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Interaction of Polysaccharides with Lipid Monolayers

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The interactions of model neutral lipids such as lecithin and dipalmitoyl phosphatidylcholine (DPPC), and of the positively charged lipid dioctadecyl dimethyl ammonium bromide (DOMA) with neutral (dextrans) and acidic polysaccharides (carrageenans and xanthan), representing the hydrophilic solutes occurring in natural aquatic systems, have been monitored electrochemically and by monolayer techniques. Surface pressure-area (π-*A*) and surface potential-area (ΔV-*A*) isotherms have been measured. The values for compressibility of mixed films and the dipol moments (effective dipole moment μ_T and polar head group dipole moment μ_α) have been calculated from π-*A* and ΔV-*A* isotherms, respectively. In electrochemical experiments lipid-coated mercury electrodes have been used. The influence of polysaccharides on the monolayers structure has been studied by capacitance measurements and by using an electrochemical probe (redox processes of cadmium) with phase-sensitive ac voltammetry. The results presented here are part of more general studies of the interaction of organic solutes naturally occurring in the aquatic systems with hydrophobic lipids at different phase boundaries. These investigations are of great importance for the interfacial properties of mixed monolayers and for understanding the influence of hydrophilic and hydrophobic substances on the physicochemical properties of natural surface films.

Key Words: **polysaccharides; lipid monolayers; air/water interface; π-*A* and ΔV-*A* isotherms; capacity measurements; ac voltammetry.**

INTRODUCTION

Natural aquatic systems contain a complex mixture of organic substances such as lipids, proteins, peptides, polysaccharides, humic substances, and artificial compounds with different functional groups and different hydrophobic properties. A large fraction of organic substances in seawater is surface active and can adsorb at natural interfaces such as seawater boundaries with atmosphere, living and nonliving dispersed and particulate matter, and sediment. Due to the accumulation of surface-active substances onto the sea surface, the sea surface microlayer, being the interfacial region where many important biophysicochemical processes and flux of gases are taking place, is forming. The hydrophobic fraction of surface-active material is expected to be more enriched in the surface microlayer collected at the natural air/seawater interface compared to the total surfactants and total DOC (dissolved organic carbon) values, as was found in the investigations of organic surface-active substances in seawater and sea surface microlayer samples from the North Adriatic Sea (1). However, the hydrophilic fraction in surface-active material in the sample of microlayer which was taken during the bloom of diatoms was found to be suprisingly high (1). It is known that these phytoplankton species excrete high quantities of carbohydrates (2). Many studies and determination of polysaccharides in marine environment have been done in recent years (3–5) and special attention was paid to the role of polysaccharides derived from algal and microbial sources in forming the gelatinous aggregates (mucilages) observed during the phytoplankton blooms (6, 7).

In adsorption at interfaces there exist hydrophilic, electrostatic, hydration, and hydrophobic interactions which determine the surface excess of solute species. Among these various intermolecular interactions, hydrogen bonds also play an important role in arranging different molecules to large supramolecular assemblies. Although carbohydrates are water-soluble compounds they can form highly insoluble films due to hydrogen bonding and nonpolar interactions with lipid-insoluble components. In the case of charged polyelectrolytes the interactions with functional groups of lipid films can be expected too.

Recently, the adsorption behavior of selected model polysaccharides (dextran sulfate, dextrans, κ-, λ-, ι-carrageenans, and xanthan) on different model interfaces such as hydrophilic -Al_2O_3 particles (8) and hydrophobic mercury electrode surfaces (8–10) was studied. Studies of adsorption of polysaccharides at different surfaces, as well as those of the interactions between lipid monolayers and the selected polysaccharides, are of great importance for a better understanding of the influence of hydrophilic and hydrophobic substances on physicochemical properties of surface films and the possible mechanism of polysaccharide transformation and deposition from the bulk seawater to the sea bottom.

Monolayer techniques used for the study at the air/water interface provide the methods to organize appropriate molecules in a

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planned way and to study the interactions at the interface under controlled conditions (11). Interactions of lipid monolayers with various species from the bulk solution can also be studied electrochemically using lipid-coated mercury electrodes prepared by transferring the lipid films from the air-water interface to a mercury surface (12–18). Ion and charge transfer across the film, as well as the interactions in the film, has been detected by using phase-sensitive alternating current (ac) voltammetry. The lipid-coated electrode represents a very sophisticated system for studying the structure and functioning of biological membranes (19–21) and for investigating the aquatic chemistry of organic and inorganic micropollutants (22–24).

In this work, the interactions of model neutral lipids such as lecithin and dipalmitoyl phosphatidylcholine (DPPC) as well as those of the positively charged lipid dioctadecyl dimethyl ammonium bromide (DOMA) with neutral (dextrans) and acidic polysaccharides (carrageenans and xanthan), which represent the hydrophilic solutes naturally occurring in the aquatic system, have been monitored electrochemically and by monolayer techniques.

EXPERIMENTAL

Monolayer Studies

Lipid films were formed at the air/water and air/polysaccharide solutions interface and measurements of surface pressure-area (π-A) and surface potential-area (ΔV-A) isotherms were performed in a rectangular Teflon trough enclosed in a tight box and thermostated. A Wilhelmy balance (15-mm-wide filter paper) was used to measure the surface pressure, and the surface potential was measured using a vibrating plate condenser (11). Measurements have been done at the temperature of 20°C.

