using electrochemical techniques can provide the capability to change, in situ, the surface tension of an aqueous solution. Suzuki and Saji [39] were the first to introduce anthraquinone as an electroactive group for redox-active amphiphiles. They have applied these surfactants for the formation of organic thin films.

In this study, we report the synthesis of two new redox-active nonionic surfactants, α-anthraquinonyloxyhexyl-ω-hydroxy-*oligo*(ethylene oxide) (ACPEG) and α-anthraquinonyl-ω-hydroxy-*oligo*(ethylene oxide) (APEG), both containing an anthraquinone group (Scheme 1). The molecular characterization of the amphiphiles is attempted in terms of the surface activity, the micellization properties and the redox activity. The properties of ACPEG are compared with those of APEG to understand the distinctive features of the differences in the hydrophobic moieties. ACPEG, with six methylene groups linked between the anthraquinone group and the poly(ethylene oxide) chain, efficiently



Scheme 1 Preparation of the potassium salt of 1-hydroxyanthraquinone (KHA), 1-(6-bromohexanoyl)-anthraquinone (AQ-C_6-Br), α-anthraquinonyloxyhexyl-ω-hydroxy-*oligo*(ethylene oxide) (ACPEG) and α-antraquinonyl-ω-hydroxy-*oligo*(ethylene oxide) (APEG)

lowers the surface tension, in contrast to APEG, where anthraquinone, serving as both the redox-active and the hydrophobic group, is linked directly with the poly(ethylene oxide) chain. Both ACPEG and APEG are redox-active in both aqueous and organic media, with the difference arising from their surface activities due to the difference in the molecular geometry, the extent of aggregation and the nature of the medium.

Experimental

Materials

1-Hydroxyanthraquinone (TCI), 1-chloroanthraquinone (Junsei), NaH (55% dispersion in oil, Yoneyama), potassium-*tert*-butoxide (TCI), 18-crown-6 ether (TCI), 1,6-dibromohexane (TCI) and HCl were used without further purification. All solvents [DMF, tetrahydrofuran (THF), $CHCl_3$, 1,2-dimethoxyethane (DME) and 1-butanol] were distilled using standard procedures and were kept over molecular sieves of suitable mesh sizes. Polyethylene glycol (PEG, nominal molecular weight = 1000) was purchased from Kanto and was made water-free by azeotropic distillation prior to use for the preparations of the surfactants. A weighed amount of PEG was mixed with toluene, evaporated and dried under vacuum at 60 °C. Prior to use, 1-chloroanthraquinone and 1-hydroxyanthraquinone were also dried under vacuum to remove water.

0.16 M NaCl aqueous solution was prepared by using Millipore Milli-Q grade water (R = 18.0 MΩ cm and γ = 72.5 mN/m at 25 °C) and NaCl. Aqueous solutions of the surfactants of varying concentrations were prepared by proper dilution of stock solutions with 0.16 M NaCl aqueous solution.

Dehydrated acetonitrile (Kanto) with a water content of less than 0.05% was used for the electrochemical measurements. Tetrabutylammonium perchlorate (TBAP, TCI) was used without further purification. A stock solution of 0.1 M TBAP solution in acetonitrile was prepared and used for the preparation of the surfactant solutions.

Potassium salt of 1-hydroxyanthraquinone (KHA)

For the preparation of KHA (Scheme 1), we followed the same procedure as reported by Gustowski et al. [6]. 1-Hydroxyanthraquinone (11.2 g, 0.05 mol) and DMF (125 ml) were stirred in a 500-ml round-bottomed flask at 60 °C for the dissolution. Potassium-*tert*-butoxide (6.25 g, 0.055 mol) was added in small portions over a period of 30 min with vigorous stirring. The reaction mixture was allowed to cool for 1 h and was then transferred to a freezer for precipitation. The precipitate was filtered and dried under vacuum for 12 h. KHA (a purple solid, 11.7 g, 90%) was used for the next step without further purification.

