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Scientific paper

Binding of Cationic Surfactants by Carrageenans. A Study of the Influence of Polyelectrolyte Charge Density[†]

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[†] Dedicated to Prof. Dr. Jože Škerjanc on the occasion of his 70th birthday

Abstract

Binding isotherms for the binding of dodecyl- (DPC) and cetylpyridinium chloride (CPC) to κ-, ι-, and λ-carrageenan were determined in aqueous solution without added salt by using a potentiometric technique based on surfactant-selective membrane electrodes. The potentiometric curves in the case of CPC were used in the first place to determine the number of charges on the monomer unit of polysaccharides. This procedure showed that κ- and ι- carrageenan samples have structures close to the ideal ones, whereas λ-carrageenan sample bears around 2.8 (instead of ideally 3) charges per disaccharide repeating unit. The CAC values, determined from the binding isotherms, are around two orders of magnitude lower in the CPC case than in the DPC one. At the same time, CPC is practically completely associated with all polyions, whereas the amount of bound DPC is lower and depends on the carrageenan charge density. However, the degree of binding in the plateau region of binding is very similar for both surfactants. This finding can be explained by proposing lamellar type of ordering between rigid carrageenan chains and surfactants. The experimental CAC values were compared with those predicted by a theoretical approach based on the cell model of a polyelectrolyte solution with two monovalent counterions of different size. A satisfactory agreement between experimental and calculated values was obtained.

Keywords: Surfactant-polyelectrolyte interactions, binding isotherms, carrageenans, charge density, critical association concentration

1. Introduction

Carrageenans are water soluble, linear sulphated polysaccharides extracted from different species of marine red algae of the class Rhodophyceae.[1] In aqueous solutions, these macromolecules are charged and therefore exhibit polyelectrolyte behavior. The main reason for the wide industrial application of these compounds is their ability to induce thickening and gelation of the solutions under various experimental conditions, in particular by varying the temperature and the type of the counterion and the coion.[3–4] Three major groups of carrageenans have been recognized: κ-carrageenan, ι-carrageenan, and λ-carrageenan. They differ in chemical composition, which affects the linear charge density of the polysaccharides in aqueous solution. Thus, ideally κ-carrageenan in solution has only one elementary charge per disaccharide repeating unit, ι-carrageenan two, and λ-carrageenan can bear two or three (on the average 2.7) of these charges per disaccharide unit. Furthermore, κ-carrageenan and ι-carrageenan form gels, whereas no gel formation has been observed for the most highly charged λ-carrageenan.

In many industrial applications, both polymers and surfactants are used as ingredients. It is therefore important to recognize how the properties of the polymer and those of the amphiphile affect their mutual interaction. In the case when both species are (oppositely) charged, very strong interaction is expected primarily due to charge neutralization and this normally leads to the precipitation of a polyelectrolyte-surfactant complex. It is generally recognized that this complexation is of a highly cooperative nature and depends on the specific characteristics of both the polyelectrolyte and the surfactant.[5–7] Whereas in the case of surfactant the length of its hydrocarbon tail is the decisive factor, one has to consider several characteristics of the polyion in the interpretation of experimental observations. These characteristics are: charge density, flexibility, conformation, types of charges and their distribution along the chain, the presence (and the distribution) of hydrophilic and hydrophobic segments and others. From these standpoints, interactions between various carrageenans and certain drugs (with an amphiphilic character and with different hydrophobicity) have been addressed in detail over the past years.[8–11] These drugs differed in their hydrophobic parts, which were composed of three condensed, partly aromatic, ring systems. This is in variance with what is most frequently encountered in the study of polyelectrolyte/surfactant interaction. Usually, the hydrophobic part of the surfactant molecule is a long hydrocarbon chain. Such more common types of cationic surfactants were employed in studies of phase behavior in mixtures with κ-, ι-, and λ-carrageenan[12,13] (dodecylammonium chloride) or in characterization of microstructures by synchrotron small-angle X-ray scattering in complexes with κ- and ι-carrageenan, where cetylpyridinium chloride was used.[14] For this type of surfactants, no detailed quantification of the degree of binding, e. g. in the form of binding isotherms, is available.

