Effect of Poly(oxyethylene) Chain Length on Electrosorption of Hexa and Octa(ethylene glycol) Mono *n*-Dodecyl Ethers at the Polarized Nitrobenzene-Water Interface

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The interfacial tension at the interface between a nitrobenzene solution of 0.1 mol dm^{-3} tetrapentylammonium tetraphenylborate and an aqueous solution of 0.05 mol dm^{-3} lithium chloride has been measured as a function of the applied voltage across the interface at 25 °C in the presence of hexa- and octaethylene glycol monododecyl ethers, C12E6 and C12E8, in the nitrobenzene phase. Both C12E6 and C12E8 strongly adsorbed over the entire potential range of the polarized interface. The adsorption of C12E6 and C12E8 was stabilized by complex formation with Li^+ ions in the aqueous phase, as is the case of C12E4 (T. Kakiuchi, T. Usui, and M. Senda, *Bull. Chem. Soc. Jpn.*, **63**, 2044 (1990).). The difference in the standard adsorption Gibbs energies between n=6 and 8, where n is the number of oxyethylene units, was twice as large as that between n=4 and 6, indicating that a chain length longer than 6 is preferable for the complex formation with Li^+ ions at the interface. The surface activities of both C12E6 and C12E8 were markedly enhanced by a positive increase in the potential of the aqueous phase with respect to the potential in the nitrobenzene phase. This dependence of adsorption on the electrical potential difference indicates that the adsorbed C12E6 and C12E8 molecules behave as cationic surfactants, owing to the complex formation at the interface.

It was recognized, even before the first report of macrocyclic crown ethers,[1] that acyclic poly(oxyethylene) derivatives can form complexes with various ions.[2,3] This unique capability of the poly(oxyethylene) moiety has been the subject of numerous studies,[3–10] which have revealed that not only polyethylene glycol but also nonionic surfactants having a poly(oxyethylene) moiety as a hydrophilic moiety are capable of forming complexes with ions; this type of surfactant can function as a surface-active ionophore. In fact, polyethylene glycol alkylphenyl ethers have been utilized as extractants in liquid–liquid extraction[4,5,7,11] and as ion exchangers in the selective detection of ions with ion-selective electrodes.[12] The biological significance of this complexing ability of the nonionic surfactants has also been pointed out.[9,13] In contrast, little has been kwown regarding the effect of the complexation of surfactants with ions on their interfacial activities, though it is generally accepted that the adsorption of surfactants at interfaces is one of the decisive factors in determining various interfacial phenomena, e.g., emulsification.[14] In an earlier stage of the study of nonionic surfactants,[15] the effects of electrolyte additives on the interfacial properties were mainly interpreted in terms of salting-in and salting-out effects as well as the electrostatic shielding effect, without resorting to the idea of surfactant-ion complex formation at the interface. On the other hand, surface and interfacial activities of surface active crown ethers have been investigated relatively recently in relation to complex formation with ions at interfaces.[16–21] In a previous study using a polarized oil–water interface we showed that the adsorbed tetraethylene glycol monododecyl ether, C12E4, forms at the interface a complex with a lithium ion residing in the aqueous side of the interface; this complex formation led to a marked dependence of C12E4 adsorption on the potential drop across the interface.[22] The fact that the stability of the complex between the poly(oxyethylene) moiety and ions depends on the length of the oxyethylene unit in methanolic and in aqueous solutions[4,5,7,9] motivated us to investigate the effect of the poly(oxyethylene) chain length on the electrosorption behavior of the nonionic surfactants at the polarized oil–water interface. In this communication we present studies concerning the electrosorption of hexa and octa(ethylene glycol) mono *n*-dodecyl ethers, C12E6 and C12E8, at the polarized nitrobenzene–water interface using electrocapillarity measurements.

