

Adsorption of Carrageenans on Mercury Surface in Sodium Chloride Solution and Seawater*

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Adsorption of natural sulphated polysaccharides from algal sources, ι-, κ- and λ-carrageenans, on mercury surface was studied by out of phase a.c. voltammetry. Adsorption studies were performed in a wide concentration range (10 mg/L up to 15 g/L) and the influence of the adsorbed layer on the reduction of cadmium ions, used as a probe, was studied as well. The adsorption was measured at two potentials, -0.2 V and -0.6 V vs. Ag/AgCl reference electrode. The stronger, one step adsorption, was obtained at the potential of -0.2 V. At the potential of -0.6 V, the first adsorption plateau was established at the concentration of app. 100 mg/L of added polysaccharide while at the concentration of few g/L a second adsorption plateau was established. The oxido-reduction processes of Cd^{2+} ions were influenced by the presence of sulphopolysaccharides only in the concentration range of a few grams/L. At the potential of $E = -0.6$ V after the first adsorption plateau, adsorption is a slow process, determined by both the concentration of polymer in the solution and the time of adsorption. It is most probable that transformations of the adsorbed layer occur.

INTRODUCTION

Natural polysaccharides represent a well recognized and important part of the organic matter present in aquatic environment.¹ In literature, special attention has recently been paid to natural sulphated polysaccharides,^{2,3,4,5,6}

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since they are recognized as exocellular polysaccharides observed during marine diatom blooms. Diatom blooms are most common phytoplankton blooms appearing in the Northern Adriatic,⁷ which are occasionally accompanied by the appearance of mucilages. Carrageenans are a family of galactans extracted from marine red algae. Their ability to act as thickeners or to form aqueous gels make them extensively used in food and cosmetic technology as well as in pharmaceutical industry. Individual members of this family show subtle differences in chemical structure that have far-reaching effects on their ability to form cohesive network structures both *in vitro* and *in vivo*. Carrageenans are alternating copolymers of α -(1 \rightarrow 3) and β -(1 \rightarrow 4) galactose units, with different fractions having different sulphate contents. The main gel-forming carrageenan fractions are known as ι - and κ -, while the third main fraction, λ -, is non-gelling.^{8,9} The relative molecular mass of carrageenans are estimated to vary from 3.5×10^5 up to 7.5×10^5 .¹¹

In the Northern Adriatic (Gulf of Trieste), the appearance was detected of the red alga *Hypnea Musciformis* from which κ -carrageenan can be successfully isolated.¹⁰

We have recently studied the adsorption behaviour of ι -, κ - and λ -carrageenan on hydrophilic (γ -Al₂O₃ particles) and hydrophobic surfaces (mercury electrode).¹² The investigations performed by a.c. voltammetry were made in a relatively low concentration range (1 mg/L to 100 mg/L). Great affinity of carrageenans to both surface was observed under the conditions investigated. The concentration range was below the range in which the viscosity and aggregation number in solutions play a role.

In this paper, the adsorption study of carrageenans has been extended to hydrophobic mercury surface in a higher concentration range, up to a few grams/L, which can be of significance for situations in which the concentrations of sulphated polysaccharides are highly increased.

EXPERIMENTAL

Measurements were made using the phase sensitive a.c. voltammetry (PSACV). The method makes it possible to measure the capacitive current (*i.e.* the current needed to build up a certain potential on the electrode) selectively. The decrease of the capacitive current below the value obtained for pure electrolyte in the presence of surface active organic material is a measure for the amount of this material adsorbed on the electrode.¹³

The experiments were performed with a stationary hanging mercury drop electrode (HMDE, surface area 5.4×10^{-3} cm²) in a three electrode cell (Metrohm VA 663) connected either to a Metrohm E-506 (Switzerland) or ECO-CHEM (The Netherlands) electroanalytical instruments. Phase sensitive a.c. voltammetry with a frequency of 75 Hz, amplitude 10 mV and phase angle of 90° was used to measure the adsorbed amount of carrageenans on the HMDE electrode. We recorded current *vs.* potential voltammetric curves after different accumulation times or current *vs.* time voltam-