The purpose of this work is to investigate the binding of two cationic surfactants, dodecyl-, DPC, and cetylpyridinium chloride, CPC, to the above mentioned κ-, ι-, and λ-carrageenans. The study is confined to the case of aqueous carrageenan solutions without added salt and concentrates on the influence of charge density of the polyion on the interaction with surfactant. Potentiometric measurements using the surfactant-selective membrane electrode were used to determine the degree of binding of both surfactants to carrageenan polyions. The binding isotherms derived therefrom were used to determine the critical association concentration (CAC) values, which were compared with theoretical predictions. The latter were derived from the calculated distributions of counterions around the polyions of varying charge densities. The distribution of the counterions around the polyion was obtained from the solution of the Poisson-Boltzmann equation for the cell model of a polyelectrolyte solution with two kinds of monovalent counterions differing in size.[15]

2. Experimental

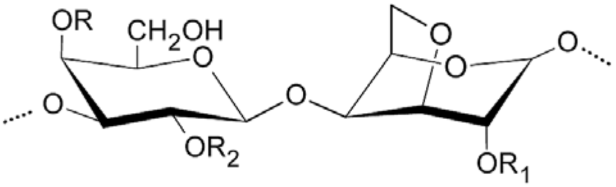
2. 1. Materials

The κ-, ι-, and λ-carrageenan samples were commercial products from Sigma Chemicals Co. (Bornem, Belgium), Types III, (No. 127H-1222), V (No. 27F-0373), and IV (No. 58F-0604), respectively. They were purified and transformed into sodium salts by the procedures reported in the literature.[2] The solid salts were stored refrigerated. N-dodecylpyridinium chloride (DPC, Merck, Darmstadt, Germany) and N-cetylpyridinium chloride (CPC, Kemika, Zagreb, Croatia) were purified by repeated re-crystallization from acetone and dried under vacuum at 50 °C.[15a] They were stored in a desiccator.

Polysaccharide stock solutions were prepared by carefully following the procedures reported in the literature.[2,3] A calculated amount of a polymer was weighed into a volumetric flask and dissolved in water at room temperature. Solution was heated to 75 °C and kept at this temperature under continuous stirring for at least one hour. After cooling it to room temperature, the volumetric flask was filled with pure water to the graduation mark to get the desired polymer concentration. All solutions were prepared in triple distilled water with no added salt. It has been shown that under these conditions and with Na^+ as the counterion all carrageenans are in their random coil conformations.[4,16,17]

2. 2. Potentiometry

The equilibrium concentration of free surfactant ions (c_S^{free}) in aqueous carrageenan solutions was determined potentiometrically with a surfactant-selective membrane electrode. The preparation of the electrode reversible to dodecyl- and cetylpyridinium cation, DP^+ and CP^+, respectively, was as described before.[18] As a reference, the saturated calomel electrode was used and the voltage difference E was measured with an ISKRA MA 5740 pH meter. A titration technique was employed to determine both, the E vs. the logarithm of total surfactant concentration (c_S^{tot}) curve in solvent without added polyelectrolyte and the corresponding curves in the presence of polyelectrolytes. The voltage E reached a constant value a few minutes after the change in surfactant concentration. The response of the electrode in DPC and CPC solutions without added polymer was linear in a wide concentration range: i.e., from around 1×10^{-6} mol/L to the critical micelle concentration, CMC, (with a slope 57 ± 1 mV/decade) and from around 1×10^{-5} mol/L to the CMC (with a slope 59 ± 1 mV/decade) in the CPC and DPC case, respectively. These slopes are close to the theoretical value of 59.2 mV/decade at 25 °C that follows from the Nernst equation. The binding of DPC and CPC by κ-, ι-, and λ-carrageenan was studied at a polymer concentration, c_p, equal to 5×10^{-4} moles of the repeating disaccharide unit per volume. This concentration unit is usually abbreviated as monomol/L. The monomolar concentrations were calculated by taking into account the idealized structures of carrageenans shown in Scheme 1.