Electrochemical Studies

Lipid films were prepared by spreading from hexane solutions onto the electrolyte solution, and then transferred to the mercury surface by vertical dipping of the electrode through the film. The technique of transferring the lipid film from the air/water interface to the mercury surface is described in more detail elsewhere (14, 15, 22). Afterward, the films were studied using *out-of-phase* (capacity current measurements) and *in-phase* (Faradaic current measurements) ac voltammetry. The values of differential capacitance were calculated from the measured capacity current. In a separate experiment we calibrated electrochemical instruments with a series of capacitors (precision of capacitors is $\pm 1\%$).

Measurements were performed with a Polarecorder PAR 170 (Princeton Applied Research Co., Princeton, NJ). A standard polarographic Metrohm cell of 100 cm^3 equipped with a three electrode system was used. A hanging mercury drop electrode (HMDE, Metrohm, Switzerland) of the surface area $A = 0.0141\ cm^2$ was used as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire as the auxiliary electrode.

Pure nitrogen was used for deaeration of the solutions. All measurements were made in 0.55 mol dm^{-3} NaCl as the supporting electrolyte. Accumulation of polysaccharides was performed with stirring.

Chemicals

Lipids. Dipalmitoyl phosphatidylcholine, egg lecithin, and dioctadecyl dimethyl ammonium bromide were purchased from Sigma Chemical Co. (U.S.A.) and used as received.

Polysaccharides. The schematic structure of polysaccharides used in this work is presented in Fig. 1.

Carrageenans (κ-, λ-, ι-) are natural polysaccharides isolated from red algae (Rhodophyta). They are sulfonated glycans and contain A and B units, i.e., β-D- and α-D-galactopyranose residues arranged in an alternating sequence $(AB)_n$ (25). They differ in position and number of sulfated groups and in their properties regarding the formation of gels. κ-Carrageenans form rigid gels, λ-carrageenans do not form gels, and ι-carrageenans form flexible and compiliant gels. Mean molecular weight values for carrageenans are between 3.5×10^5 and 7×10^5 (26).

Xanthan is a water-soluble biopolymer ($M_w = 2 \times 10^6$) of microbial origin having polyelectrolyte properties. It has a five sugar repeat unit, two types of carboxyl groups, and a celulose backbone (27).

Both carrageenans and xanthan were purchased from Sigma Chemical Co. Dextrans were obtained from Serva, Heidelberg, Germany. Dextrans are neutral polymers isolated from bacteria from the *Lactobacilleae* family. In this work we used Dextran T-4 ($M_w = 4000$) and Dextran T-500 ($M_w = 500{,}000$).

Other Chemicals

Chloroform (HPLC), p.a. grade from Baker Chemicals, Holland, and *n*-hexan, p.a. grade from Kemika, Croatia, were used as spreading solvent. Deionized water from a Milli-Q system (Millipore Corp.) was used to prepare the subphase.

RESULTS AND DISCUSSION

Air/Water Interface

It is reasonable to expect that the difference in the interfacial behavior of the lipid monolayers formed at the air/water interface and at the air/polysaccharides solutions interface, respectively, will be reflected in the surface pressure-molecular area (π-A) and surface potential-molecular area (ΔV-A) isotherms.

The surface pressure-molecular area (π-A) isotherms for DPPC and DOMA monolayers spread on water and on subphases containing different polysaccharides are measured and the thermodynamic parameters, limiting, specific area A_0, compressional modulus Cs^{-1} and compressibility $1/Cs^{-1}$, have been calculated (presented in Table 1). The values for surface potential ΔV at $=40$ mN/m are also given in Table 1. From the measured values of surface potential the effective dipole moment μ_T is