1-(6-Bromohexanoyl)-anthraquinone (AQ-C_6-Br)

KHA (5.24 g, 0.02 mol), 1,6-dibromohexane (30 ml, 0.2 mol) and 18-crown-6 ether (5.28 g, 0.02 mol) were heated at 100 °C for 54 h (Scheme 1). The reaction mixture was then allowed to cool. $CHCl_3$ (100 ml) and HCl (100 ml, 3 N) were added and shaken well in a separating funnel. The mixture was extracted 3 times with brine, dried over $MgSO_4$ and evaporated. Column chromatography (silica gel 60, Merck, 160 g, $CHCl_3$/hexane, 2/3) yielded the compound as a yellow solid (3.80 g, 9.81 mmol, 49.1%). The ^{1}H NMR data ($CDCl_3$) showed peaks at 1.4–2.1 ppm [$(CH_2)_n$], 3.4 ppm (CH_2Br) 4.2 ppm (OCH_2) and 7.2–8.4 ppm (anthraquinone, AQ protons). The relative NMR peak areas agreed with these assignments. The purity of the product was confirmed by the single, sharp peak at the retention time of 27 min in the gel permeation chromatogram.

α-Anthraquinonyloxyhexyl-ω-hydroxy-oligo(ethylene oxide)

PEG (4.66 g, 4.66 mmol) was heated at 60 °C in a 500-ml flask. NaH (0.203 g) in DME (4 ml) was added dropwise to the system in small portions over a period of 30 min with continuous stirring. After the bubbling due to the evolution of H_2 was over, AQ-C_6-Br (1.8 g, 4.6 mmol) dissolved in DME (55 ml) was added to the reaction mixture and refluxed at 110 °C for 12 h. After having cooled, the mixture was filtered, and the filtrate was evaporated. 1-Butanol (100 ml) and a few drops of HCl (10 N) were added to this, transferred to a separating funnel and shaken well with brine (100 ml). After the phase separation, the aqueous portion was washed with 1-butanol (50 ml), and the organic phase was extracted 3 times with brine (100 ml) and dried over $MgSO_4$. In order to exclude ionic impurities, a solid base (Kyowaad 300, 2.01 g) was added to the mixture and the mixture was stirred at 60 °C for 30 min, followed by the addition of a solid acid (Kyowaad 700, 5.51 g) under identical conditions. The mixture was cooled and filtered, evaporated and dried under vacuum at 70 °C. Column chromatography (silica gel 60: 100 g, $CHCl_3$/hexane, 7/3) yielded the compound (a brown solid, 1.70 g, 1.2 mmol, 52.8%). The ^{1}H NMR data ($CDCl_3$) showed peaks at 1.4–2.1 [$(CH_2)_n$], 3.4–4.0 ppm [$(OCH_2CH_2)_m$] and $CCCH_2O$), 4.2 ppm (AQ-OCH_2), 4.3 ppm ($CCOCH_2CH_2O$) and 7.2–8.4 ppm (AQ protons). The assignments were verified from the relative NMR peak areas and the purity of the product was checked by the single peak at the retention time of 21 min in the gel permeation chromatogram.

α-Anthraquinonyl-ω-hydroxy-oligo(ethylene oxide)

NaH (0.484 g) in THF (30 ml) was added dropwise to PEG (11.1 g, 11.1 mmol) in a 500-ml flask at 60 °C with stirring over a period of 30 min. After the bubbling was over, 1-chloroanthraquinone (2.7 g, 11.1 mmol) dissolved in THF (40 ml) was added to the reaction mixture and the mixture was refluxed at 110 °C for 12 h. The mixture was filtered, washed well with THF and evaporated. The solvent was then extracted with the same procedure as for ACPEG. Column chromatography (silica gel 60:100 g, $CHCl_3$) followed by freeze-drying using benzene yielded a brown compound (9.3 g, 8.24 mmol, 74.2%). The ^{1}H NMR data ($CDCl_3$) showed peaks at 3.4–4.0 ppm [$(OCH_2CH_2)_n$], 4.3 ppm (AQ-OCH_2CH_2O), and 7.2–8.4 ppm (AQ protons). The relative NMR peak areas were consistent with these assignments. The single peak at the retention time of 22 min in the gel permeation chromatogram was a confirmation of the purity of the product.