metric curves, both of which gave us information on the amount of substance adsorbed. Experiments were performed either in 0.55 M NaCl (precleaned from organic contaminants) or in seawater. All potentials were referred to the Ag/AgCl reference electrode. The measurements were performed at two electrode potentials, $E = -0.2$ V and $E = -0.6$ V. At the potential of -0.2 V, the mercury electrode is positively charged and favours adsorption of negatively charged organic substances while at the potential of -0.6 V, which is close to the electrocapillary maximum, adsorption of neutral molecules is to be expected.¹⁴ Investigations were performed at pH = 5.0 (0.55 M NaCl) and at pH = 8.0 (in seawater). The pure chemical ι -carrageenan (Type V) was from Sigma (USA) isolated from red algae and already used in previous work.¹² Besides this pure chemical, for measurements in a higher concentration range, two additional, commercial grade chemicals (Sigma, USA) were used, namely: Type I carrageenan blended from various seaweeds to produce rigid gels, containing predominantly κ -carrageenan and lesser amounts of λ -carrageenan and Type II blended from various seaweeds to produce flexible gels, containing predominantly ι -carrageenan. The solutions were prepared by weighing a certain amount of chemical. For pure chemicals, solutions of 1–2 g/L were prepared while for commercial grade chemicals solutions of 5–17 g/L were prepared. Solutions with higher concentrations of added polysaccharide were highly viscous.¹⁵ In literature, formation of gels is reported for solutions containing 3% of dissolved solids.¹¹

Differential pulse voltammetry (DPV) was used to measure the influence of the adsorbed amount of sulphated polysaccharide on the oxido-reduction processes of cadmium ions. In DPV, the adsorbed amount of surface active material on the electrode surface usually diminishes the rate of electrode reaction, which is observed as a suppression of the height of the voltammetric wave (oxidation or reduction / or both) of metal ions used as a probe.¹⁶ DPV was also applied for studying the existence of the faradaic process for carrageenans. The experimental conditions for DPV applied on the ECO-CHEM electroanalytical system were: modulation time 0.04 s, interval time 0.20 s, step potential 0.001 V and modulation amplitude 0.025 V at different accumulation times (as indicated in Figures.). Scan rate was 5 mV/s (calculated from the step potential and interval time).

RESULTS AND DISCUSSION

Figure 1 presents the capacitive current Δi (*i.e.* the difference between the capacitive current for the pure electrolyte and the capacitive current in the presence of carrageenan) *vs.* added amount of ι -carrageenan in a wide concentration range. Curve 1 was obtained for the measurement of capacitive current at the potential of $E = -0.6$ V after an accumulation time $t_a = 60$ s. Two adsorption plateaus are visible on the curve. One was established at the concentration of ≈ 0.1 g/L and the other at about 8 g/L. Measurements at the potential of $E = -0.2$ V for the same accumulation time $t_a = 60$ s showed only one adsorption plateau, established at a lower concentration range of ι -carrageenan (20–30 mg/L) and remaining unchanged over the entire concentration range investigated (curve 2). Curve 3 was constructed from measurements of the capacitive current *vs.* time at the potential of -0.6 V.

The data presented are for the accumulation time of $t_a = 600$ s. Although recorded at the potential of -0.6 V, the data for the decrease of the capacity current (curve 3) resemble more the adsorption behaviour of carrageenan as obtained at the potential of -0.2 V (compare with curve 2). The experiment showed that the adsorption process of ι -carrageenan is variable, being dependent both on the time and potential of the electrode under constant conditions of the concentration and ionic environment. Figure 2 shows the adsorption curves for κ -carrageenan at potentials of $E = -0.6$ V (0.55 M NaCl (O), seawater (□)) and $E = -0.2$ V (Δ) for the accumulation time $t_a = 60$ s. The same feature as in Figure 1 is visible: one step adsorption at the potential of -0.2 V and two step adsorption at the potential of -0.6 V regardless of the electrolyte employed (0.55 M NaCl or seawater). The presence of calcium and magnesium ions in seawater did not influence the adsorption process under the given conditions of the experiment. In our previous work,¹⁷ it was shown that the presence of calcium and magnesium ions in seawater partially neutralized the negative charges of the sulphate groups and thus

