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Cationic-surfactant transfer facilitated by DNA adsorbed on a polarized 1,2-dichloroethane/water interface

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Abstract

The voltammetric behaviour of high-molecular-weight DNA at a polarized 1,2-dichloroethane/water (DCE/W) interface was investigated in the presence of a cationic surfactant, dimethyldistearylammonium in DCE. A well-developed adsorption wave was obtained for salmon sperm DNA (purified) and herring sperm DNA (commercial and purified). The peak current showed a Langmuir-type dependence on the DNA concentration. The half-peak width was relatively small (∼30 mV). To explain the voltammetric behaviour, a reaction model was proposed, in which the transfer of surfactant ions from DCE to W is facilitated by DNA adsorbed on the DCE/W interface. Theoretical simulation of the voltammetric wave was performed by assuming a Frumkin isotherm for the DNA–surfactant binding. When the interaction parameter g' was set to be 2, the theoretical value (38 mV) for the half-peak width was closest to the experimental value of ∼30 mV. The g' value of 2 suggested that there were strongly attractive interactions among the surfactant ions on DNA.

1. Introduction

In recent years, growing interest has been dedicated to electrochemical transfer of biological polyions such as heparin [1] and proteins [2–7] at the interface between two immiscible electrolyte solutions (the so-called oil/water interface). In our recent study [6, 7], it was found that some proteins, including cytochrome c (Cyt c), ribonuclease A, and protamine, could be transferred at a polarized 1,2-dichloroethane/water (DCE/W) interface, by complex formation with an anionic surfactant, bis(2-ethylhexyl) sulfosuccinate (AOT). At low pH values (e.g., pH 3.4), a well-developed voltammetric wave for the transfer of a protein could be obtained;

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however, the protein–surfactant complex (at least for Cyt c) seemed to be unstable in DCE and liable to aggregate at the interface. At neutral pH (∼7.0), though the wave for the formation of unfilled reverse micelles was overlapped with that for the protein transfer, the protein–surfactant complex appeared to be effectively stabilized, probably via fusion with unfilled reverse micelles.

In the present study, we tried to apply reverse-micelle electroextraction to deoxyribonucleotide (DNA) by using a cationic surfactant, dimethyldistearylammonium ($2C_{18}QA^+$). One of the authors (Goto) and co-workers [8] reported that DNA was most efficiently extracted into isooctane with $2C_{18}QA^+$ in a conventional (i.e., non-electrochemical) reverse-micelle extraction system. At the present stage, however, our attempt was unsuccessful; any electrochemical evidence for transfer of DNA at the DCE/W interface has not yet been obtained. Nevertheless, we could obtain a well-defined voltammetric wave, which appeared to be due to the transfer of $2C_{18}QA^+$ facilitated by DNA adsorbed at the interface. In this paper, we present a theoretical reaction model to explain the voltammetric behaviour of DNA at the interface. Previously, Horrocks and Mirkin [9] observed voltammetric behaviours of DNA and oligonucleotides at micro DCE/W interfaces. The binding of DNA to a certain cation in the W phase was found to decrease the current for transfer of the cation. It was also reported that the transfer of a cation from DCE to W was facilitated by oligonucleotides (fragments of DNA) that were probably adsorbed on the interface. This is similar to our present observation, but they did not study the reaction with high-molecular-weight DNA.

The binding (or intercalation) of bioactive compounds to DNA is a current topic in the field of electroanalytical chemistry. Nitrogen-containing compounds such as environmental pollutants [10–12] and anticancer and antibacterial drugs [12–14], usually existing as cations at physiological pH, were investigated for their binding affinities to DNA in solution and at electrode surfaces. A variety of DNA-modified electrodes [10–13] were developed for determining the cationic compounds. To our knowledge, however, the cation binding to DNA at the electrified oil/water interface has rarely been studied so far. Since the oil/water interface is the simplest model of a biomembrane, the present observation for the interfacial DNA–surfactant interaction seems to be useful for understanding the activities of drugs or pollutants acting on DNA *in vivo*.