Surface tension measurements

Measurements of surface tensions of the aqueous solutions of the surfactants over a wide range of concentrations were performed to determine the critical micelle concentration (cmc) and to study the interfacial behavior at the air/water interface. A surface tensiometer (Kyowa CBVP-Z) with a platinum Wilhelmy plate was used for this purpose. Surface tensions were measured within several hours of the preparation of the solutions. The accuracy of the measurement, checked by replicate experiments and by frequent measurement of the surface tension of pure water, was ±0.1 mN/m. Sets of measurements were taken at 10-min intervals until no significant change in the value of the surface tension occurred. In the concentration range studied, equilibrium times of 10–20 min were found to be sufficient for the micellar solutions prior to the measurements, whereas at lower concentrations longer times of up to 90 min were required to attain equilibrium.

Electrochemical measurements

Electrochemical measurements were performed using a glassy carbon electrode (BAS) with an area of 0.071 cm^2 as a working

electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as a counter electrode in a three-compartment cell. The surface of the working electrode was polished with 0.05 μm alumina (Buehler) before each run. The surfactant solutions were deaerated with N_2 and the inert atmosphere was maintained during the course of the measurements. An electrochemical workstation (BAS 100B/W) equipped with IR compensation was used for the cyclic voltammetric measurements. The measurements in aqueous media were performed using 0.16 M NaCl aqueous solution, while those in the organic phase were conducted in 0.1 M TBAP acetonitrile solution. The background measurements were carried out for both the 0.16 M NaCl aqueous solution and the 0.1 M TBAP acetonitrile solution and were subtracted from the cyclic voltammograms of the surfactant solutions. All measurements were carried out at 25 °C.

Light scattering measurements

The static light scattering measurements were conducted on a dynamic light scattering spectrophotometer (Otsuka Electronics, DLS-7000) equipped with a He-Ne laser with a wavelength of 632.8 nm. The scattering angle was changed from 50 to 160°. The calibration constant of the instrument was determined with reference to the reduced intensity of light scattered from pure water with a Rayleigh ratio of $R_{90} = 9.2 \times 10^{-7}$ at 632.8 nm [40]. The surfactant solutions and the solvents to be measured were filtered 3 times through Millipore membrane filters with 0.2-μm pores before the measurements. A cell of 21-mm diameter was used for the scattering experiments. The increment in the specific refractive indices for the surfactant solutions in 0.16 M NaCl aqueous solution was measured using a double-beam differential refractometer (Otsuka Electronics, DRM-1021). Proper corrections were made for the absorptivity for the surfactants at 632.8 nm by spectrophotometric measurements. The temperature was maintained at 25 ± 0.1 °C in both the light scattering goniometer and the differential refractometer by circulating water of constant temperature from a thermostat (Lauda).

Results and discussion

Synthesis

The preparation of the surfactants ACPEG and APEG is depicted in Scheme 1. Suzuki and Saji [39] also reported a scheme for the preparation of similar surfactants without the use of any phase-transfer catalyst; however, no experimental details were available. We tried to prepare AQ-C_6-Br following the scheme reported by Suzuki and Saji; however, in spite of repeated efforts, the yield was always less than 0.5%. Nakatsuji et al. [41] also reported that the reaction of the sodium salt of 1,8-dihydroxy anthraquinone with triethylene glycol ditosylate in refluxing xylene gives only 0.6% yield of the bis(anthraquinone) crown-8 ether. The ion pairing interaction in KHA makes it a poor nucleophile, making in the conversion of KHA to a nucleophilic substituted compound unfeasible. The poor nucleophilicity of the KHA necessitates the use of a phase-transfer catalyst. In this study, we carried out the reaction between the KHA with 1,6-dibromohexane using 18-crown-6 ether as a phase-transfer catalyst, which gave a reasonable yield of 49.1%. 18-Crown-6 ether can strip the potassium cation from the anthraquinone anion by forming a complex, thereby increasing its nucleophilicity resulting in a substantial increase in the yield. Gustowski et al. [6] also carried out the reaction of KHA with CH_3I in the presence of 18-crown-6 ether and obtained 48% of 1-methoxyanthracene-9,10-dione. A large excess of dibromohexane was used to prevent the formation of the dimer, AQ-C_6-AQ, from the reaction with KHA.