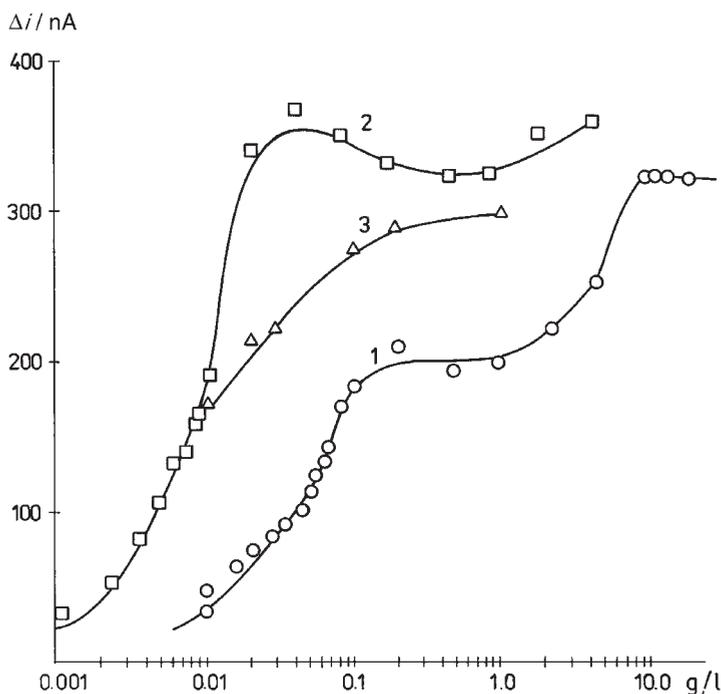


Figure 1. Apparent adsorption isotherms for ι -carrageenan in 0.55 M NaCl, pH = 5.0, for 60 s of accumulation with stirring (chemical used: for < 1 g/L Type V, for > 1 g/L Type II). (1) $E = -0.6$ V, (2) $E = -0.2$ V, and for 600 s of accumulation with stirring (3) $E = -0.6$ V. Δi = the difference between the capacitive current for pure electrolyte and in the presence of added carrageenan.

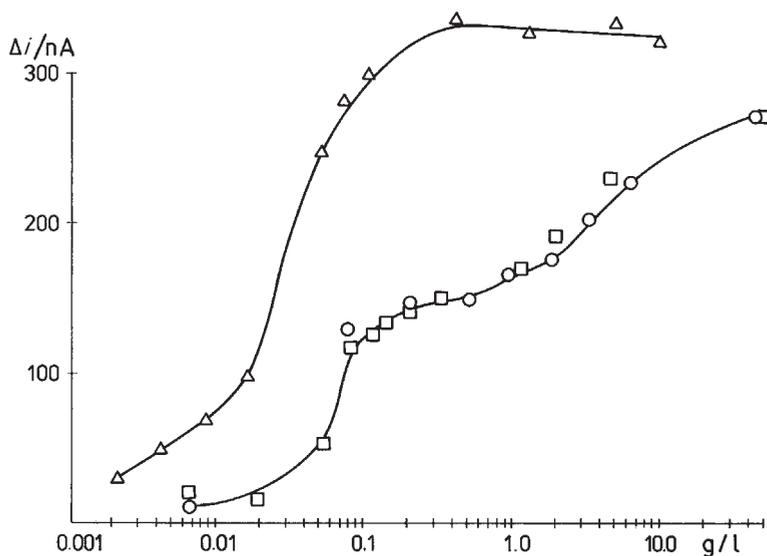


Figure 2. Apparent adsorption isotherms for κ -carrageenan in 0.55 M NaCl (pH = 5.0) for 60 s of accumulation with stirring at $E = -0.6$ V (o) and $E = -0.2$ V (Δ) and in seawater (pH = 8.0) $E = -0.6$ V (\square). Chemical used: Type I carrageenan.

enhanced the adsorption of ι -carrageenan at lower concentrations (<10 mg/L).

The same as for ι - and κ -carrageenans, one step adsorption at the potential of -0.2 V was obtained in the adsorption experiment for λ -carrageenan, not presented here.