Scheme 1. Idealized disaccharide repeating unit of carrageenans: κ-carrageenan: R = SO_3^-; R_1, R_2 = H; ι-carrageenan: R, R_1 = SO_3^-; R_2 = H; λ-carrageenan: R, R_1, R_2 = SO_3^-. Hydrogen atoms are not explicitly shown.

3. Theoretical Approach for the Calculation of CAC Values

A well known phenomenon in polyelectrolyte solutions is a pronounced accumulation of counterions in the vicinity of the polyion, which is a consequence of strong attraction between highly charged polyion and oppositely charged counterions. The variation of the local concentration of counterions with the distance from the polyion depends strongly on the charge density of the polyion. In the case treated herein, two monovalent counterions (Na^+ and the surfactant cation, DP^+ or CP^+) that differ in their size are present in solution. Their distribution was calculated following the approach reported in the literature.[15] The Poisson-Boltzmann equation was solved for the cell model of a polyelectrolyte solution with two kinds of monovalent counterions differing in their size (see the relevant equations in ref. 15a). The smaller ions were Na^+, the larger ones were either DP^+ or CP^+, and the calculations were performed for the mole fraction of the larger counterions, X_c, approaching unity. It has been stated that the value of X_c does not influence much the general course of the radial distribution of the counterions.[15a] The following values for the structural parameters were used in these calculations: the polyion radius was $a = 1.1$ nm and the distances of the closest approach of the counterions to the polyion were $b = 1.3$ and $c = 1.4$ nm. The value of b was obtained from the polyion and sodium ion radii in solution.[15a] The value of c applies to both, CP^+ and DP^+, and was obtained by taking into account the radius of the pyridinium cation in solution.[15a]

The value for the linear charge density parameter, ξ (for the definition of ξ see for example ref. 15a), of the κ-carrageenan was calculated from the length of the disaccharide repeating unit, b_m, carrying unit charge. The value of b_m obviously depends on the conformation of the chain. There is a general agreement that b_m equals 1.03 nm for κ-carrageenan in a quasi-extended conformation,[19–21] resulting in a value $\xi = 0.693$ in water at 25 °C. The b_m values for the random-coil conformation of ι- and λ-carrageenan were obtained from the b_m value for κ-carrageenan (as one half and one third of 1.03 nm, respectively) and resulted in $\xi = 1.386$ and 2.08 for ι- and λ-carrageenan, respectively.

In Figure 1, the calculated distributions of larger (surfactant) counterions (expressed as the ratio c/c_{aver}, where c is the local concentration of ions at a radial distance r from the axis of the polyion cylinder and c_{aver} is their average concentration in the cell) are plotted as a function of the radial distance r for all three polyions. For better visibility, the distributions of smaller counterions (Na^+) are not included. The polyion concentration is in all cases 5×10^{-4} monomol/L. As expected, the concentration of surfactant cations at the cell boundary increases with decreasing charge density of the polyion. More important for the present case are surfactant concentrations in layers close to the polyion; for example, at distances from the polyion that correspond to the length of surfactants' hydrocarbon chains. The relevant distances in the present case are 2.6 and 3.1 nm for DPC and CPC, respectively. They were obtained by adding up the lengths of fully extended dodecyl or cetyl chains (1.5 or 2.05 nm,[22] respectively) and the radius of the polyion (a = 1.1 nm). These two distances are designated by dashed and dotted lines in Figure 1b and are situated very close to the polyion surface.