Williamson synthesis reactions of AQ-C_6-Br and 1-chloroanthraquinone were carried out with a stoichiometric excess of the sodium salt of PEG to suppress the formation of dianthraquinonyl surfactant. Furthermore column chromatography allowed the separation of the dimers and unreacted compounds from the crude product.

cmc of ACPEG and APEG

The relationships between surface tension and the logarithm of the concentration of the surfactants in 0.16 M NaCl aqueous solution is shown in Fig. 1. The breakpoint allows the ready evaluation of the cmc as 0.2 mM for ACPEG. Takeoka and coworkers [34–38] reported the value of the cmc for α-(ferrocenylundecyl)-ω-hydroxy-oligo(ethylene oxide) in 0.16 M NaCl aqueous solution to be 0.012 mM. The high cmc value in the case of ACPEG can be attributed to the shorter hydrophobic group and longer poly(oxyethylene)(POE) chain length. It is evident that a decrease in the total hydrocarbon number in the lyophobic part and also an increase in the number of ethylene oxide groups results in a shift in the cmc to a higher concentration. Although the difference in the redox-active moiety, which is hydrophobic as well, makes a realistic comparison difficult, a rough account could easily be made. A comparison was also available for a nonionic surfactant, $CH_3(CH_2)_5CO(OCH_2CH_2)_nOH$

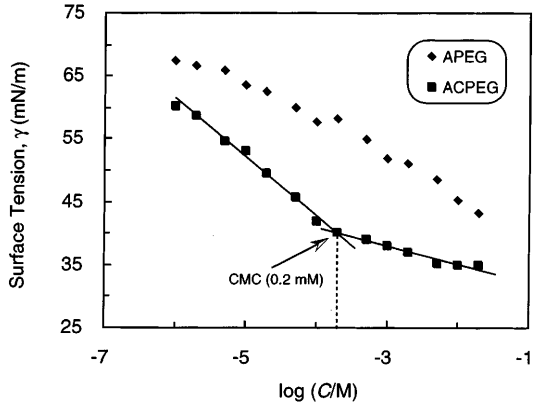


Fig. 1 Surface tension versus the logarithm of the concentration of α-anthraquinonyloxyhexyl-ω-hydroxyl-*oligo*(ethylene oxide) (ACPEG) and α-anthraquinonyl-ω-hydroxy-*oligo*(ethylene oxide) (APEG) in 0.16 M NaCl aqueous solution

(LE) containing the same POE chain length as that of ACPEG [42]. The reported cmc of LE from surface tension measurements was 8.71 mM at 300 K in aqueous solution. Although the cmc of a solution is shifted to a lower concentration with the addition of salts, the much smaller cmc compared with that of LE can be attributed to the difference in the hydrophobicity; the anthraquinone group being more hydrophobic compared to a methyl group promotes micellization. Such promotion was also reported for an azobenzene-linked surfactant by Kozlecky et al. [43]. The cmc value for ACPEG is therefore reasonable.

It can be noted from Fig. 1 that the surface tension for ACPEG continues to decrease at concentrations above the cmc. For thermodynamic reasons, a slight decrease in the surface tension is usual. With increasing concentration, the change in entropy can cause a lowering of the surface tension, but to a lesser extent. The comparatively large and linear decrease in surface tension upon increasing the concentration above the cmc is not usual. A similar observation was reported for a number of surfactants without any explanation [44, 45]. The only explanation available was for a cationic surfactant linked with a phenothiazine group wherein this decrease was ascribed to an increasing degree of aggregation with increasing surfactant concentration [46]. In this system, we presume the decrease to be due to the change in the configurational entropy with increasing concentration of ACPEG (vide infra).

For APEG, no breakpoint is seen in the plot of surface tension as a function of the logarithm of the concentration, which is indicative of no cmc value for the surfactant. It is well established that hydrophobic interaction between the hydrocarbon chains is the driving force for micellization and is dominant in surface activity. APEG has only one anthraquinone group as the hydrophobic moiety in contrast to ACPEG where six methylene groups are also linked between anthraquinone and the POE chain. The same POE chain in ACPEG and APEG opposes micellization to the same extent. Significant variation in the micellization properties therefore results from the difference in the hydrophobic part. The cmc and the micellization of ACPEG lead to the conclusion that six methylene groups along with an anthraquinone group in ACPEG can provide the necessary hydrophobic interaction to the surfactant molecules that can easily overcome the opposition of micellization by the POE chain. In contrast, APEG molecules cannot aggregate appreciably to form micelles, indicating insufficient hydrophobic interaction from the terminal anthraquinone group.