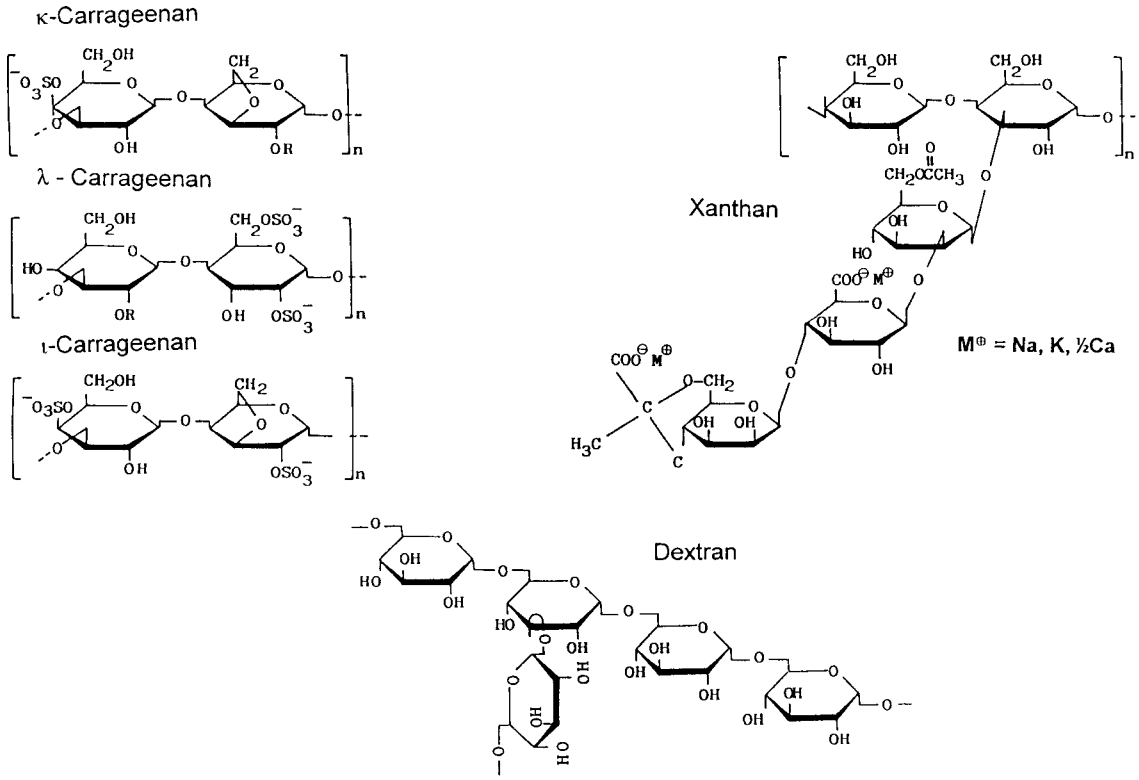

FIG. 1. Schematic structure of used polysaccharides.

calculated according to the Helmholtz equation (28),

$$\mu_T = \varepsilon_0 \Delta V A,$$

where A is the mean area per molecule, ΔV is surface potential, and ε_0 is permittivity of the vacuum. The term μ_T can be subdivided into the head group and the hydrophobic tail region dipole moments,

$$\mu_T = \mu_\alpha + \mu_\omega.$$

For aliphatic chains only the terminal $-CH_3$ group contributes to this term and was determined by a partial dipole compensation approach to be $\mu^{CH_3} = 0.35 \pm 0.01$ D (29). With the known

TABLE 1

The Calculated Thermodynamic Parameters (Limiting Specific Area A_0 and Compressibility), Measured Values of Surface Potential (ΔV) at $\pi = 40$ mN/m, and Calculated Values of Total Dipole Moment μ_T and Polar Head Group Dipole Moment μ_α for DPPC and DOMA Monolayers on Different Subphases

Monolayer	Subphase	A_0 (nm^2)	Compressibility (m/mN)	A (nm^2)	ΔV (V) at $\pi = 40$ mN/m	Dipole moment	
						μ_T (D)	μ_α (D)
DPPC	Water	0.51	0.007	0.45	0.60	0.72	0.02
	Dextran	0.56	0.011	0.47	0.61	0.76	0.06
	λ-Carrageenan	0.56	0.008	0.47	0.58	0.72	0.02
	ι-Carrageenan	0.53	0.008	0.46	0.57	0.70	0.00
	κ-Carrageenan	0.53	0.010	0.45	0.59	0.71	0.01
	Xanthan	0.72	0.018	0.59	0.60	0.94	0.24
DOMA	Water	0.64	0.030	0.52	1.05	1.45	0.75
	Dextran	0.68	0.040	0.54	0.91	1.30	0.60
	λ-Carrageenan	0.69	0.020	0.53	0.76	1.07	0.37
	ι-Carrageenan	0.72	0.035	0.56	0.66	0.98	0.28
	κ-Carrageenan	0.77	0.016	0.60	0.60	0.95	0.25
	Xanthan	1.19	0.034	0.76	0.60	1.21	0.51

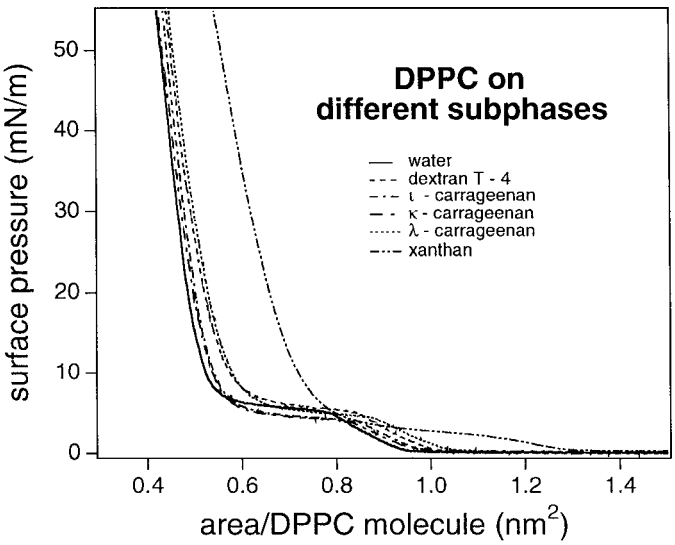

FIG. 2. Surface pressure-area (π-A) isotherms for DPPC monolayers on different subphases. Concentration of polysaccharides in the subphase was 100 mg dm^{-3}. Temperature $T = 20°$C.

contribution μ^{CH_3} per $-CH_3$ group at the monolayer/air interface to the total dipole moment μ_T, the contribution μ_α of the polar head groups can be calculated from surface potential data. The calculated values of μ_T and μ_α for DPPC and DOMA monolayers on water surface and on polysaccharides solutions are also given in Table 1.