The adsorption curves presented in Figure 1 and Figure 2 are nonequilibrium ones since they are recorded for a certain time of adsorption before the equilibrium is reached.

Adsorption of sulphated polysaccharides at the mercury electrode is strongly influenced by the electrode surface charge. At potentials more positive than the electrocapillary maximum, which is in chloride solutions around -0.6 V (-0.56 V reported for 1.0 M NaCl),¹⁸ the electrode surface bears a positive charge and favours adsorption of negatively charged sulphated polysaccharides, as it is shown for adsorption of different carrageenans at the potential of -0.2 V. With accumulation time of $t_a = 60$ s, the adsorption plateau is reached for ι -carrageenan at concentrations between 10 and 20 mg/L. With increasing adsorption time, the adsorption is shifted towards lower concentrations. As it is shown on the $i-t$ curves presented in Figure 3, recorded at $E = -0.2$ V, in solutions with 1–2 mg/L of ι -carrageenan maximum adsorption can be achieved in adsorption times of 20–30 min. An interesting feature of $i-t$ curves was observed for higher concentrations of ι -carrageenan (>10 mg/L), *i.e.* after the first adsorption event

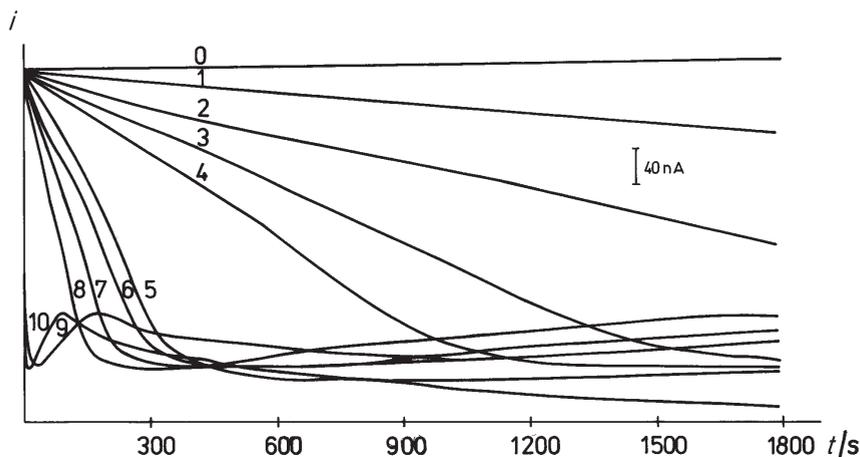


Figure 3. $i-t$ curves at $E = -0.2$ V for 0.55 M NaCl, pH = 5.0 (0) and with 0.22 mg/L (1), 0.55 mg/L (2), 1.11 mg/L (3), 1.66 mg/L (4), 2.77 mg/L (5), 5.54 mg/L (6), 7.76 mg/L (7), 11.08 mg/L (8), 110.08 mg/L (9), 166.20 mg/L (10) of added ι -carrageenan. Chemical used: Type V ι -carrageenan.

reaching the adsorption maximum, further changes in the capacity current were observed which could be ascribed to the association process and transformation of the adsorbed layer of carrageenan. A similar feature of $i-t$ curves was reported for adsorption of commercial sodium dodecyl sulphate (SDS) in the concentration range where the expected formation of associates and hemimicelles at the electrode surface was given as the most likely explanation.¹⁹

At -0.6 V, the mercury electrode is slightly negatively charged, which has a strong influence on the adsorption behaviour of negatively charged sulphated polysaccharides. Adsorption curve is shifted towards higher concentrations, reaching the first plateau of adsorption at about 100 mg/L. Further adsorption is possible by increasing either the concentrations up to a few grams per liter, or by increasing the time of adsorption, which means that some rearrangements of the adsorbed polymeric material are prerequisites for further adsorption of the negatively charged polymer to the slightly negatively charged electrode surface. It is reasonable to expect that counter ions may play an important role in these processes, the same as reported for gelation processes.^{15,20,21}

It is known that sugars can be reduced on the mercury electrode due to the presence of keto or aldehydic groups.¹⁸ We have investigated the faradaic processes of ι -carragennan and their relations to the adsorption behaviour at the mercury electrode.