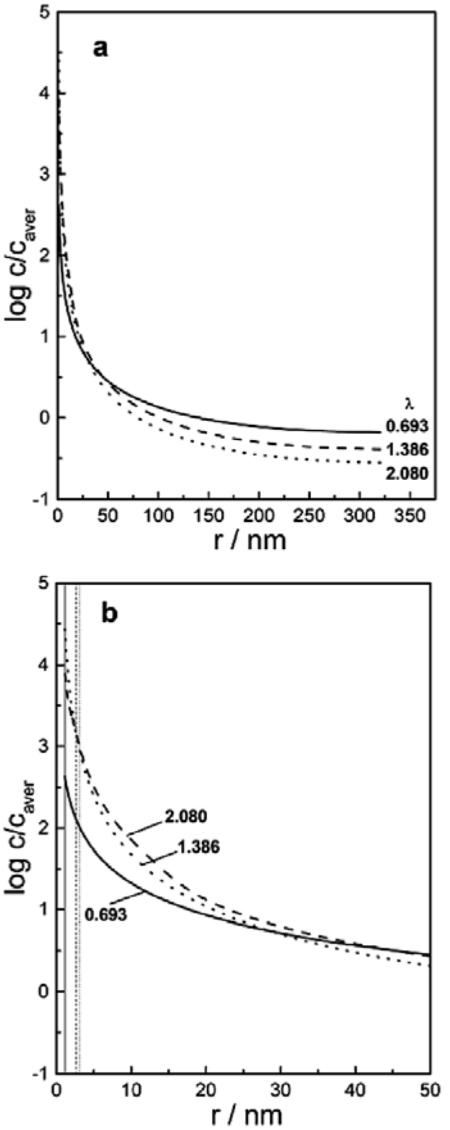


Figure 1. The dependence of c/c_{aver} for surfactant counterions in a mixture with Na^+ counterions on the radial distance r from the axis of the polyion; the radius of the polyion is a = 1.1 nm and the radii of the counterions are 0.2 and 0.3 nm. The linear charge density parameter values (ξ = 0.693, 1.386, and 2.080) correspond to structural values derived from the idealized structures of κ- , ι-, and λ-carrageenan (see Scheme 1). Polymer concentration: $c_p = 5 \times 10^{-4}$ monomol/L; value of the mole fraction of surfactant counterions $X_C = 1$; a) in the whole region of the cell; b) in the region close to the polyion. The solid, dashed and dotted lines in Figure 1b designate the radius of the polyion (a = 1.1 nm) and distances 2.6 and 3.1 nm from the center of the cell (see text).

Evidently, the local concentration of larger counterions at these distances is considerably higher than their average concentration in the cell. It is known that sufficient accumulation of surfactant unimers ultimately leads to aggregation/micellization.[5–7,15] In the present approach, it was assumed that polyion induced micellization of surfactant in layers close to the polyion will take place when their local concentration at these distances reaches (or exceeds) the surfactant's CMC. From the distribution curves, the ratio c/c_{aver} was read and the CAC values were calculated by putting c = CMC (the value for the particular surfactant in H_2O at 25 °C; these values are 1.52×10^{-2} and 6.3×10^{-4} mol/L for DPC and CPC, respectively[7,15a]) and c_{aver} = CAC. The theoretical predictions for CAC values of DPC and CPC are reported in Table 1 and will be commented together with the ones determined experimentally. At present it is sufficient to say that surfactant aggregation can take place close to the polyion even when the average surfactant concentration in solution is considerably lower than the CMC.