The measurements were performed with high concentrations of polysaccharides (100 mg dm^{-3}) to avoid the influence of kinetics. Kinetics study of cholesteryl/pullulan derivatives (hydrophobized derivative of naturally occurring polysaccharide) at the air/solution interface showed that adsorption kinetics of such amphiphilic macromolecules was difussion-controlled only at low solution concentrations (2×10^{-7}–5×10^{-6} mol dm^{-3}) (30). Taking in account the relative molecular masses for polysaccharides used in this work, the concentrations of carrageenans solutions were between 1.3 and 2.8×10^{-5} mol dm^{-3} and those of Dextran T-4 and xanthan were 2.5×10^{-3} and 5×10^{-3} mol dm^{-3}, respectively. We assumed that kinetics will not play any rule in this high concentration range. Preliminary measurements have been done 5 and 30 min after the evaporation of the solvent. There was almost no difference in surface pressure and the difference in surface potential was negligible, especially at small areas regarding accumulation time, thus the results presented here are those measured 5 min after spreading.

DPPC spread on water exhibits an π-A isotherm with a LE/LC phase transition around 5 mN/m (Fig. 2, full line). The isotherm of the DPPC monolayer shows only small differences if spread on solutions of ι- and κ-carrageenans; i.e., the phase transition is present and the increase in area/DPPC molecule is almost negligible. A DPPC monolayer spread on dextran and λ-carrageenan, respectively, also shows the phase transition at the same pressure, and the area/DPPC molecule at $=10$ mN/m is larger by only 0.05 nm^2 on the solutions of these sugars than on water. By further compressing, this increase in molecular area becomes smaller, and in condensed layers at $=40$ mN/m it is about 0.025 nm^2. A completely different behavior was observed if xanthan is present in solution. The π-A isotherm is an expanded type without phase transition, and the area/DPPC molecule at $\pi = 10$ mN/m is 0.2 nm^2 larger than that of the DPPC monolayer on water. From the results presented in Table 1 it is obvious that the values for compressibility, as well as those for surface potential and surface dipole moment, are almost identical for DPPC monolayers spread on water and on sugar solutions, except in the case of DPPC monolayers spread on xanthan solutions, where the values for compressibility are about two times larger than the values for DPPC monolayers spread on water and on solutions of other polysaccharides. Although the value for the surface potential of condensed monolayer ($\pi = 40$ mN/m) is the same as for DPPC monolayers at the water surface, both dipole moments are bigger than for DPPC monolayers on water. Such a phenomenon may be interpreted as a partial incorporation of the polyelectrolyte molecule into the matrix monolayer due to a hydrophobic interaction through hydrogen bonding of the solute xanthan with the DPPC monolayer.

Specific effects of counterions on the π-A isotherms of DOMA monolayers have been well established and described in the literature (31, 32). The surface pressure-area (π-A) isotherm of a DOMA monolayer spread on water is of the liquid expanded type, with a phase transition around 14 mN/m which changes to a liquid condensed state upon compression (Fig. 3, full line). The π-A isotherm of a DOMA monolayer on a dextran subphase (curve 1) did not differ from that on the water surface. However, other polysaccharides investigated showed a significant influence on the behavior of DOMA monolayers.

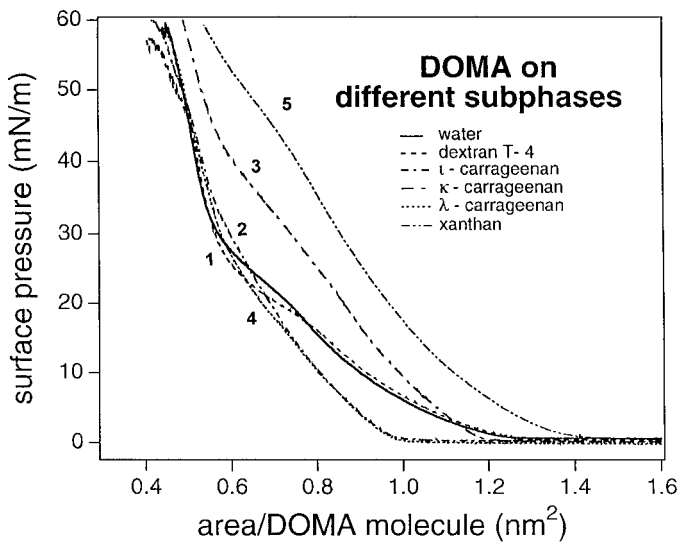

FIG. 3. Surface pressure-area (π-A) isotherms for DOMA monolayers on water (full line), Dextran T-4 (1), ι-carrageenan (2), κ-carrageenan (3), λ-carrageenan (4), and xanthan (5). The concentration of polysaccharides in the subphase was 100 mg dm^{-3}. Temperature $T = 20°$C.