2. Experimental details

2.1. Chemicals

Sodium salts of DNA from salmon sperm and herring sperm were purchased respectively from Sigma Chemical Co. and Wako Pure Chemical Industries, Ltd. The commercial preparations of DNA were used as received or purified in a conventional manner. The commercial DNA was dissolved in 10 mM (M = mol dm^{-3}) Tris-HCl (pH 8.0) by stirring overnight so that the DNA concentration became 2 g L^{-1} (L = dm^3). To this solution were added sodium chloride (0.1 M) and proteinase K (20 mg L^{-1}; from Sigma), and the solution was incubated at 37 °C for 30 min. Then, the solution was subjected to phenol–chloroform extraction, for which the phenol–chloroform solution was prepared in advance by equilibrating phenol containing 0.1% quinolinol with an equal amount of 50 mM Tris-HCl (pH 8.0) and then collecting the lower layer. The extraction was performed one or more times until the white middle layer containing protein was not observed. Ethanol was added to the resultant aqueous phase (upper layer) so that the concentration became 70%, and then the solution was kept in a refrigerator overnight to precipitate DNA. The resulting precipitate was separated from the solution by centrifugation (3000 rpm; 20–30 min) and then washed with 70% cold ethanol in a similar

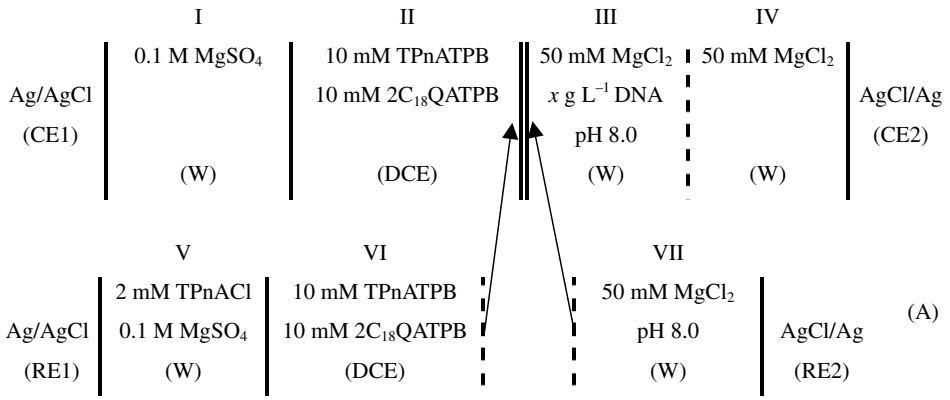
manner. Finally, the remaining solvent was evaporated by reduced pressure to obtain purified DNA. The purity of DNA was checked by UV/visible spectroscopy [15]. It is known that pure DNA has an $A_{260\ \mathrm{nm}}/A_{280\ \mathrm{nm}}$ ratio $\geqslant$1.8. The unpurified and purified samples of salmon sperm DNA and those of herring sperm DNA had ratios of 1.76, 1.82, 1.82, and 1.82, respectively. The molecular weights (MWs) of DNA samples were determined by agarose gel electrophoresis. The MWs of salmon sperm and herring sperm DNAs were, respectively, around 4500 kDa (= 7000 bp; bp = base pair) and 5200 kDa (= 8000 bp) for either unpurified or purified sample.

Dimethyldistearylammonium tetraphenylborate ($2C_{18}$QATPB) was prepared by equimolar addition of ethanol solutions of dimethyldistearylammonium chloride (Tokyo Kasei Kogyo, Co., Ltd) and sodium tetraphenylborate (Dojindo Laboratories, Co., Ltd). The resulting precipitate was washed several times with deionized water and recrystallized from acetone–ethanol (1:1). The preparation and purification of tetrapentylammonium tetraphenylborate (TPnATPB) and the preparation of an aqueous solution of tetrapentylammonium chloride (TPnACl) have been described previously [16]. DCE for high performance liquid chromatography (Wako) was used as received. All other chemicals were of the highest grade available and used as received.