Experimental

The interfacial tension was measured at 25±0.05 °C using a computer-aided pendant drop method.[23,24] Details of this method were described elsewhere.[22,24] The potential drop across the interface was controlled by a laboratory-made four-electrode potentiostat.[22] Auxiliary measurements of the cyclic voltammetry were made in order to check the polarized range of the interface using a two-electrode cell with a flat nitrobenzene–water interface (area of 0.096 cm^2). High-purity C12E6 and C12E8 were purchased from Nikko Chemicals (Japan) and used without further purification. Nitrobenzene was first distilled under reduced pressure and then treated with active alumina. Water was treated with a NANOpure II system (Barnstead, MA., USA) and then distilled from a potassium permanganate solution. Tetrapentylammonium tetraphenylborate, TPnATPB, was prepared as described elsewhere.[22] An aqueous solution of tetrapentylammonium chloride, TPnACl, was saturated with silver chloride. The TPnACl concentration was determined with a potentiometric titration of chloride ions.

Lithium chloride monohydrate (a Merck's Spurapur grade) was used without further purification. A nitrobenzene solution of TPnATPB containing various amounts of C12E*n* (n=6 or 8) was shaken with an aqueous solution of lithium chloride overnight at 25 °C for ensuring partition equilibrium. The concentration of C12E8 in the aqueous phase in partition equilibrium with a nitrobenzene solution containing 100 mmol dm^{-3} C12E8 was determined by using cyclic voltammetry; the current due to the transfer of C12E8–Li$^+$ complexes from the aqueous to the nitrobenzene phase was monitored. The concentration of C12E8 in the aqueous phase was found to be 0.1 mmol dm^{-3}, and was negligible in the analysis of electrocapillary curves using the electrocapillary equation.[22] Since C12E6 is more lipophilic than C12E8, its concentration in the aqueous phase should also be negligibly small.

Results

The electrochemical cell used for the electrocapillary curve and cyclic voltammetry measurements is represented by:

I	II	III	IV	V	VI	VII
		0.02 M†)	0.1 M TPnATPB	0.05 M		
Ag	AgCl	TPnACl	+	LiCl	AgCl	Ag
			x mM C12E*n*			
		(water)	(nitrobenzene)	(water)		

The interface between Phases IV and V is the polarized interface. The electrical potential difference between Phases IV and V was controlled using a four-electrode potentiostat.[22] The potential of the right-hand side terminal of the cell with respect to the left is hereafter denoted as E. Cyclic voltammograms recorded with this cell in the presence of 1 mmol dm^{-3} C12E*n* (n=6 or 8) in Phase IV are shown in Fig. 1. The current was taken to be positive when positively charged species were transferred from the aqueous to the nitrobenzene phase. The potential window (i.e., the range of the applied potential in which no significant current passes through the interface and the interface can be polarized externally) was narrowed by current increase at the positive end of the window (Fig. 1). This current can be ascribed to the transfer of lithium ions from the aqueous to the nitrobenzene phase, facilitated by C12E*n* (n=6 or 8),[25] similar to the facilitated ion transfer with Triton X.[26]

The interfacial tension was recorded at intervals of 20 mV within the potential window for eight different concentrations of C12E*n* between 1 mmol dm^{-3} and 100 mmol dm^{-3} (Figs. 2a and 2b). Figures 2a and 2b show that C12E6 and C12E8 lowered the interfacial tension over the entire range of the potential window. The degree of interfacial tension suppression is compared at 10 mmol dm^{-3} and 100 mmol dm^{-3} for n=4, 6, and 8 in Fig. 3. In Fig. 3 and the following, our previously reported data for C12E4[22] are included for a comparison. Figure 3 clearly indicates that an elongation of oxyethylene unit enhances the adsorption of C12E*n*. This trend accords with the adsorption behavior of 2-[2-[4-(1,1,3,3-tetramethyl butyl)phenoxy]ethoxy]ethanol with different oxyethylene chain lengths at the isooctane–water interface,[27] but is in