The isotherm of the DOMA monolayer spread on the subphase containing ι- and λ-carrageenans (curves 2 and 4) shows a contraction with respect to DOMA monolayers spread on water at the areas $A \geq 0.65$ nm^2 ($\pi = 25$ mN/m). Further compression until $A = 0.55$ nm^2 leads to a strong increase in surface pressure, and no LE/LC phase transition of monolayer was observed. The area/DOMA molecule for the monolayer spread on solution of ι- and λ-carrageenans in the tightly packed state is almost identical to that of DOMA spread on water. Surface pressure data indicate that ι- and λ-carrageenans adsorption drives the liquid expanded to liquid condensed phase transition in the DOMA monolayer by decreasing the available area per lipid, being thus equivalent to mechanical compression of the monolayer. The condensation of the DOMA monolayer isotherm can be attributed to the decrease in repulsive forces between the head groups of DOMA due to the neutralization of positive charge via electrostatic interaction with OSO_3^- from carrageenans in solution. The influence of κ-carrageenan and xanthan in the subphase on the behavior of DOMA monolayers is observed not only in the expanded phase but also in the condensed phase of the monolayer. The π-A isotherm of the DOMA monolayer spread on the subphase containing κ-carrageenan (curve 3) shows a contraction with respect to the DOMA monolayer spread on water only at very large areas, between 1.15 and 1.25 nm^2. By further compression at higher surface pressures, an expansion of the DOMA monolayer spread on subphase containing κ-carrageenan with respect to DOMA spread on water is observed. The expansion of the DOMA isotherm in the whole range of the area (<1.4 nm^2) is observed for the DOMA monolayer spread on xanthan solution (curve 5).

Such expansion of π-A isotherms as a result of lipid/solute interaction has usually been interpreted in terms of penetration or incorporation of solute molecules in the monolayer (33–35). However, an expansion of the area can also be observed when electrostatically adsorbed multivalent molecules are located underneath the lipid monolayer, pulling the lipid molecules apart (36–39). The strong interaction of DOMA monolayers with negatively charged solutes from the subphase was expected and can be attributed to electrostatic binding.

This can also be seen from the surface potential-area isotherm presented in Fig. 4. In the whole area range, the values of ΔV are less positive for DOMA monolayers on subphases containing polysaccharides compared to DOMA monolayers on water. The smallest difference is observed for DOMA on dextran (curve 1), which is a neutral molecule, and electrostatic interactions are not expected. From the results of the surface potential and dipole moments collected in Table 1, it is obvious that DOMA monolayers in the condensed phase show a pronounced decrease in the potential values and dipole moments on polysaccharide solutions in comparison to the value for DOMA monolayers on water, due to the neutralization of positive charge of DOMA polar head groups. The strongest effect is observed with carrageenans, which decrease the positive charge of head groups more than 50%.

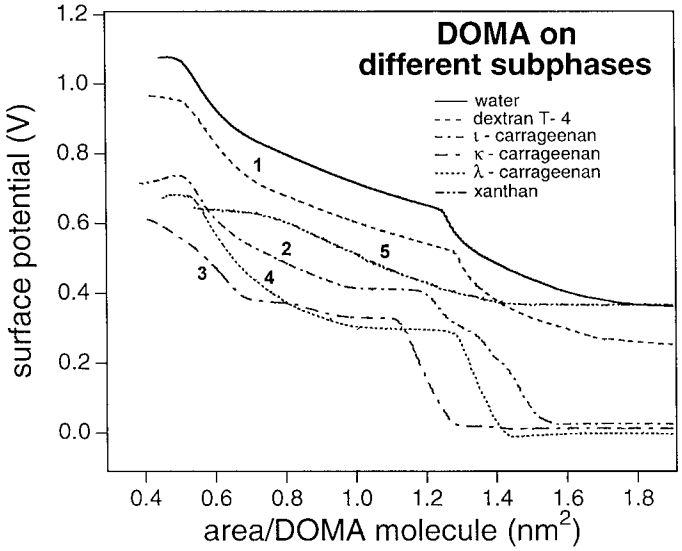

FIG. 4. Surface potential-area (ΔV-A) isotherms for DOMA monolayers on water (full line), Dextran T-4 (1), ι-carrageenan (2), κ-carrageenan (3), λ-carrageenan (4), and xanthan (5). Concentration of polysaccharides in the subphase was 100 mg dm^{-3}. Temperature $T = 20°$C.

Mercury Surface

The interaction of lipid monolayers with polysaccharides from the bulk solution was also studied electrochemically with phase sensitive ac voltammetry using lipid-coated mercury electrodes. All investigated lipid monolayers transferred to the mercury surface show in the potential region from -0.6 V toward more negative potentials a capacitance minimum and capacitance peaks which are influenced by the presence of polysaccharides in solution. The capacitance-potential curves for the monolayer of lecithin (surface concentration of 0.485 g cm^{-2}) formed on the solution of 0.5 mol dm^{-3} NaCl (full line) and on the solutions of Dextran T-500 (dashed line) and ($\kappa + \lambda$) carragennans (dotted line) are shown in Fig. 5.