Aggregation of ACPEG and APEG above the cmc

Static light scattering measurements were employed for the determination of the aggregation number of the surfactants. Typical Zimm plots [47] of ACPEG in 0.16 M NaCl aqueous solution at different concentrations above the cmc were used for the estimation of the molecular weight of the aggregated states in the micellar solutions as well as the radius of gyration and the second virial coefficient. The aggregation number was calculated by simply dividing the relative molar mass of the aggregated states by that of the monomeric state. For ACPEG the value was evaluated as 289 (Table 1).

Table 1 Critical micelle concentration (cmc), area per molecule at the interface, molecular weight of the aggregated state (M_w) and aggregation number (N) for α-anthraquinonyloxyhexyl-ω-hydroxy-*oligo*(ethylene oxide) (ACPEG) and α-anthraquinonyl-ω-hydroxy-*oligo*(ethylene oxide) (APEG) in 0.16 M NaCl aqueous solution

Surfactant	cmc (mM)	Area (Å^2/molecule)	M_w	N
ACPEG	0.2	101	3.786×10^5	289
APEG	–	167	5.119×10^3	4

In the concentration range studied (3–15 mM), angular dissymmetry [48], $Z_{60} = R_{60}/R_{120}$, for a micellar solution of ACPEG in 0.16 M NaCl was found to range between 1.34 and 1.46. For spherical micelles the value is close to unity and for rigid rods the value is $\sqrt{3}$, i.e. 1.73. It can therefore be concluded that some dimensions of the micelle had become larger than $\lambda/20$, i.e. 31.64 nm, in this case [49]. The calculated radius of gyration was 66.97 nm which is not compatible for spherical bodies, but can rather be assigned to the rodlike micelles. The ratio of the radius of gyration to that of the hydrodynamic radius (R_G/R_H) has been evaluated as 1.14. The value is much higher than $\sqrt{(3/5)}$, i.e. 0.77, for spherical micelles [50]. This further supports the presence of nonspherical micelles in the system. Furthermore, the second virial coefficient evaluated from the Zimm plots for an aqueous solution of ACPEG in 0.16 M NaCl aqueous solution was 2.078×10^{-5} mol cm^3 g^{-2}. The value is positive but is smaller than usually found for spherical nonionic micelles. All these results suggest asymmetry in the micellar structure; however at all concentrations straight lines gave the angular dependence. Ikeda et al. [50] also observed such linear angular dependence for asymmetric micelles and explained this as the influence of the contribution from the spherical micelles possibly coexisting with rodlike micelles; therefore, the system can be treated as a polydisperse one with spherical and rodlike micelles existing together. This is further evidenced by the polydispersity index of ACPEG micellar solutions which has been calculated as 0.156. The value is not essentially "zero" to indicate the system to be a monodisperse one.

Zimm plots of APEG solutions could not be constructed with high accuracy for the evaluation of second virial coefficients and the radius of gyration; however,

the aggregation number of APEG at higher concentrations could be approximated (Table 1). The aggregation number of APEG was found to be much lower than that of ACPEG.

Adsorption of ACPEG and APEG at the air/water interface

The plots of surface tension as a function of concentration for both ACPEG and APEG (Fig. 1) show an effective reduction in the surface tension in 0.16 M NaCl aqueous solution. This is consistent with the efficient positive adsorption at the air/water interface. The lowering of surface tension with increasing concentration of the surfactants was more pronounced in the case of ACPEG compared to that of APEG. This can be explained in terms of surface activity. It is well known that for nonionic surfactants, the amphiphilic molecules orient at the air/water interface with the hydrophobic part above the interface and the POE chains residing in the aqueous phase. The relative ease with which a surfactant molecule migrates to the interface depends on the solubility in the bulk phase. The absence of methylene groups in APEG increases its solubility towards the bulk phase, simultaneously decreasing the tendency to migrate towards the interface, resulting in a decrease in surface activity. The lower surface activity of APEG does not allow it to lower the surface tension sufficiently compared to ACPEG.