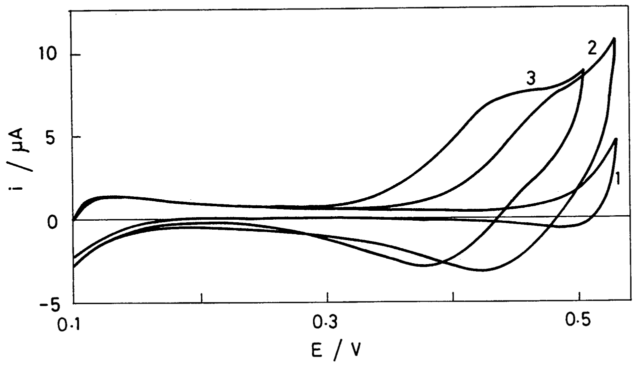

Fig. 1. Cyclic voltammograms at the nitrobenzene–water interface at 25 °C; 1: base solutions; 2: 1 mmol dm^{-3} C12E6; 3: 1 mmol dm^{-3} C12E8 in nitrobenzene, scan rate=20 mV s^{-1}.

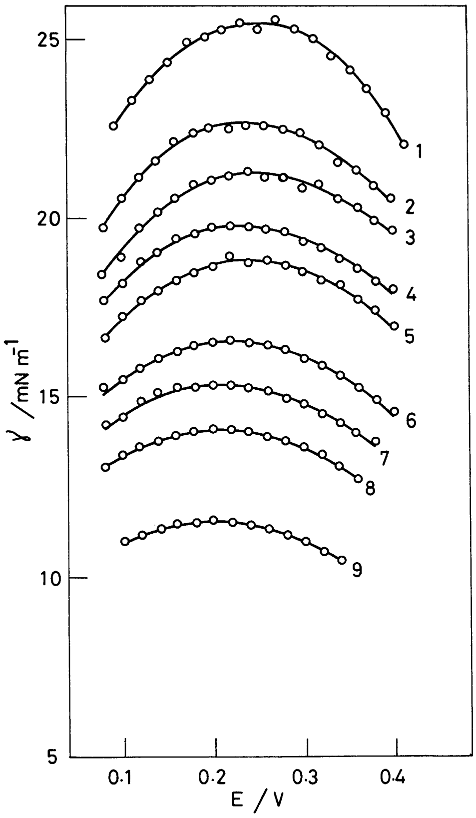

Fig. 2a. Electrocapillary curves at 25 °C for the interface between the nitrobenzene solution of 0.1 mol dm^{-3} TPnATPB and aqueous solution of 0.05 mol dm^{-3} in the presence of x mmol dm^{-3} C12E6 in nitrobenzene: x=0(1), 1(2), 2(3), 5(4), 10(5), 20(6), 30(7), 50(8), 100(9).

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†) M=mol dm^{-3}

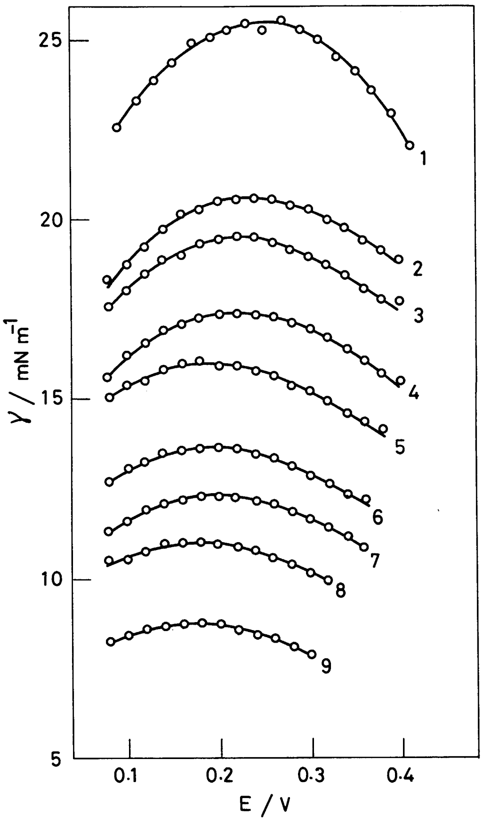

Fig. 2b. Electrocapillary curves for C12E8. x=0(1), 1(2), 2(3), 5(4), 10(5), 20(6), 30(7), 50(8), 100(9).