2.2. Voltammetric measurements

Voltammetric measurements were performed using a computer-assisted measurement system [17]. A four-electrode electrolytic cell [17] was used, in which a reproducible flat DCE/W interface (surface area, 0.075 cm^2) was formed. The test DCE/W interface was polarized using a potentiostat (model HA10100mM1A, Hokuto Denko Co.) equipped with a positive-feedback circuit for IR compensation [17].

Unless noted otherwise, the electrochemical cell studied was



where ‖ represents the test DCE/W interface. The potential difference of the interface was controlled using the two reference electrodes (RE1 and RE2) immersed in the respective phases by means of Luggin capillaries whose tips were located near the test interface. The current flowing through the test interface was detected by means of the counter electrodes (CE1 and CE2). The pH of the W phase (III) was adjusted to 8.0 with 10 mM Tris-HCl buffer. The electrolytic cell was water-jacketed to maintain the temperature at 25 ± 0.1 °C.

The potential difference E applied between RE1 and RE2 is related to the Galvani potential difference across the test DCE/W interface, $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$ ($\equiv\phi^{\mathrm{W}} - \phi^{\mathrm{O}}$), as $E = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi + \Delta E_{\mathrm{ref}}$, where ΔE_{ref} stands for the constant which is determined only by the reference electrodes employed. For an electrochemical cell that is approximately equivalent with cell (A), ΔE_{ref} was reported to be +0.233 V [6, 7].

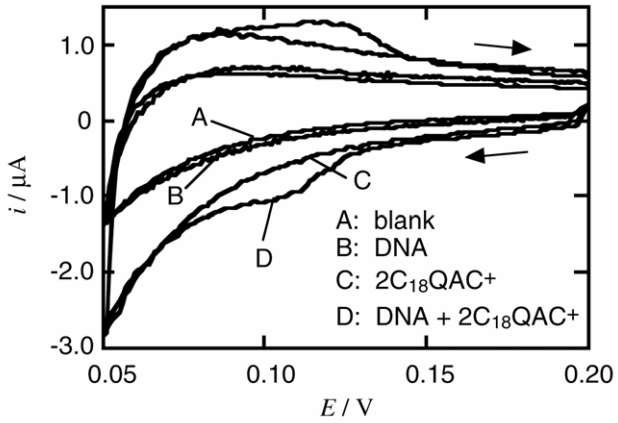


Figure 1. Cyclic voltammograms obtained for (A) blank, (B) 0.115 g L^{-1} purified salmon sperm DNA in W, (C) 10 mM $2C_{18}$QATPB in DCE, and (D) 0.115 g L^{-1} purified salmon sperm DNA in W + 10 mM $2C_{18}$QATPB in DCE. The scan rate was 100 mV s^{-1}.

3. Results and discussion

3.1. Voltammetric behaviour

A typical example for voltammetric behaviour of DNA is shown in figure 1. When neither DNA nor $2C_{18}QA^+$ was present, only residual current was observed, as shown by curve (A). This residual current might be partially due to the charging up of the interface and mostly due to the interfacial transfer of supporting-electrolyte ions. The cathodic (negative-current) final descent on the forward scan corresponds to the transfer of (mainly) $TPnA^+$ from DCE to W, whereas the anodic (positive-current) rise on the reverse scan corresponds to its back transfer to DCE. The residual current was hardly affected by the addition of DNA, as shown by curve (B), but increased by the presence of 10 mM $2C_{18}QA^+$ in DCE, as shown by curve (C). This current increase was proportional to the square root of the scan rate (v) in the range 10–200 mV s^{-1} (data not shown), suggesting that it should be due to the simple, diffusion-controlled transfer of $2C_{18}QA^+$ across the interface. Further addition of 0.115 g L^{-1} salmon sperm DNA (purified) to W led to the appearance of well-developed current peaks on both forward and reverse scans, as shown by curve (D).