Regarding the behavior of lipid layers the decrease in capacitance for lipid monolayers at the potential of -0.6 V with respect to the capacitance of the pure electrolyte provides information about the adsorption of lecithin present on the top of the electrolyte solution, while the presence of three ac voltammetric waves at the potentials of -0.9, -1.3, and -1.47 V indicates the reorientation of the layer on the electrode (14, 15). However, peaks at the potential more negative than -1.3 V are not simply reorientation peaks. There is evidence that they are representative of a ferroelectric-type transition (40) in the lipid film which can be understood as switching processes (14). Low capacity values at the potential of -0.6 V also indicate that lecithin is adsorbed in this region with the hydrocarbon chains oriented toward mercury. However, there is some contradiction between theoretical values for capacity if all hydrocarbon chains are oriented toward mercury and the measured values. We found the capacity value of 3.2 μF cm^{-2} which is higher than the calculated capacity value of 0.7 μF cm^{-2}, which was expected for a

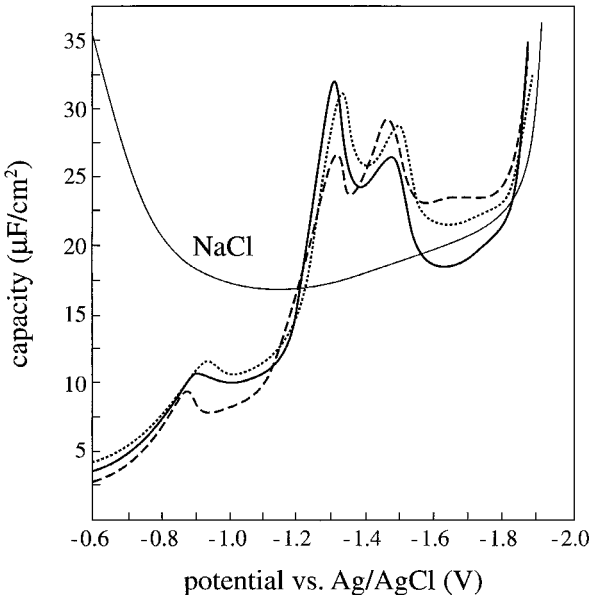

FIG. 5. Capacity-potential curves for a monolayer of lecithin, surface concentration 0.485 μg cm^{-2}, on the solution of 0.55 mol dm^{-3} NaCl (full line) and on the solutions of 18 mg dm^{-3} Dextran T-500 (dashed line) and 80 mg dm^{-3} $(\kappa+\lambda)$-carrageenans (dotted line). Accumulation potential was -0.6 V. Accumulation time was 60 s.

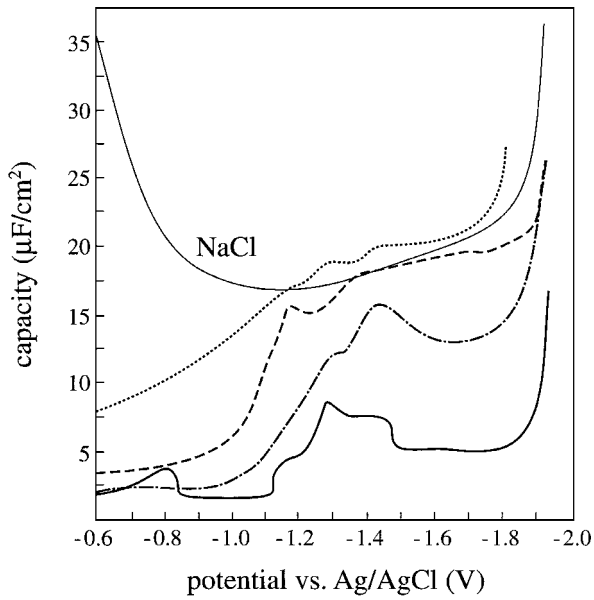

FIG. 6. Capacity-potential curves for DOMA monolayers, surface concentration 0.45 μg cm^{-2}, on the solution of 0.55 mol dm^{-3} NaCl (full line) and on the solutions of 36 mg dm^{-3} ι-carrageenan (dashed line), 89 mg dm^{-3} $(\kappa+\lambda)$-carrageenans (dotted line), and 30 mg dm^{-3} xanthan (dashed-dotted line). Accumulation potential was -0.6 V vs Ag/AgCl. Accumulation time was 60 s.

2.5-nm-long carbon chain perpendicular to the mercury and a dielectric constant of $\sim$2. A similar discrepancy between measured and calculated capacity values for a condensed layer of lecithin ($C_d \sim 2\ \mu$F cm^{-2}) was also observed by A. Nelson and I. R. Miller (14, 40). This may be explained by folding and overlapping of the hydrocarbon chains on the mercury surface, resulting in thinning of the layer, and consequently in an increase in capacitance.

In the presence of Dextran T-500, the capacity of the lipid layer at -0.6 V decreases negligibly and the reorientation waves are moved toward more positive potential by about 50 mV. In the presence of $(\kappa+\lambda)$ carrageenans, the capacity increases negligibly and the reorientation peaks are moved toward negative potential by ca 50 mV. All of these changes are not significant, and therefore those polysaccharides do not have any important influence on the lecithin monolayer. At potentials more negative than -1.6 V, curves for lecithin monolayers on polysaccharides show higher capacity values in comparison to the curves for pure lecithin and for electrolyte. Such behavior can be ascribed to the faradaic process. It is known that saccharides can be reduced on the mercury electrode at potentials more negative than -1.5 V due to the presence of keto or aldehydic groups (42). The influence of some other polysaccharides, such as dextran sulfate, Dextran T-4, xanthan, and ι-carrageenan on the structure of lecithin monolayers has also been studied (data not shown here), and very similar results have been obtained. In general, it can be concluded that the influence of the investigated polysaccharides on lecithin monolayers was not significant; i.e., in their presence only a negligible effect on the reorganization and the capacity of the layer is observed.