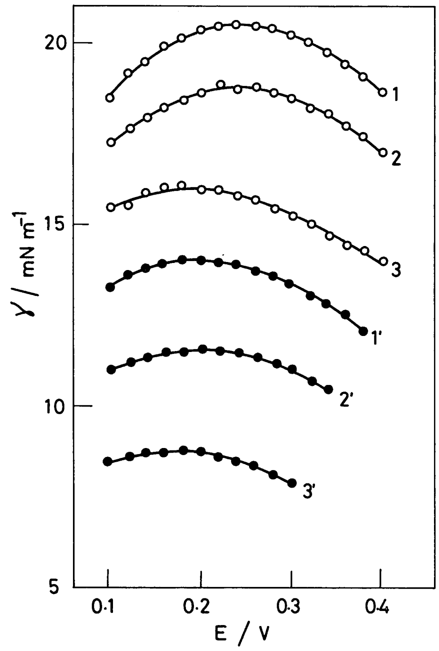

Fig. 3. Comparison of the electrocapillary curves for C12E4 (1,1′), C12E6 (2,2′), and C12E8 (3,3′) at 10 (○) and 100 (●) mmol dm^{-3} C12En in nitrobenzene.

contrast with the case of the adsorption of poly(oxyethylene) derivatives at the air–water interface.[28] Plots

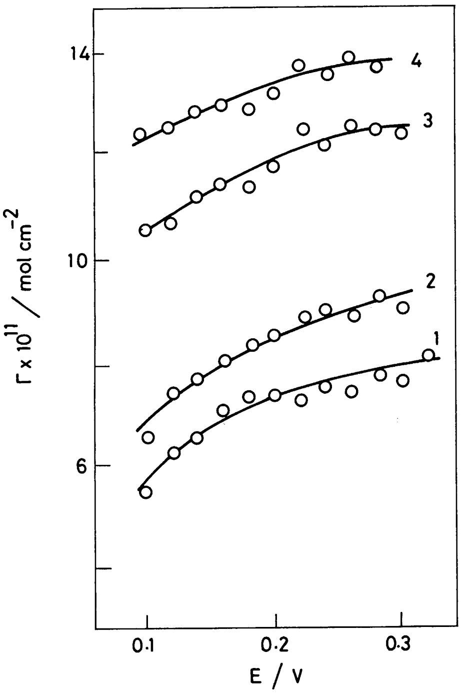

Fig. 4a. Dependence of surface excess of C12E6 on E at x=5(1), 10(2), 20(3), and 50(4).

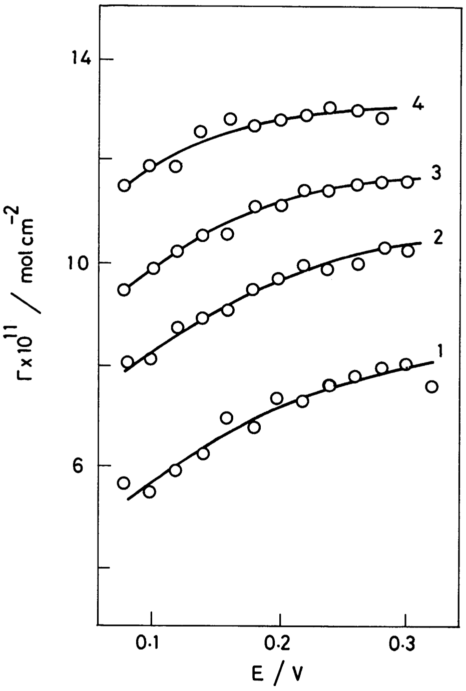

Fig. 4b. Dependence of surface excess of C12E8 on E at x=2(1), 5(2), 10(3), and 50(4).