The differential pulse voltammetry was applied to these measurements and a faradaic wave for carragennan at the half-wave potential of -1.29 V

was observed, which is a value similar to the half-wave potentials of other sugars (monosaccharides or disaccharides) quoted in literature.¹⁸ The reduction wave for ι-carrageenan was observable in the concentration range between 300 mg/L – 1 g/L of the added polysaccharide (Figure 4). For a lower concentration range (up to 100 mg/L), a very small faradaic current was observed even for longer accumulation times. For the concentration range higher than 1 g/L, no faradaic current was observable. The peak height of DP voltamograms slightly depends on the accumulation potential. A slightly higher DP voltamogram was observed for 60 s accumulation at the potential of -0.2 V than at -0.6 V (for 324 mg/L of ι-carrageenan for 60 s of accumula-

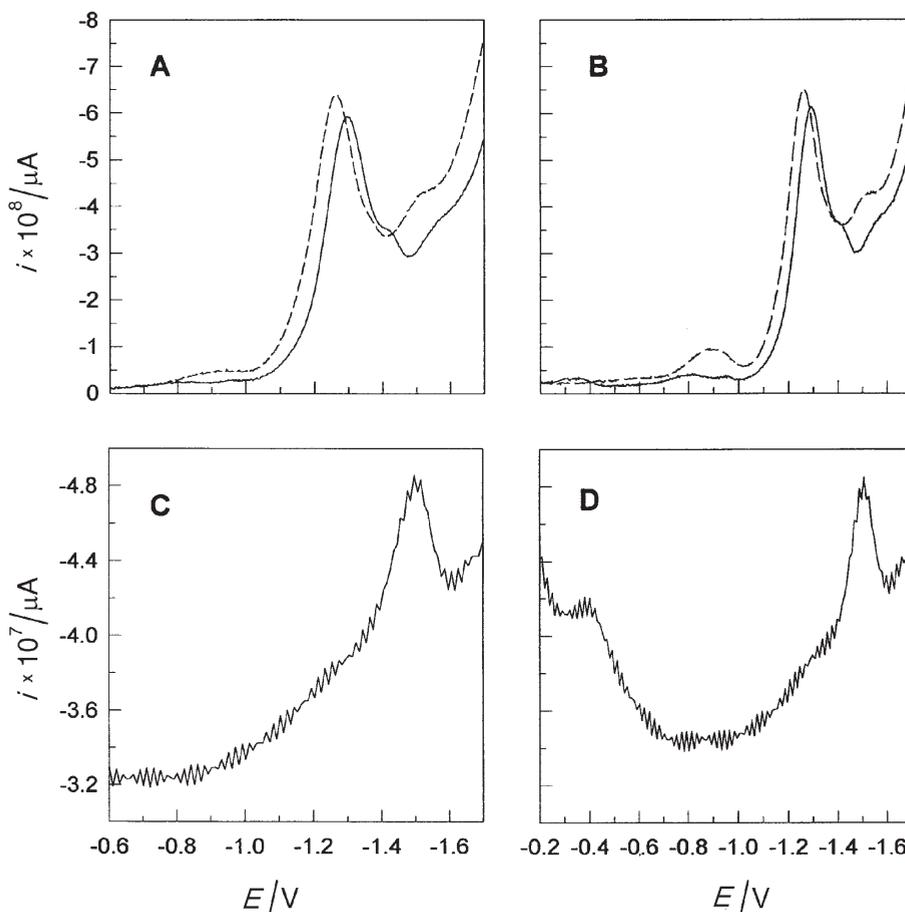


Figure 4. DP voltamograms for 324 mg/L of ι-carrageenan (Type II) in 0.55 M NaCl recorded at accumulation potentials $E = -0.6$ V (A) and $E = -0.2$ V (B); --- $t_a = 60$ s; — $t_a = 300$ s. Alternating current out of phase voltamograms recorded after accumulation at $E = -0.6$ V (C) and $E = -0.2$ V (D) with $t_a = 60$ s.

tion at -0.6 V the height of the voltammetric wave is 37.7 nA, and at -0.2 V the height of the voltammetric wave is 40.7 nA (Figures 4A and 4B), though the difference is very small and could be within the experimental error. The relatively low reduction current for the added amount of polysaccharide of about 40 nA is in accordance with the fact that in a large polysaccharide molecule a small amount of free reducible groups is present. In the same concentration range (300 mg/L – 1 g/L), also in recording a.c. out of phase voltammetric curves, a pronounced desorption wave was observed at app. -1.5 V for both accumulation potentials (-0.2 V and -0.6 V) (Figure 4C and Figure 4D), which was not visible in the concentration range lower than 300 mg/L and in the concentration range greater than 1 g/L.