The scan-rate dependence of the voltammetric peaks was investigated. The cathodic and anodic peak currents (i_{pc} and i_{pa}), corrected for the base current (curve (C)), were proportional to v in the range 10–200 mV s^{-1}, suggesting that the voltammetric wave observed should be related to a certain adsorption process. The cathodic peak potential did not appreciably depend on v to show that the charge-transfer reaction was a reversible process, although the anodic peak potential was somehow shifted to positive potentials with increasing v (due to a possible kinetic effect). The peak separation ranged between 15 and 25 mV. It should be noted that the half-peak width for the cathodic peak was not very dependent on v, and its approximate value was 30 mV.

The dependence of i_{pc} on the bulk concentration of DNA in W (C^*_{DNA}) is shown in figure 2. As is seen in the figure, i_{pc} was saturated at around 0.1 g L^{-1}. This concentration dependence could be well explained by a Langmuir isotherm [18]:

$$i_{pc} = i_s \frac{\beta C^*_{DNA}}{1 + \beta C^*_{DNA}}. \quad (1)$$

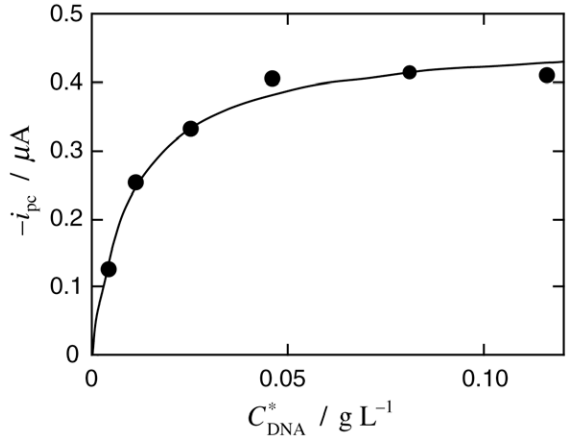


Figure 2. Dependence of the cathodic peak current on the bulk concentration of salmon sperm DNA (purified) in W. The peak current was measured at 100 mV s^{-1}.

The solid curve in figure 2 represents the regression curve obtained using equation (1) with $i_s = -0.468$ μA and $\beta = 96.7$ L g^{-1}. Although the data are not shown, a similar dependence was observed for the charge passed, obtained from the cathodic peak area.

The above-mentioned results were obtained using the purified sample of salmon sperm DNA; however, the unpurified (commercial) sample did not give well-developed voltammetric peaks. As shown in figure 3(a), the peak pair for the unpurified sample was not clear and appeared at more negative potentials than that for the purified one. This suggested that the commercial sample was possibly contaminated by proteins. This seems to be in harmony with the lower $A_{260\ nm}/A_{280\ nm}$ ratio of 1.76 (< 1.8) for the commercial sample. On the other hand, the unpurified and purified samples for herring sperm DNA showed almost the same result in their voltammetric data, as shown in figure 3(b). It was thus suggested that the commercial sample was pure enough. Also, for herring sperm DNA, a similar i_{pc} versus C^*_{DNA} curve as in figure 2 was observed, and the following parameters were obtained: $i_s = -0.465$ μA and $\beta = 129$ L g^{-1}.

3.2. Reaction model

As described above, the DNAs studied gave a so-called 'adsorption' wave at the oil/water (O/W) interface in the presence of $2C_{18}QA^+$ in O. However, the adsorption wave cannot be explained by a simple analogy of the adsorption wave at solid electrodes [19, 20]. If DNA being adsorbed on the W-phase side surface of the interface was transported to the O-phase side surface by potential application, the DNA as a polyanion should give a spike-like wave, contrary with the observed wave. Thus we assumed that DNA itself did not move from the W-phase side of the interface, but $2C_{18}QA^+$ in O should be transferred to W with the help of DNA adsorbed at the interface.

For the theoretical explanation of the adsorption wave, we propose the reaction model shown in figure 4 and then assume the following.

(a) The interfacial transfer of a monovalent cation (here $2C_{18}QA^+$, denoted by R^+) is very fast.
(b) The bulk concentration of R^+ in O ($C^*_{R^+}$) is in excess and thus equal to its surface concentration in the observed potential range, where the amount of R^+ transferred across the interface is limited to only a small fraction of the total amount of R^+.