of interfacial tension, γ, vs. logarithm of the C12En concentration, $c^{\mathrm{NB}}_{\mathrm{C12E}n}$, in the nitrobenzene phase at a given value of E showed no breaks, indicating the absence of appreciable micelle formation in the nitrobenzene phase up to 100 mmol dm^{-3} C12En. For a calculation of the surface excess, Γ, γ vs. log $c^{\mathrm{NB}}_{\mathrm{C12E}n}$

curves were numerically differentiated with respect to $\log c^{\mathrm{NB}}_{\mathrm{C12E}n}$ using the B-spline function. Data for the activity coefficients of C12E*n* in nitrobenzene were not available; we equated the activity with the concentration of C12E*n* in this evaluation of Γ. The resultant Γ values are plotted against *E* in Fig. 4a for C12E6 and in Fig. 4b for C12E8. In these figures a remarkable fact is that both Γ_{C12E6} and Γ_{C12E8} are strongly dependent on *E* and are increasing functions of *E*, as was the case of C12E4 adsorption.[22] The adsorption isotherms at constant *E* were analyzed using the Langmuir isotherm, assuming that the adsorbed amounts of C12E*n* were simply given by the Γ values. The maximum adsorption, Γ^{m}, and the adsorption Gibbs energies, $\Delta G_{\mathrm{a}}^{0}$, thus obtained, are shown in Figs. 5 and 6 as a function of *E*. The standard states for $\Delta G_{\mathrm{a}}^{0}$ are 1 mol dm^{-3} for the aqueous phase and full coverage of the interface for the adsorbed state; both of them refer to infinite dilution. Γ^{m} remained constant over the range of the potential window, while $\Delta G_{\mathrm{a}}^{0}$ negatively increased with a positive shift of *E*.

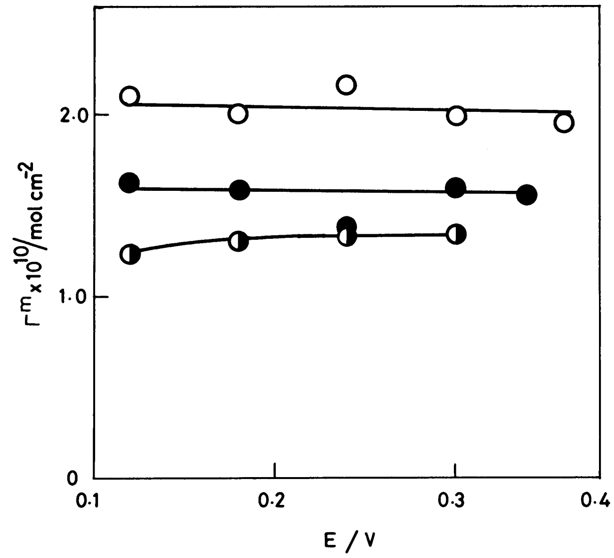

Fig. 5. Plots of the maximum adsorption vs. *E* for C12E4 (○), C12E6 (●), and C12E8 (◑).

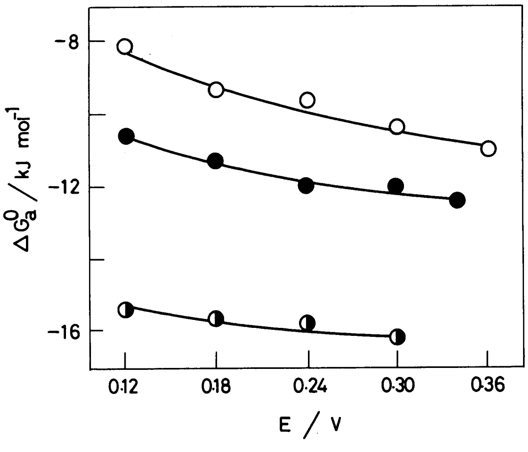

Fig. 6. Dependence of $\Delta G_{\mathrm{a}}^{0}$ on *E* for C12E4 (○), C12E6 (●), and C12E8 (◑).