The Gibbs adsorption isotherm was used for the estimation of the limiting area occupied by one molecule of ACPEG and APEG at the air/water interface. The simplified Gibbs adsorption equation in terms of concentration can be expressed as

$$\Gamma_{ex} = -(1/RT)(d\gamma/d\ln c) \ , \quad (1)$$

where Γ_{ex} is the excess concentration of surfactant molecules at the interface, i.e. the amount of surfactant adsorbed per unit area (mol/cm^2), γ is the surface tension of the solution, c is the concentration of the surfactant in the bulk of the solution, T is the temperature and R is the gas constant. The slope of the γ versus log c plot (Fig. 1) (below the cmc for ACPEG) was used to estimate Γ_{ex}. The limiting area per molecule was then calculated from the equation

$$A_{min} = 1/(N\Gamma_{ex}) \ , \quad (2)$$

where N is Avogadro number.

The limiting areas calculated for ACPEG and APEG were 101 and 167 Å^2/molecule, respectively. This suggests poorer packing of surfactant molecules at the interface. Similar behavior has been reported for conventional nonionic surfactants with longer PEG chains [51]. This can be explained in terms of the excluded-volume effect. The long POE moiety is flexible and does not permit ACPEG and APEG molecules to come to close approach at the interface thus forcing the surfactant molecules to occupy a larger space. Also the large size of the redox-active moiety may also inhibit any closer packing of the hydrophilic group [46].

Gibbs free energy change for micellization and adsorption

The change in the standard free energy associated with the micellization process, ΔG°_{mic}, was evaluated according to the equation [42, 52]

$$\Delta G^\circ_{mic} = RT \ln \text{cmc} \ . \quad (3)$$

ΔG°_{mic} for ACPEG was calculated as −21.10 kJ/mol. The standard free-energy change of adsorption at the air/water interface, ΔG°_{ads}, can also be obtained from the relationship [42]

$$\Delta G^\circ_{ads} = \Delta G^\circ_{mic} - (\Pi_{cmc}/\Gamma_{ex}) \ , \quad (4)$$

where Π_{cmc} refers to the surface pressure of the surfactant at the cmc. Π_{cmc} can be calculated by subtracting the surface tension of the surfactant solution at the cmc from that of the solvent. ACPEG molecules were found to adsorb at the air/water interface with a change in the standard free energy of −37.58 kJ/mol. Maiti and Chatterji [42] reported ΔG°_{ads} and ΔG°_{mic} for aqueous solutions of LE at 300 K as −11.93 and −24.44 kJ/mol, respectively. The less negative values indicate that adsorption as well as micellization is more spontaneous for ACPEG compared to LE. The differences are reasonable based on the differences in the surface properties of the surfactants already explained.

Redox activity of ACPEG and APEG in aqueous media

Both ACPEG and APEG having one anthraquinone group as a redox-active site were electrochemically active. The cyclic voltammetric behavior for both ACPEG and APEG in 0.16 M NaCl aqueous solution with scan rates 1–500 mV/s was studied. The cyclic voltammogram of 1.0 mM ACPEG in 0.16 M NaCl aqueous solution at a scan rate of 100 mV/s is shown in Fig. 2. The cyclic voltammograms show a single reduction wave and a corresponding oxidation wave. Similar cyclic voltammograms were obtained for APEG solutions as well. The half-wave potentials and separations of the cyclic voltammetric peak potentials between the reduction and oxidation peaks for ACPEG and APEG are tabulated in Table 2. Bailey and Ritchie [17] also reported the cyclic voltammetric behavior of some quinone derivatives in aqueous media and showed that the process involves two-electron reduction. This indicates the possibility of two formal potentials; however,

the existence of only one reduction peak comes from the fact that the second electron is more positive than the first [53]. The larger separation of the peak potentials can be ascribed to the slow electron transfer in the system for an accompanying chemical reaction.