4. Results and Discussion

Potentiometric curves that were determined with the CPC electrode in the absence and in the presence of carrageenans are shown in Figure 2. The curves in the presence of polysaccharides can be used in the first place to determine the molar concentration of charges on the polyion by proposing stoichiometric binding between surfactant ions and charges on the polyion, i.e. binding of one surfactant cation per one charged group on the polyanion. This is a reasonable assumption in the CPC case, because binding of CP^+ to various polyanions is generally very strong and considered to be stoichiometric, thus leading to the formation of a 1:1 polyelectrolyte-surfactant complex.[5–7] The curves in Figure 2 were therefore treated as "classical" titration curves for the titration of carageenan polyanions with CP^+. The inflection point in these curves corresponds to the molar concentration of negative charges on the polyion. The following values were obtained for κ-, ι-, and λ-carrageenan: 5×10^{-4}, 1×10^{-3}, and 1.4×10^{-3} moles of negative charges/L. By taking into account the idealized carrageenan structures (Scheme 1), this gives the following monomolar concentrations: 5×10^{-4}, 5×10^{-4}, and 4.7×10^{-4} monomol/L for κ-, ι-, and λ-carrageenan, respectively. These values indicate that structures of carrageenan samples used in this study are indeed close to the ideal ones. A small deviation from the ideal structure is observed only for λ-carrageenan. Our result indicates that the disaccharide repeating unit in this case bears around 2.8 elementary charges.

This method may thus be regarded as an alternative for the determination of charges on carrageenans by the classical procedure reported in the literature (i.e. titration of sulphate groups by NaOH).[8] Note that the potentiometric curves for the DPC binding to carrageenans (not shown) indicate that binding of DPC to these polysaccharides cannot be used for the determination of carrageenan concentration. This will be evident also from the binding results reported below.

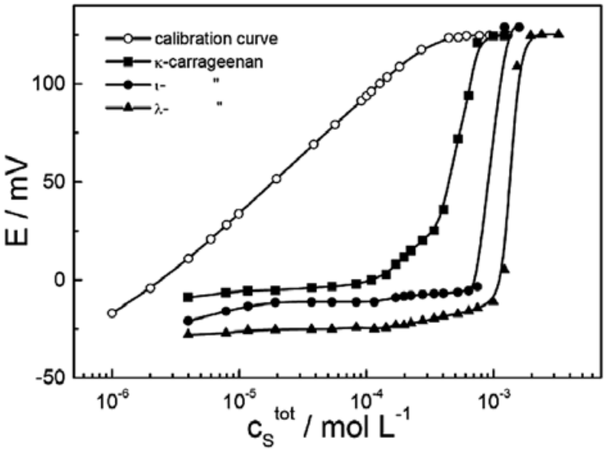


Figure 2. Response of the CP^+ electrode to the change in CPC concentration in 5×10^{-4} monomol/L solutions of κ- (■), ι-(●), and λ-(▲) carrageenan in water. Open circles: calibration curve.

Our major purpose was to use the E vs. c_S^{tot} curves for the construction of the binding isotherms,[18] which are shown in Figure 3 for the CPC and DPC binding to κ-, ι-, and λ-carrageenan. In Figure 3a, the degree of binding, β, defined as

$$\beta = \frac{c_S^{tot} - c_S^{free}}{c_p} \tag{1}$$

is given in terms of moles of surfactant bound per mole of repeating disaccharide unit (by taking into account the monomolar polyelectrolyte concentration, c_p). By replacing c_p in Eq. 1 by the molar concentration of charges ($c_{charge} = nc_p$, where n = 1, 2, and 3 for the idealized structures of κ-, ι-, and λ-carrageenan; see Scheme 1) the degree of binding is expressed per mole of charges on the polyion (see plots in Figure 3b). In the case of λ-carrageenan, the isotherms were in addition corrected by taking into account the experimental concentration of charges on the λ-carrageenan chain ($c_{charge} = 1.4 \times 10^{-3}$ charge/L). The corrected isotherms are plotted in Figure 3b as dashed and dotted lines. It can be seen that the two curves are altered only in the final region of binding, but remain virtually the same in the initial region of the steep increase of β, which defines the CAC.[5–7,22]

It can bee seen from Figure 3b that the degree of binding in the plateau region of binding, where the β vs. c_S^{free} curve levels off, is very similar for both surfactants. This is usually not the case, i.e. the so-called saturation degree of binding, β_{sat},[7,23] of surfactants with shorter chain lengths is usually lower. The reason for this may be the