Much stronger effects of polysaccharides on the structure of lipid monolayers are observed with DOMA monolayers. Capacity-potential curves for DOMA monolayers on water (full line) and on solutions of carrageenans, xanthan, and dextrans are shown in Figs. 6 and 7. The capacity-potential curve for

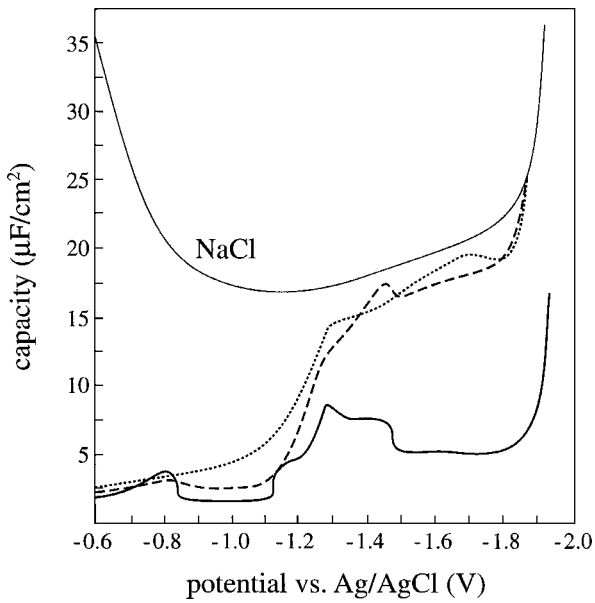

FIG. 7. Capacity-potential curves for DOMA monolayers, surface concentration 0.45 μg cm^{-2}, on the solution of 0.55 mol dm^{-3} NaCl (full line) and on the solutions of 12 mg dm^{-3} Dextran T-4 (dashed line) and 44 mg dm^{-3} Dextran T-500. Accumulation potential was -0.6 V vs Ag/AgCl. Accumulation time was 60 s.

DOMA monolayers on NaCl is completely different from those of phospholipids. The capacity of 1.78 μF cm^{-2} at the potential of -0.6 V is lower than the capacity values for lecithin, and is much closer to the value of the capacity when all hydrocarbon chains are oriented toward the mercury surface. At the potentials between -0.8 and -1.1 V, a marked pit appears which is caused by compact film formation due to strong intermolecular interactions between DOMA molecules, thus indicating a condensation process in DOMA monolayers. Such two-dimensional condensations are well known and described in the literature (42–45). At more negative potentials a reorientation of the DOMA monolayer is taking place (probably because of its positive charge), resulting in reorientation peaks at -1.3 V. In the region between -1.45 and -1.9 V, where desorption occurs, a new pit appears, indicating that a condensation of the reoriented monolayer is taking place. This condensed layer has a higher capacity (4.6 μF cm^{-2}), probably due to overlapping of hydrocarbon chains. It is obvious that the DOMA monolayer adsorbed at the mercury electrode undergoes marked structural changes depending on the applied potentials. Adsorption of DOMA on mercury is very strong in the whole region of potentials, from -0.6 V to the desorption at -1.9 V, resulting in much lower capacitance values compared to the capacity of sodium chloride. The more condensed monolayers of DOMA may be caused by hydrogen bonding between the head groups and by saturated hydrocarbon chains (46). It is also known that the longer the hydrocarbon chains, the lower the capacitance at the equilibrium spreading pressure (47).

All the investigated polysaccharides showed a strong influence on the structure of DOMA monolayers. Since xanthan and carrageenans are negatively charged polysaccharides, a significant interaction with positively charged DOMA monolayers was expected. The influence of carrageenans and xanthan on DOMA monolayers can be seen from the results presented in Fig. 6. The pits observed with the DOMA monolayer have disappeared, indicating that the condensation of the monolayer is prevented in the presence of carrageenans or xanthan in solution. The capacity is increased in the whole region of potentials, and desorption of the monolayer is taking place at more positive potentials compared to the monolayer at the water surface. Similar behavior (disappearing of pits and higher capacity at the potentials more negative than -1.0 V) has been observed with DOMA monolayers on solutions of dextran sulfate (data not shown here). In all these cases, the effects should be caused by electrostatic interactions. However, DOMA monolayers on the solutions of noncharged dextrans (Fig. 7) also show a similar behavior (disappearing of pits and higher capacity values at the potentials more negative than -1.3 V) which cannot be ascribed to electrostatic interactions but probably to hydrophobic and hydrogen binding contributing to the interaction. The condensation of DOMA monolayers occurring in adsorption of DOMA molecules at the mercury electrode can be ascribed to strong electrostatic interaction of positively charged DOMA with negatively charged mercury. If some other solutes like sugars are present in the subphase, their interaction with DOMA monolayers is in competition with the interaction with mercury, thus diminishing the condensation process. By comparing the adsorption of DOMA at the mercury surface with its adsorption at air/water and air/solution interfaces the following can be concluded. At the free air/water interface there is no charge which can contribute to the condensation of DOMA monolayers; however, at subphases containing carrageenans the condensation of DOMA monolayer was noted.