The amplitude for the reduction current of ACPEG and APEG increases linearly with the square root of the scan rate as expected for a diffusion-controlled species. The apparent diffusion coefficients at 25 °C were therefore calculated using the Randles–Sevcik equation [54],

$$i_{pc} = (2.69 \times 10^5) n^{3/2} A D_{app}{}^{1/2} v^{1/2} c \ , \quad (5)$$

where i_{pc} is the cathodic peak current, n is the number of electrons taking part in the electrochemical reaction, A is the geometric area of the electrode surface, D_{app} is the apparent diffusion coefficient, v is the potential scan rate and c is the concentration of the reactive species in the bulk of the solution. The apparent diffusion coefficient of 1.0 mM ACPEG is much lower than that evaluated for APEG (Table 2) under identical experimental conditions. In solutions of flexible polymers the diffusion coefficient depends on the molecular weight of the polymers according to the relationship $D \propto M^{-0.50 \sim -0.65}$ [55]. Both ACPEG and APEG are surface-active oligomers that do not allow us to make a direct comparison of the diffusion coefficients in terms of the molecular weights using the above relationship because of molecular aggregation; however, it can help to make an approximation for the correlation. The lower diffusivity of ACPEG compared to APEG comes from the fact that the relative molar mass of the aggregated ACPEG is much higher than that of APEG (Table 1).

Redox-activity of ACPEG and APEG in the organic phase

The cyclic voltammogram (v = 100 mV/s) of 1.0 mM ACPEG in 0.1 M TBAP acetonitrile solution is shown in Fig. 3. The electrochemical reduction resulted in the observation of two quasi-reversible redox waves for both ACPEG and APEG. The first and second redox potentials (taken as the average of the anodic and cathodic potentials) for ACPEG were observed at –0.96 V and –1.37 V versus the SCE. The corresponding potentials for APEG are also tabulated in Table 2. The close similarity in the values indicates that the hydrocarbon chain length does not substantially influence the redox process in acetonitrile. Echegoyen et al. [5] also reported two quasi-reversible redox waves with almost identical redox potentials for 1-methoxyanthracene-9,10-dione, 1-((1-oxaanthracene-9,10-dione)methyl)-15-crown-5 ether and some other 1-substituted anthraquinones. In acetonitrile, the double waves suggest a reduction reaction of anthraquinone through the anthraquinone radical anion ($AQ^{\cdot -}$) to the anthraquinone dianion (AQ^{2-}). Meisel and Fesseden [56] through their electron spin resonance study on the reduction mechanism also showed that the first wave is a reversible one-electron

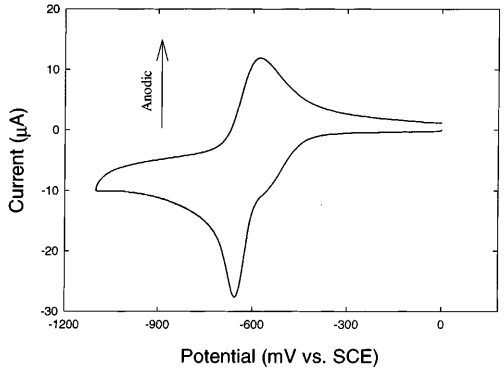


Fig. 2 Cyclic voltammogram (v = 100 mV/s) of 1.0 mM ACPEG in 0.16 M NaCl aqueous solution

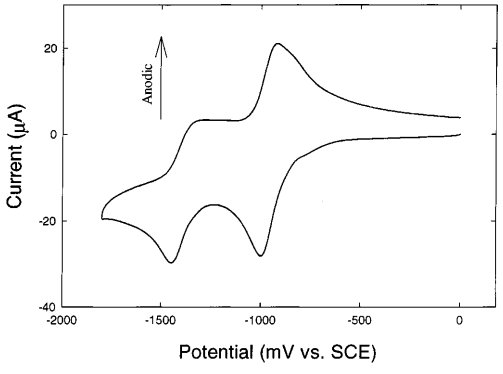


Fig. 3 Cyclic voltammogram (v = 100 mV/s) of 1.0 mM ACPEG in 0.1 M tetrabutyl ammonium perchlorate acetonitrile solution

Table 2 Redox potentials (versus the saturated calomel electrode SCE) (v = 100 mV/s) and apparent diffusion coefficients of 1.0 mM ACPEG and APEG in 0.16 M NaCl aqueous solution and in 0.1 M tetrabutyl ammonium perchlorate acetonitrile solution