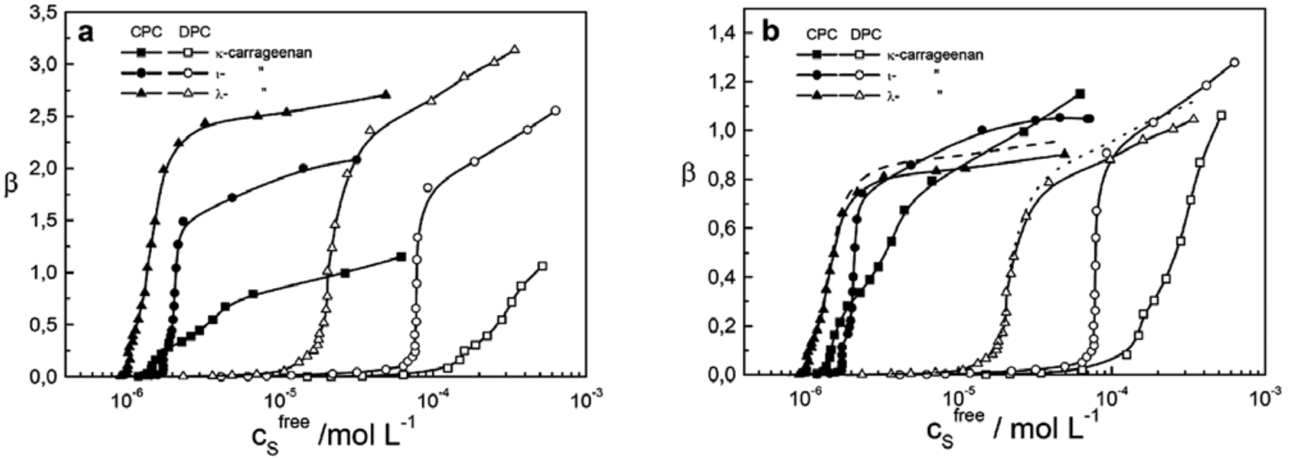


Figure 3. Binding isotherms for the CPC and DPC binding to κ-, ι-, and λ-carrageenan: $c_p = 5 \times 10^{-4}$ monomol/L; a) the degree of binding β is calculated per mole of repeating disaccharide unit; b) the degree of binding β is calculated per mole of charges on the polyion. The dashed and dotted lines are the isotherms for the CPC and DPC binding to λ-carrageenan, corrected by taking into account the experimental concentration of charges (see text).

specific mode of structural organization of surfactants in conjunction with rigid carrageenan chains. It has been demonstrated by SAXS measurements that CPC forms highly ordered lamellar structures in conjunction with stiff carrageenan chains.[14] We presume that this type of surfactant association does not depend considerably on the surfactant chain length, but is mainly governed by the tendency of the carrageenan chains to align.

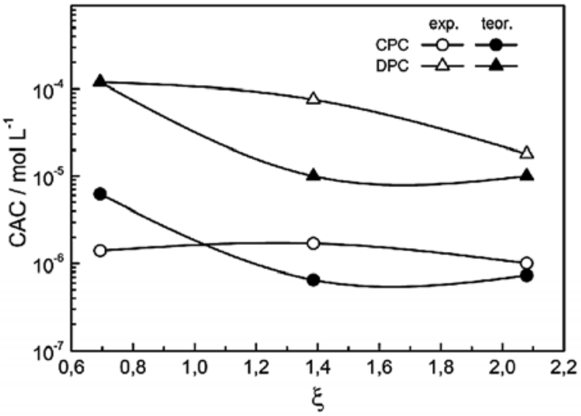


Figure 4. The dependence of the CAC values for CPC and DPC binding to κ-, ι-, and λ-carrageenan ($c_p = 5 \times 10^{-4}$ monomol/L) on the charge density parameter ξ; open symbols: experimental values; solid symbols: theoretical predictions (see text).