Additional investigations on the influence of polysaccharides on the structure of DOMA monolayers have been done by using an electrochemical probe. We chose cadmium as a model electrochemical probe for its very good polarographic characteristics and since it is a potential pollutant in aquatic systems. ac voltammograms of cadmium in sodium chloride solution without and with DOMA monolayers are shown in Figs. 8a and 8b (curves 0 and 1). It is obvious that DOMA monolayers decrease the height of voltammogram of cadmium, showing that an inhibition of electrode reduction of cadmium is taking place in the presence of DOMA monolayers. It can also be seen that after the cadmium wave at -0.67 V another wave at the potential of -0.85 V is appearing. We know that at this potential, capacity-potential curve for DOMA monolayer has a reorientation wave. Therefore we assume that at this potential, due to reorientation of the monolayer, the transport process of cadmium is changed. However, on the current-potential in-phase curve for a DOMA monolayer in the absence of cadmium in solution (data not shown here) this wave is appearing too, indicating that at this potential not only reorientation but also some faradaic process of the layer is taking place. More detailed studies of this phenomena will be done in the near future.

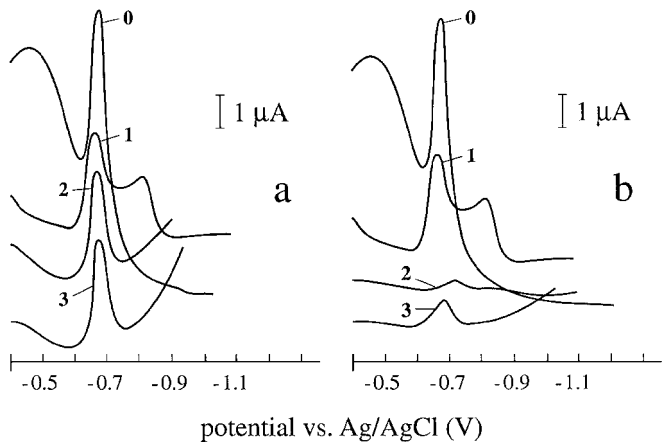

FIG. 8. (a) ac voltammetric wave of 10^{-5} mol dm^{-3} cadmium in 0.55 mol dm^{-3} NaCl (curve 0), in the presence of a DOMA monolayer without polysaccharide in subphase (curve 1) and in the presence of a DOMA monolayer spread on the solution of ($\kappa + \lambda$)-carrageenans (curve 2) and ι-carrageenan (curve 3). Accumulation potential was -0.45 V vs Ag/AgCl. Accumulation time was 60 s. (b) ac voltammetric wave of 10^{-5} mol dm^{-3} cadmium in 0.55 mol dm^{-3} NaCl (curve 0), in the presence of a DOMA monolayer without polysaccharide in subphase (curve 1) and in the presence of DOMA monolayer spread on the solution of Dextran T-4 (curve 2) and xanthan (curve 3). Accumulation potential was -0.45 V vs Ag/AgCl. Accumulation time was 60 s.

Although a DOMA monolayer inhibits the reduction of cadmium, the inhibition is not complete; i.e., at full coverage of the surface with a monolayer the ratio I/I_0 (current of cadmium when monolayer is present/current of cadmium in the absence of the monolayer) is 0.41. This means that a condensed monolayer of DOMA is partially transparent for cadmium ions in contrast with lecithin monolayers which completely inhibit the reduction of cadmium (15).

Mixed layers of DOMA with polysaccharides have different effects on cadmium reduction. In the presence of carrageenans, the inhibition of cadmium is not changed (Fig. 8a, curves 2 and 3), indicating that carrageenans do not increase the inhibition effects of a DOMA monolayer although the structure of the layer is modified. If Dextran T-4 and xanthan are present in solution, the ac voltammetric wave of cadmium is much more suppressed with mixed layers than with pure DOMA monolayers (Fig. 8b, curves 2 and 3). It is known that xanthan does not inhibit cadmium reduction in the absence of the DOMA monolayer since $I/I_0 = 0.94$ (48). Dextran T-500 shows an inhibition effect and the $I/I_0 = 0.43$ (49). From the results shown here, the inhibition effect of a mixed layer of DOMA and xanthan is $I/I_0 = 0.14$ and that of mixed layer of DOMA with Dextran T-500 $I/I_0 = 0.06$ in comparison with the effect of pure DOMA, which is $I/I_0 = 0.52$. This shows that the transport of cadmium is strongly blocked, since the change of the DOMA monolayer structure due to the interaction with xanthan and dextran, respectively, causes the formation of completely nontransparent film.

CONCLUSION

The results described here are part of more general studies of the interaction of hydrophilic solutes naturally occurring in the aquatic systems, like polysaccharides, with hydrophobic lipids. These observations are of great importance both to the interfacial properties of mixed lipid-polysaccharide monolayers and to the understanding of the influence of hydrophilic and hydrophobic substances on the physicochemical properties of natural surface films.

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