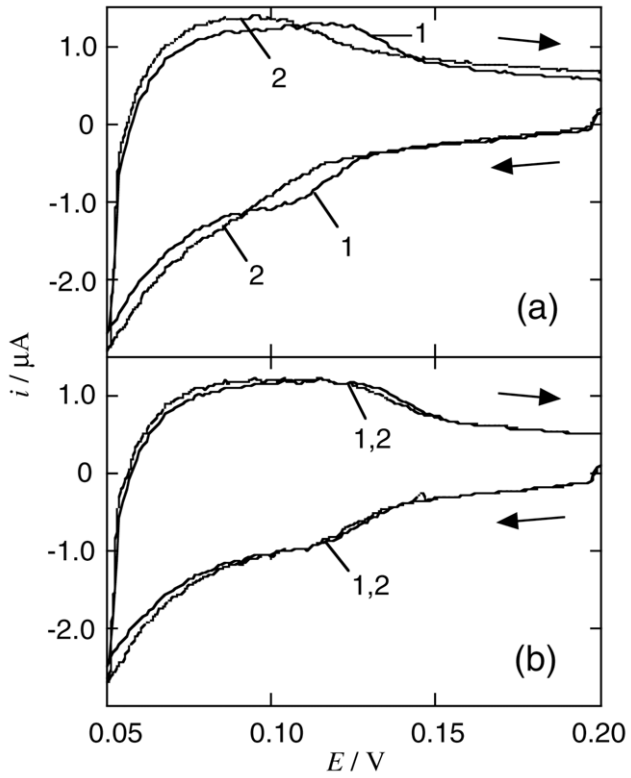


Figure 3. Cyclic voltammograms obtained for (a) 0.115 g L^{-1} salmon sperm DNA and (b) 0.115 g L^{-1} herring sperm DNA in the presence of 10 mM $2C_{18}$QATPB in DCE. Curves 1 and 2 in each panel represent the voltammograms for purified and unpurified samples, respectively. The scan rate was 100 mV s^{-1}.

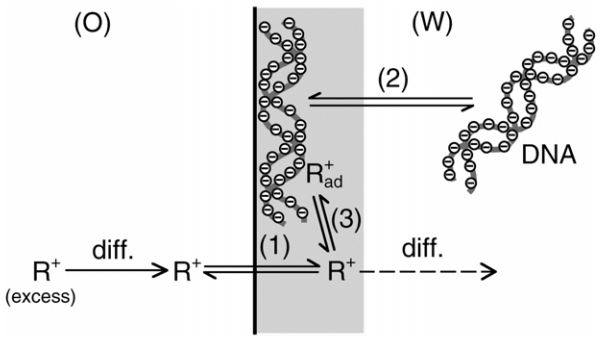


Figure 4. Proposed model for the facilitated transfer of monovalent cation (R^+) by DNA adsorbed at the O/W interface. diff. = diffusion. For further details, see the text.

(c) The adsorption of DNA at the W-phase side surface obeys a Langmuir isotherm.

(d) The adsorption of R^+ onto the adsorption sites of DNA on the W-phase side surface is very fast and obeys a Frumkin isotherm, in which an intermolecular interaction factor is taken into account.

For process (1) in figure 4, we can write the Nernst equation, based on assumption (a), as

$$E = E^{\circ'}_{R^+} + \frac{RT}{F} \ln \frac{[R^+(O)]}{[R^+(W)]} \tag{2}$$

where $E^{\circ'}_{R^+}$ is the formal potential of the transfer of R^+ (which includes the standard ion-transfer potential, the term of activity coefficients, and ΔE_{ref}), $[R^+(O \text{ or } W)]$ is the surface concentration of R^+ in O or W, and R, T, and F have their usual meanings. Because $[R^+(O)]$ is approximated by $C^*_{R^+}$ from assumption (b), $[R^+(W)]$ can be obtained from equation (2) as

$$[R^+(W)] = C^*_{R^+} \exp\left[-\frac{F}{RT}(E - E^{\circ'}_{R^+})\right]. \tag{3}$$