These experiments have shown that the changes in the structure of the adsorbed layer of polysaccharides occur between 100 mg/L – 1 g/L. The faradaic process of polysaccharide, observable in the same concentration range, is influenced by the adsorption process. At low polysaccharide concentrations (below 100 mg/L), the very low current is due to the very slow transport of the bulky molecules to the electrode. At higher concentrations (in the range 100 mg/L – 1 g/L), the current is due to electroreduction of the polysaccharide accumulated by adsorption at the electrode surface. At very high concentrations of polysaccharide (greater than 1 g/L), the adsorption of macromolecules in multilayers is such that the transport to and from the electrode is minimized and the electroactive groups in the adsorbed state are not favourably oriented for the faradaic process to take place.

We also tested the permeability of the adsorbed layer for the oxido-reduction processes of cadmium ions. Below the second adsorption plateau, *i.e.* for concentrations below a few grams/L, there is no suppression of the voltammetric reduction wave of Cd^{2+} ions (at -0.4 V), which indicates that the layer of adsorbed polysaccharide is permeable for Cd ions at a lower concentration range (Figure 5) while at certain concentration ranges (few g/L) a change in the permeability of adsorption layer occurs which is visible through suppression of the Cd^{2+} reduction wave.

Permeability of the adsorbed layer of carrageenan for Cd ions up to a few g/L of added polysaccharide indicates that negatively charged sulfate groups are oriented to the solution, enabling reduction of cadmium ions while galactose units of polysaccharide are close to the mercury surface. When the concentration of carrageenans is high enough (greater than 1 g/L) and the formation of gel structure starts, sulfate groups are not in a favourable position any more and the reduction process of cadmium ions becomes inhibited to a certain extent. The behaviour of the already mentioned SDS, showing similar *i-t* curves to carrageenans, regarding oxido-reduction processes of metal ions, shows different features. At lower concentrations of SDS, the oxido-reduction processes of metal ions (Cd, Pb) becomes inhibited while after hemimicelles and micelles are formed on the electrode, the layer