Media	Surfactant	$E_{1/2,1}$ (V)	$\Delta E_{p,1}$ (mV)	$E_{1/2.2}$ (V)	$\Delta E_{p,2}$ (mV)	$D_{app} \times 10^6$ (cm^2/s)
Aqueous	ACPEG	−0.62	76	–	–	1.84
	APEG	−0.62	71	–	–	4.39
Acetonitrile	ACPEG	−0.96	75	−1.37	129	9.08
	APEG	−0.95	76	−1.30	214	11.20

process corresponding to the formation of $AQ^{\cdot-}$ and the second wave corresponds to the reduction to AQ^{2-}.

At 1.0 mM concentration of ACPEG and APEG, the amplitude of the waves increases linearly with the square root of v indicating that this process is also a diffusion-controlled one. The cyclic voltammetric cathodic peak current for the first wave (10–500 mV/s) was used for the evaluation of D_{app} for both ACPEG and APEG. The D_{app} values of the surfactants calculated using Eq. (5) are tabulated in Table 2. As the medium is acetonitrile, i.e. an organic one, no micellization is feasible and the peak current therefore corresponds to the diffusion of the monomeric species of the surfactants. The small difference in the diffusivity arises from the difference in the molecular weight of the surfactants in the monomeric states.

Comparative study of the redox behavior of ACPEG and APEG in aqueous and organic media

In the redox process in acetonitrile, two-electron reduction took place leading to the successive formation of $AQ^{\cdot-}$ and AQ^{2-} at two formal potentials. In contrast in the aqueous system the cyclic voltammograms were characterized by single waves resulting from two-electron reduction. The rate of protonation of $AQ^{\cdot-}$ should be greater than the rate of diffusion and therefore $AQ^{\cdot-}$ can readily react with a proton to give AQH which can be further reduced to give the anion AQH^{-}. The diffusion current of this reduction step then corresponds to the addition of one more electron. The voltammetric response for ACPEG and APEG can therefore be treated as a convolution of two, closely spaced one-electron waves. By digital simulation of the cyclic voltammetric results of anthraquinone-2-sulfonate in basic aqueous solution, Wipf et al. [16] also reported the process to be of such a convolution.

The D_{app} values of APEG and ACPEG in aqueous media are found to be much smaller than the corresponding D_{app} values in the organic phase. As the concentration is the same, the difference in diffusivity arises mainly from their characteristic difference in aggregation depending on the medium. Micellar aggregates of ACPEG and APEG in aqueous solution are less diffusive compared to the monomeric states of the surfactant molecules in acetonitrile solution; however, the large difference in the magnitude of the D_{app} values (Table 2) cannot simply be explained in terms of aggregation; the difference in the viscosity should also be considered. The viscosity of acetonitrile (0.325 cP at 30 °C) is much lower than that of water (0.797 cP at 30 °C); therefore, ACPEG and APEG molecules can diffuse faster to the electrode surface when they are in less viscous acetonitrile solution compared to the aqueous medium.

Conclusions

The nonionic surfactants ACPEG and APEG containing an anthraquinone group as a redox-active site have been synthesized. The results of surface tension measurements show that linkage of methylene groups with an anthraquinone group in the hydrophobic moiety has a profound influence on the surfactant behavior of aqueous solutions of the surfactants. The anthraquinone group being hydrophobic in nature promotes micellization when linked at the end of a hydrophobe as seen in the case of ACPEG; however, when linked directly with a long poly(ethylene oxide) chain such as APEG, it fails to provide the necessary hydrophobic interaction to the surfactant molecules for micellization. ACPEG having a cmc value of 0.2 mM in 0.16 M NaCl aqueous solution can form larger aggregates while APEG having no cmc forms smaller aggregates. ACPEG is found to be more surface-active at the air/water interface compared to APEG. The surfactants undergo two-electron reduction in aqueous solution, with aggregation having a pronounced effect on the redox processes. In contrast, both ACPEG and APEG undergo reduction reactions through $AQ^{\cdot-}$ to AQ^{2-} in acetonitrile solution. The redox processes depend only on the nature of the medium and the molecular geometry, as micellization in the organic medium is not feasible.

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