Regarding process (2), assumption (c) yields an expression for the surface concentration of DNA (in mol cm^{-2}):

$$\Gamma_{DNA} = \Gamma_s \frac{\beta C^*_{DNA}}{1 + \beta C^*_{DNA}} \tag{4}$$

where Γ_s stands for the surface concentration at saturation. If a DNA molecule has N binding sites for R^+, the surface concentration (mol cm^{-2}) of binding sites is then given by

$$\Gamma_{bs} = N\Gamma_{DNA} = N\Gamma_s \frac{\beta C^*_{DNA}}{1 + \beta C^*_{DNA}}. \tag{5}$$

Regarding process (3), we can write the Frumkin isotherm [18], based on assumption (d), as

$$\beta' a^W_{R^+} = \frac{\Gamma_{R^+}}{\Gamma_{bs} - \Gamma_{R^+}} \exp\left(-\frac{2g\Gamma_{R^+}}{RT}\right) \tag{6}$$

where $a^W_{R^+}$ is the activity of R^+ on the W-phase side surface of the interface and, for simplicity, assumed to be equal to $[R^+(W)]$. Γ_{R^+} denotes the surface concentration (mol cm^{-2}) of R^+ ions adsorbed at the binding sites of DNA on the interface. Using the surface coverage θ ($\equiv \Gamma_{R^+}/\Gamma_{bs}$), equation (6) is then rewritten as

$$\beta'[R^+(W)] = \frac{\theta}{1 - \theta} \exp(-g'\theta) \tag{7}$$

with $g' = 2g\Gamma_{bs}/RT$. The parameter g' is intrinsically dependent on potential, but here assumed to be constant within a narrow potential range around the voltammetric peak of interest. The range of g' is generally $-2 \leqslant g' \leqslant 2$. If g' is positive, the interactions between neighbouring adsorbed molecules (here R^+ ions) on the surface are attractive; and if g' is negative, the interactions are repulsive.

Substituting equation (3) into (7) gives

$$\beta' C^*_{R^+} \exp\left[-\frac{F}{RT}(E - E^{\circ'}_{R^+})\right] = \frac{\theta}{1 - \theta} \exp(-g'\theta). \tag{8}$$

Taking the logarithm of this equation one obtains

$$\ln(\beta' C^*_{R^+}) - \frac{F}{RT}(E - E^{\circ'}_{R^+}) = \ln\left(\frac{\theta}{1 - \theta}\right) - g'\theta. \tag{9}$$

Rearranging leads to

$$E = E^{\circ'}_{R^+} + \frac{RT}{F} \ln\left(\beta' C^*_{R^+}\right) - \frac{RT}{F} \ln\left(\frac{\theta}{1 - \theta}\right) - \frac{RTg'\theta}{F}. \tag{10}$$

The second term on the right-hand side (rhs) of this equation shows that the transfer of R^+ from O is facilitated by the binding with DNA. When the equilibrium parameter β' is larger,

the wave shifts to more positive potentials. Equation (10) cannot be solved analytically for θ as a function of E; however, the value of E can be numerically obtained by substituting into it the values of θ from 0 to 1.

The voltammetric current i due to the transfer of R^+ from O to W would be the sum of the component due to the diffusion of R^+ into the bulk W phase (i_{IT}) and the component due to the adsorption onto DNA (i_{ad}):

$$i = i_{IT} + i_{ad}. \tag{11}$$

The component i_{IT} corresponds to the current difference between curves (A) and (C) in figure 1, while the component i_{ad} corresponds to that between curves (C) and (D), i.e., the current of the adsorption wave. The latter is given by the time variation of Γ_{R^+} as

$$\frac{i_{ad}}{FA} = -\frac{\partial \Gamma_{R^+}}{\partial t} = -\frac{\partial(\theta \Gamma_{bs})}{\partial t} = -\Gamma_{bs}\frac{\partial \theta}{\partial t} \tag{12}$$

where A is the surface area of the interface. The potential E for the forward (cathodic) and reverse (anodic) scans is given by

$$E = E_i \mp vt \tag{13}$$

where E_i is the initial potential. The minus and plus signs in the rhs of equation (13) are related to the cathodic and anodic scans, respectively. Since $\partial E/\partial t = \mp v$ from equation (13), equation (12) yields

$$\frac{i_{ad}}{FA} = \pm v\Gamma_{bs}\frac{\partial \theta}{\partial E}. \tag{14}$$