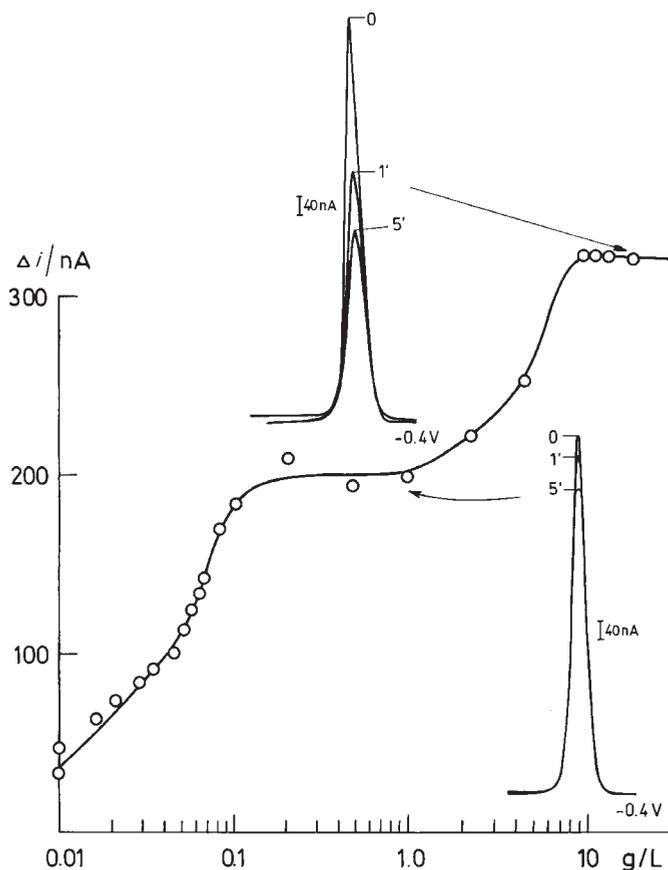


Figure 5. Apparent adsorption isotherm for ι -carrageenan in 0.55 M NaCl (Type V carrageenan for concentrations < 1 g/L and for concentrations > 1 g/L Type II carrageenan) (pH = 5.0) for $t_a = 60$ s at $E = -0.6$ V together with DP voltamograms for 10^{-5} M Cd^{2+} ions measured in the presence of ι -carrageenan in concentrations as indicated by arrows. Cathodic current for cadmium was recorded after $t_a = 0, 1$ or 5 min at $E_a = -0.4$ V.

of adsorbed SDS becomes permeable for reduction of metal ions since the now negatively charged sulfate groups are oriented to the solution, forming »bridges« for easier reduction of metal ions.¹⁹

Regarding the adsorption of carrageenans and other polysaccharides with sulphate groups on hydrophylic $\gamma\text{-Al}_2\text{O}_3$ particles, it was estimated that the sulphate groups are oriented to the surface of alumina particles while the adsorption densities on the alumina surface, expressed as the amount of sulphate units/ m^2 , were the same for Dextran sulphate and ι -carrageenan,¹² although there are differences in adsorption densities calculated for these compounds, taken as whole molecules.

CONCLUSION

Sulphated polysaccharides from algal sources, ι -, κ - and λ -carragennans, are adsorbed to a high extent onto the mercury surface. Different adsorption behaviour at two different potentials, $E = -0.2$ V and $E = -0.6$ V, was observed. A stronger, one step adsorption at the potential of $E = -0.2$ V can be ascribed to the interaction between the negatively charged polymers and the positively charged electrode surface. At the potential $E = -0.6$ V, *i.e.* at a slightly negatively charged electrode surface, two step adsorption was observed for accumulation time of 60 s. Further adsorption is a slow process that is determined by both the concentration of the polymer in solution and the time of adsorption. It is most likely that some transformations of the adsorbed layer occur, which is indicated by the out of phase measurements (capacity current *vs.* time curves) as well as by the faradaic measurements of the reduction process of carrageenan and of the reduction of cadmium ions used as an electrochemical probe. The layer of the adsorbed polysaccharide is permeable for reduction of cadmium ions at lower concentrations of carrageenan, up to a few g/L, while at the second adsorption plateau (≈ 10 g/L) partial inhibition of the reduction of cadmium ions was observed.

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SAŽETAK

Adsorpcija karagena na živinoj površini u otopini natrijevog klorida i u morskoj vodi

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U ovom radu ispitivana je adsorpcija prirodnih polisaharida sa sulfatnim skupinama, ι -, κ -, λ -karagena, na živinoj površini metodom voltametrije s izmjeničnom strujom. Adsorpcijska ispitivanja napravljena su u širokom koncentracijskom području (10 mg/L – 15 g/L). Ispitan je i utjecaj adsorbiranog sloja na redukciju kadmijevih iona. Adsorpcija je mjerena na dva potencijala $-0,2$ V i $-0,6$ V prema referentnoj elektrodi Ag/AgCl. Jača adsorpcija, koja pokazuje samo jedan adsorpcijski plato, dobivena je na potencijalu od $-0,2$ V. Na potencijalu od $-0,6$ V kod koncentracije od 100 mg/L dodanog polisaharida opaža se prvi adsorpcijski plato, a kod koncentracije od nekoliko g/L drugi adsorpcijski plato. Utjecaj polisaharida na oksido-redukcijski proces kadmijevih iona vidljiv je tek kod koncentracija od nekoliko g/L. Na potencijalu od $-0,6$ V nakon prvog adsorpcijskog platoa, adsorpcija postaje spori proces određen koncentracijom polimera u otopini i vremenom adsorpcije. Vjerojatna je promjena u strukturi adsorbiranog sloja.