In contrast with β_{sat} values, CAC values depend considerably on the surfactant chain length. The CAC values determined from the binding isotherms and those predicted theoretically are reported in Table 1 and plotted in Figure 4 as a function of the charge density parameter ξ. The experimental CAC values for CPC are nearly two orders of magnitude lower than those for DPC. They show nearly no dependence on ξ, whereas those for DPC display a decreasing trend with increasing ξ. The calculations result in CAC values that are of a correct order of magnitude, in some cases even surprisingly close to the experimental ones. The reason for this may again be the rigidity of carrageenan chains: for rigid chains structural values of ξ may be close to the actual ones. On the contrary, theoretical CAC values display a more pronounced ξ dependence, in particular at lower ξ values, than do the experimental ones. Besides, the ξ dependence of calculated CAC values has the same shape in both the CPC and the DPC case. In calculation of charge distributions, the charge on the polyion is assumed to be uniformly smeared on the surface of the polyion cylinder. However, the actual distribution of charges is discrete. It is possible that charges on different types of carrageenans (Scheme 1) are

Table 1. Experimental and theoretical values for the critical association concentration (CAC) for the CPC and DPC binding to κ-, ι-, and λ-carrageenan: $c_p = 5 \times 10^{-4}$ monomol/L.

		CPC		**DPC**	
	ξ	**CAC^a (exp)**	**CAC^a (teor)**	**CAC^a (exp)**	**CAC^a (teor)**
κ-carrageenan	0.693	1.4×10^{-6}	6.2×10^{-6}	1.2×10^{-4}	1.2×10^{-4}
ι-carrageenan	1.386	1.7×10^{-6}	6.5×10^{-7}	7.6×10^{-5}	1.0×10^{-5}
λ-carrageenan	2.079	1.0×10^{-6}	7.3×10^{-7}	1.8×10^{-5}	1.0×10^{-5}

[a] in mol/L

not all within easy reach for the approaching surfactant counterions. Besides, the model takes into account only electrostatic interactions between polyions and counterions and ignores any eventual non-electrostatic (specific) effects. All this may be the basis for some disagreement between calculated and predicted CAC values.

Finally, the amount of bound surfactant, *b*, defined as the fraction of surfactant ions bound by the polyion[7]

$$b = \frac{c_S^{tot} - c_S^{free}}{c_S^{tot}} \tag{2}$$

was calculated and is plotted in Figure 5 as a function of the total surfactant concentration for both surfactants. These plots demonstrate that the binding of CPC by all three carrageenans is indeed complete (100%: *b* is equal to 1) or stoichiometric up to surfactant concentration 5×10^{-4} mol/L, which is equivalent to the concentration of polyion charges. This result justifies the above approach of using potentiometric curves for the determination of the amount of charges on the carrageenan chains. On the contrary, parameter *b* is lower than 1 for the DPC binding to carrageenans. It reaches 0.96 at $c_s^{tot} = 5 \times 10^{-4}$ mol/L only in the λ-carrageenan case, but is around 0.84 and 0.48 in the ι- and κ-carrageenan case, respectively. These values indicate a weaker interaction between carrageenans and DPC as compared to CPC.

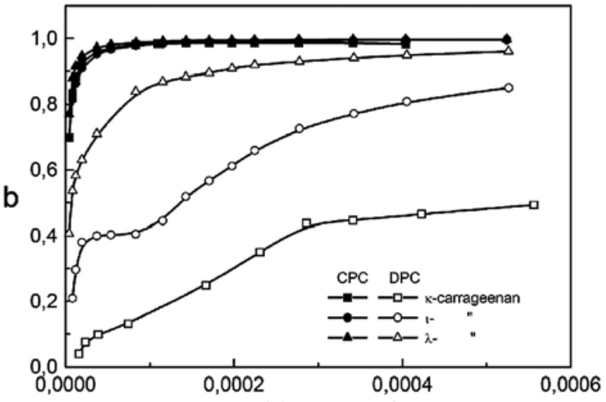


Figure 5. The amount of binding, *b*, as a function of the total surfactant concentration, c_S^{tot}, for the CPC and DPC binding to κ-, ι-, and λ-carrageenan.