The expression for $\partial\theta/\partial E$ in the rhs can be obtained by differentiating equation (9) with respect to E:

$$\frac{\partial \theta}{\partial E} = -\frac{F}{RT}\left[\frac{\theta(1-\theta)}{1-g'\theta(1-\theta)}\right]. \tag{15}$$

Substituting this into equation (14) yields

$$i_{ad} = \mp\frac{F^2 vA}{RT}\left[\frac{\theta(1-\theta)}{1-g'\theta(1-\theta)}\right]\Gamma_{bs}. \tag{16}$$

As is seen in this equation, i_{ad} should be proportional to Γ_{bs} and thus obey the Langmuir isotherm (see equations (4) and (5)). This is in accordance with the experimental result shown in figure 2.

If the parameters other than θ in the rhs of equation (16) are independent of potential, the shape of the adsorption wave should be determined by the following function:

$$\psi(\theta) = \frac{\theta(1-\theta)}{1-g'\theta(1-\theta)}. \tag{17}$$

In figure 5, the values of $\Psi(\theta)$, being calculated for different values of g', are shown against $-(RT/F)\ln[\theta/(1-\theta)]$–$RTg'\theta/F(= E - E^{o'}_{R^+} - (RT/F)\ln(\beta' C^*_{R^+})$; see equation (10)). For $g' = 0$, where there are no interactions between R^+ ions adsorbed on DNA, equation (8) is reduced to a Langmuir isotherm. In this case, the adsorption wave should have the half-peak width ($\Delta E_{p,1/2}$) of 91 mV, which is three times larger than the experimental value of ~30 mV. The theoretical values of $\Delta E_{p,1/2}$ are 146, 118, 91, 64, 38 mV for $g' = -2, -1, 0, 1, 2$, respectively. The largest $\Delta E_{p,1/2}$ value of 38 mV for $g' = 2$ is the closest to the experimental value, suggesting that there should be strongly attractive interactions between $2C_{18}QA^+$ ions on DNA. Probably, the hydrophobic interactions among the long alkyl chains of $2C_{18}QA^+$ ions result in their 'cooperative' adsorption onto DNA.

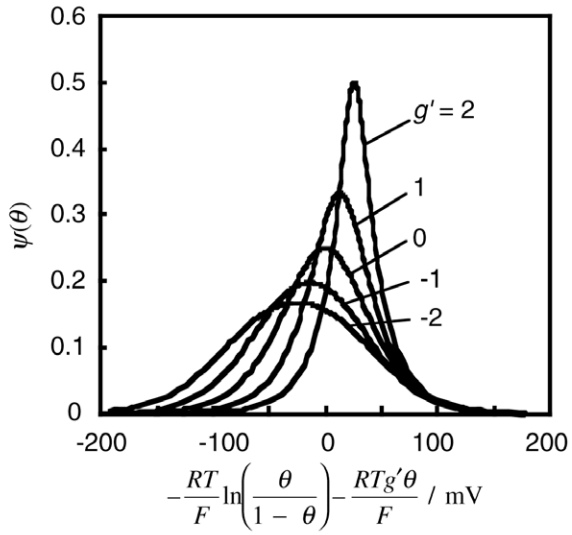


Figure 5. Theoretical voltammograms based on the Frumkin isotherm with different g' values. For the horizontal and vertical axes, see equations (10) and (17), respectively.