Discussion

Interestingly, the surface activities of C12E6 and C12E8 were markedly influenced by a potential drop across the interface (Figs. 4a and 4b). This dependence can be ascribed to a complex formation at the interface of the adsorbed C12E*n* molecules with Li^{+} ions existing in the aqueous side of the interface, as we showed in a previous study of C12E4 adsorption.[22] The $\Delta G_{\mathrm{a}}^{0}$ values at *E*=0.12, 0.24, and 0.30 V are plotted against the number of the oxyethylene units, *n*, in Fig. 7. There are two conceivable factors which may lead to a negative increase in $\Delta G_{\mathrm{a}}^{0}$ with *n*: an increase in the hydrophilicity of the poly(oxyethylene) group and an increase in the complex-forming ability of the poly(oxyethylene) moiety with Li^{+} ions. Since the adsorption Gibbs energy of the poly(oxyethylene) derivatives at the air–water interface is little changed with *n*,[28] the negative increase in $\Delta G_{\mathrm{a}}^{0}$ with an elongation of the poly(oxyethylene) moiety appears to be primarily attributable to an increased stability of the adsorbed molecules at the interface through stronger complexation with Li^{+} ions. Conductivity measurement of methanolic solution containing polyethylene glycol dodecyl ether revealed that the critical chain length is 6—7 oxyethylene units for complex formation with Na^{+} and K^{+} ions.[9] The results given in Fig. 7 exhibit the same trend. Similar conclusions have been reached in the solvent extraction studies of K^{+} ions into dichloromethane with noncyclic poly(oxyethylene) derivatives.[4,5,7]

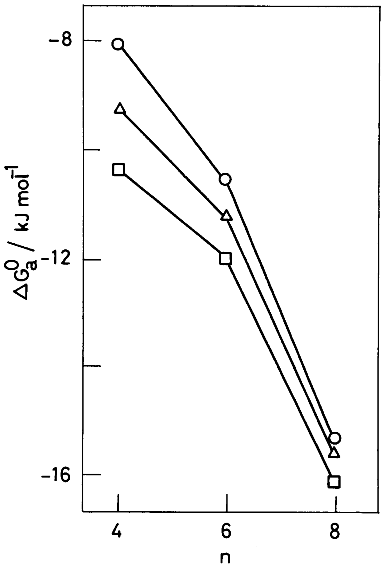

Fig. 7. Variation of adsorption Gibbs energies with the length of oxyethylene unit at *E*=0.12 (○), 0.18 (△), and 0.30 (□) V.

The curves in Fig. 6 for C12E6 and C12E8 are almost superimposable on the curve for C12E4 by vertically shifting the curves by 2.4 and 3.8 kJ mol^{-1}, respectively. In a previous study we presented, based on the Gouy–Chapman theory, a model for the surface complexation which accounts for the dependence of ΔG^0_a on the electrical state of the interface. According to this model, the larger the K value, the lower the ΔG^0_a value and the greater the dependence of ΔG^0_a on the excess surface charge density.[22] The fact in Fig. 6 that the curvatures of the three curves are not much different from each other, while the ΔG^0_a value decreases with n, suggests that other factors (e.g., the change in the polarizability of C12En molecules with n) should be taken into account. If we assume that the difference in ΔG^0_a can be ascribed solely to the difference in the magnitude of the stability constant, K, of the C12En–Li$^+$ complex at the interface, we can estimate that K values for C12E6 and C12E8 are about 4- and 25-times greater than the K for C12E4, respectively.