5. Conclusions

The binding of CPC and DPC to κ-, ι-, and λ-carrageenan was studied in aqueous solutions without added salt by using the experimental approach based on surfactant-selective membrane electrodes. The potentiometric curves measured in the case of CPC binding to carrageenans present a new and straightforward way for the determination of the amount of charges on polyion chains. Primarily however, these curves were used to construct the binding isotherms and to derive from these plots the CAC values and the saturation degree of binding, β_{sat}, for the interaction between carrageenans and CPC and DPC. The results, in particular lower CAC and *b* values for DPC, indicate that the interaction of DPC with these polysaccharides is weaker than that of CPC. Still, both surfactants attain a similar degree of binding in the saturation region, β_{sat}. There may be some controversy in similar β_{sat} values on one hand and different CAC (and *b*) values on the other. However, this result may be explained as follows: CAC is primarily determined by the tendency of surfactant towards self-association and is thus closely related to surfactant's CMC. Surfactants with higher CMC values also have higher CAC values or vice versa. Conversely, formation of lamellar structures is governed by the characteristics of the polyion chain; only stiff polyions that cannot adjust easily to the curvature of e.g. globular surfactant micelles, will form this type of structures in conjunction with surfactants, whereas more flexible ones rather form cubic or hexagonal phases that afford closer packing.[24] The role of surfactant in such lamellar ordering is merely to connect the chains by forming bilayers between them and to relieve some of the repulsion between likely charged polyanions with their cationic headgroups. The length of surfactant's tail plays a minor role. Thus, both DPC and CPC induce association/alignment between approximately the same portions of carrageenan chains (note that β actually denotes the fraction of binding sites on the polyion that are occupied by surfactant). The difference is that in the case of DPC, which generally displays lower cooperativity in association phenomena in comparison with CPC, the concentration of free surfactant in solution is higher. This is clearly demonstrated by lower *b* values in the DPC case.

Together with the above experimental results, a simple theoretical approach based on the cell model of a polyelectrolyte solution with two kinds of monovalent counterions for predicting the CAC values is presented. The resulting CAC values are in satisfactory agreement with the experimental ones.

6. Acknowledgement

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Povzetek

Določili smo izoterme vezanja za vezanje dodecil- (DPC) in cetilpiridinijevega klorida (CPC) na κ-, ι- in λ-karagene v vodnih raztopinah brez dodane soli z uporabo potenciometrične metode na osnovi membranske elektrode selektivne za surfaktantni ion. Potenciometrične krivulje v primeru CPC smo uporabili za določitev števila nabojev na monomerni enoti polisaharidov. Ta postopek je pokazal, da sta strukturi κ-, in ι-karagena blizu idealni, medtem ko λ-karagen vsebuje 2,8 naboja na ponavljajoči disaharidni enoti (namesto idealnih 3). CAC vrednosti, ki smo jih določili iz izoterm vezanja, so v primeru CPC približno dva velikostna razreda manjše kot v primeru DPC. Hkrati je CPC skoraj popolnoma asociiran z vsemi polioni, medtem ko je delež asociiranega DPC manjši in odvisen od gostote naboja na poliionu. Kljub tem razlikam pa je stopnja vezanja pri nasičenju poliionov s surfaktantom za oba surfaktanta zelo podobna. To lahko razložimo, če predlagamo lamelaren način urejevanja med togimi verigami karagenov in surfaktanti. Eksperimentalne vrednosti za CAC smo primerjali s teoretičnimi napovedmi, ki so osnovane na celičnem modelu raztopine polielektrolita z dvema enovalentnima protiionoma različne velikosti. Dobili smo zadovoljivo ujemanje med eksperimentalnimi in teoretičnimi vrednostmi.