3.3. Estimation of the electrochemically active binding sites on DNA

DNA has two negative charges per bp, each of which may act as the binding site for a monovalent cation. We estimated what percentage of the binding sites of DNA contributed to the voltammetric wave observed. For the estimation, a DNA molecule was considered as a tape with the width of 20 Å and the length of 3.4 Å per bp. If we assume that the DNA molecule is adsorbed at the interface in closest-packing arrangement, it should occupy the interface of 6.8×10^{-15} cm^2 per bp. This shows that there are 2.94×10^{14} available binding sites per cm^2. On the other hand, the charge passed, obtained from the peak area at saturation, gave the maximum number of electrochemically active binding sites: e.g., 1.34×10^{13} per cm^2 for purified salmon sperm DNA. This maximum number is only 4.6% of the available binding sites estimated above. A similar percentage (5.5%) was obtained for herring sperm DNA. These lower percentages suggest that DNA is sparsely adsorbed on the DCE/W interface even at saturation. It may be speculated that DNA molecules exists on the interface as if cotton dusts are scattered over a floor. Only a small part of the long DNA chain would get in touch with the O/W interface.

4. Concluding remarks

The adsorption wave observed for DNA in the presence of a cationic surfactant ($2C_{18}QA^+$) could be well explained by the proposed model (figure 4), in which it was assumed that the DNA–surfactant interaction should obey the Frumkin isotherm. The comparison of the half-peak width of the wave with the theoretical values suggested that there were strongly attractive interactions among surfactant molecules, which would result in the cooperative adsorption of surfactants onto DNA. In addition, it was suggested, from the charge passed for the wave, that only a limited part of the DNA chain was electrochemically active. A plausible picture for the DNA–surfactant interaction at the O/W interface is shown in figure 6. The strand of DNA locating in the vicinity of the interface is able to interact with the surfactants, which

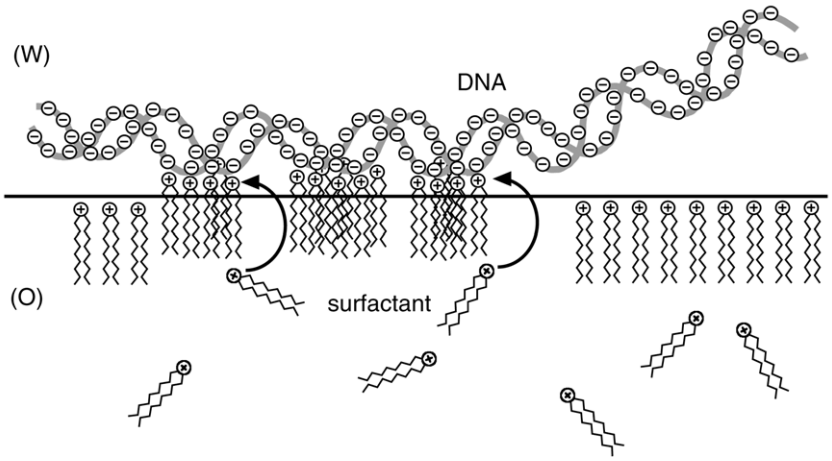


Figure 6. A plausible picture for DNA–surfactant interaction at the O/W interface. The surfactant ions transferred from the O phase to the binding site on DNA (as shown by an arrow) carry the current flowing through the interface.

aggregate to form islands on the interface. If the long alkyl chains of the surfactants are immersed in the O phase as in the picture, the binding of the surfactants with DNA may be effectively supported. A similar positive effect of the O/W interface has been suggested for oligonucleotide–cation binding [9]. It may be considered that the DNA strands, which are not accessible to the interface, do not contribute to the adsorption wave, although they probably have some ability to bind the surfactant ions.

Although the adsorption wave obtained with DNA could be analysed as shown above, our original target, i.e., the electroextraction of DNA, has not yet been achieved. Nevertheless, the present results do not deny the possibility. The complex formation between DNA and $2C_{18}QA^+$ at the O/W interface would be an initial step for the phase transfer of DNA derived by reverse-micelle formation (as a possible slow step). Goto *et al* [8] reported that DNA was successfully extracted with $2C_{18}QA^+$ or other cationic surfactants by reverse-micelle formation. Further study is now in progress.

Acknowledgments

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