The constancy of Γ^m over the E range of the potential window suggests that the change in E does not induce a change in the orientation of the adsorbed molecules and that the effect of E on the surface activity is primarily manifested through ΔG^0_a. The values of Γ^m were averaged over E and are listed in Table 1. Table 1 includes values of the area occupied by an adsorbed C12En molecule, A, calculated from the corresponding Γ^m values. Some literature values obtained at the air–water, air–formamide, and isooctane–water interfaces are also included. Although an increase in A with n is a common tendency in columns III, IV, and V in Table 1, two distinctive features of the A values regarding the present results may be discernible. First, for a given C12En species, the obtained A value is almost twice as large as the others. Second, the rate of the increase in A with n is much greater than the corresponding rate at other interfaces. All data in column IV—VII were obtained in an electrolyte-free aqueous or formamide phase, whereas in the present case the aqueous phase contained 0.05 mol dm^{-3} LiCl. Therefore, these two differences probably reflect the difference in the conformation of poly(oxyethylene) moiety with and without the complexation with Li$^+$ ions at the interface. When the aqueous phase does not contain an appreciable amount of electrolytes, the A value for an adsorbed poly(oxyethylene) derivative is determined by the size of the poly(oxyethylene) moiety, which is supposed to be in a random coil.[28] However, once a complex with an ion is formed at the interface, the size of the poly(oxyethylene) moiety would become enlarged through a change in the conformation after incorporating an ion. The area per adsorbed C12E6 molecule was estimated from the projected area of the CPK model[32] of the hexa(oxyethylene) moiety encircling one Li$^+$ ion. Indeed, a value of 1 nm^2 was obtained when the plane of the ring of the hexa(oxyethylene) moiety was parallel with the interface. This value is significantly larger than the A values in columns IV—VII in Table 1, and is comparable to the A value for C12E6 obtained in the present study.

The shift in the potential of zero charge, pzc, toward a more negative potential with increasing concentration of C12En (n=6 and 8) (Figs. 2a and 2b) is another indication of the presence of the C12En–Li$^+$ complex at the interface. Although the Li$^+$ ion, itself, does not specifically adsorb at the polarized nitrobenzene–water interface in the absence of surfactant adsorption,[33] the adsorption of C12En with its poly(oxyethylene) moiety protruding into the aqueous side of the interface in effect gives rise to a "specific" adsorption of Li$^+$ ion through complex formation. The positively charged layer thus formed at the interface should result in a shift of the pzc to a more negative potential. The specific adsorption of Li$^+$ ions to the phospholipid monolayer also causes a negative shift of the pzc.[34] In the case of the specific adsorption of a cationic surfactant at the polarized nitrobenzene–water interface from the nitrobenzene phase, the pzc shifts to the opposite side.[35]

Several experimental facts supporting the modification of the double-layer structure due to surface complexation have been reported. Lange[36] found that the spread monolayer of a poly(oxyethylene) derivative at the air–water interface was expanded upon the addition of electrolytes in the subphase, which was referred to as being "unexpected and difficult to explain". The change in the surface potential to the

Table 1. Parameters for the Adsorption of C12E4, C12E6, and C12E8 at Nitrobenzene–Water Interface at 25 °C and the Area Occupied by Poly(oxyethylene) Moiety at Other Interfaces

n	ΔG^0_a [a]	$\Gamma^m \times 10^{11}$ [a]	A/nm^2				
	kJ mol^{-1}	mol cm^{-2}	I[b]	II[c]	III[d]	IV[e]	V[f]
4	−9.6	2.0	0.81	0.47		0.48	
6	−12.6	1.6	1.04	0.52	0.59	0.57	0.63
8	−15.8	1.3	1.28	0.62		0.64	

a) At E=0.180 V. b) Present results. c) Air-water interface; data read off from Fig. 3 in Ref. 27. d) Air-water interface; data read off from Fig. 1 in Ref. 29. e) Isooctane-water interface; data read off from Fig. 9 in Ref. 27. f) Air-formamide interface; Ref. 30.

positive direction upon introduction of the poly(oxyethylene) derivative to the air–water inteface has also been reported.33) Although these phenomena have been interpreted in terms of the orientation of dipoles at the interface,36,37) the alternative model of the double layer with specific adsorption presented in this study can well explain the observed trends. The effect of surface complexation on interfacial properties has recently been demonstrated clearly from the π–A curves, surface potential, and zeta potential measurements at the oil–water interface in the presence of the adsorption of surface-active crown ethers.19–21)

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