

Scientific paper

# Binding of Cationic Surfactants by Kappa, Iota, and Lambda Carrageenans in Aqueous Solution in the Presence of Sodium Chloride

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Dedicated to the memory of Professor Ljubo Golič

## Abstract

Binding isotherms for the binding of dodecyl- (DPC) and cetylpyridinium chloride (CPC) to  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan were determined in aqueous solution without and with added NaCl at concentrations  $c_{\text{NaCl}} = 0.01, 0.05, \text{ and } 0.1 \text{ mol/L}$  by using a potentiometric technique based on surfactant-selective membrane electrodes. The critical aggregation concentration, CAC, values obtained from the binding isotherms are around two orders of magnitude lower in the CPC case than in the DPC one. They are almost independent of NaCl concentration in  $\kappa$ - and  $t$ -carrageenan solutions, but increase with increasing  $c_{\text{NaCl}}$  in the  $\lambda$ -carrageenan case. Experimental isotherms were treated by the model of cooperative binding of surfactants by polyelectrolytes. Ionic strength dependence of the cooperativity parameters  $u$  and  $Ku$  was in agreement with the rather insignificant dependence of CAC on salt concentration. The isotherms of CPC binding by  $t$ - and  $\lambda$ -carrageenan display a highly cooperative character with  $u$  values up to almost 800, whereas those for both surfactants in the presence of  $\kappa$ -carrageenan have a considerably lower cooperativity parameter (between 3 and 10). In addition, the isotherms in the CPC/ $\kappa$ -carrageenan case do not indicate any saturation of the polyion chain with surfactant ions, but proceed to values of the degree of binding larger than 1. Our observations were explained by a lamellar type of ordering of surfactant in the presence of rigid polysaccharide chains.

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

## 1. Introduction

Addition of ionic surfactants to aqueous solutions of an oppositely charged polyelectrolyte results in strong electrostatic binding, which is reinforced by a cooperative process involving aggregation of alkyl chains of the bound surfactant ions. The phenomenon is often called polyion-induced surfactant micellization or aggregation and it starts at the so-called critical association concentration, CAC.<sup>1,2</sup> CAC is usually far below the critical micelle concentration, CMC, of a particular surfactant. Research in the area of polyelectrolyte/surfactant systems is directed towards both synthetic and natural polyelectrolytes. Among the latter, carrageenans are of special interest because of the important role they play in many biomedical, pharmaceutical in technological applications.

The main reason for the wide industrial use of carrageenans is their ability to induce thickening and gelation of solutions under various experimental conditions, in particular by changing the temperature and the type of the counterion and/or the coion.<sup>3–5</sup> Three major groups of carrageenans have been recognized:  $\kappa$ -carrageenan,  $t$ -carrageenan, and  $\lambda$ -carrageenan. They differ in chemical composition, which affects the linear charge density of polysaccharides in aqueous solution. Thus ideally  $\kappa$ -carrageenan in solution has only one elementary charge per disaccharide repeating unit,  $t$ -carrageenan two, and  $\lambda$ -carrageenan can bear two or three (on the average 2.7) of these charges per disaccharide unit (see Scheme 1). Furthermore,  $\kappa$ -carrageenan and  $t$ -carrageenan form gels, whereas no gel formation has been observed for the most highly charged  $\lambda$ -carrageenan.

In many practical systems (formulations), carrageenans can come into contact with oppositely charged surfactants. One of the main goals of this work is to investigate how the carrageenan charge density affects the interaction with surfactants. Only a few reports address this issue for the series of all three carrageenans presented above.<sup>6–8</sup> Caram-Lelham and Sundelöf<sup>6,7</sup> have studied interactions between  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan and a drug amitriptyline by dialysis equilibrium measurements in water. Amitriptyline is a partly aromatic compound with amphiphilic properties. In this respect, it differs from the most frequently encountered type of surfactants for which the hydrophobic part of the molecule is usually a long hydrocarbon chain. Such more common type of surfactant was employed by Vinceković et al.<sup>8</sup> who recently investigated phase behavior in mixtures of *n*-dodecylammonium chloride, DDAC, and these three carrageenans. Structural characteristics of insoluble DDAC/carrageenan complexes revealed lamellar ordering of surfactant and formation of giant vesicles in these systems already at low carrageenan concentrations. Bilayer type of organization of another cationic surfactant cetylpyridinium chloride, CPC, in conjunction with  $\kappa$ - and  $t$ -carrageenan chains was identified also by synchrotron small-angle X-ray scattering, SAXS, measurements.<sup>9</sup> It seems that carrageenans as rather stiff chains tend to induce a lamellar-like arrangement of surfactant, which enables the chains to remain in a more or less extended conformation.

In real systems, simple salts are always present and their concentration (*i.e.* the ionic strength of the solution) may vary considerably. Therefore, additional important aspect to be explored is the effect of the added electrolyte concentration on interaction between charged surfactants and carrageenans. We have chosen to investigate  $\kappa$ - and  $t$ -carrageenan under non-gelling conditions, that is in the presence of NaCl; the same conditions were chosen for a non-gelling  $\lambda$ -carrageenan. All three carrageenans are supposed to be in the coil conformation in NaCl solutions.<sup>5,10,11</sup> Two cationic surfactants with different hydrocarbon chain length were chosen for the study, CPC and a shorter chain analogue dodecylpyridinium chloride, DPC. Potentiometric measurements using surfactant-selective membrane electrode were used to determine the degree of binding of both surfactants by carrageenan polyions.<sup>12,13</sup> The binding isotherms derived there-from were analyzed by the model of cooperative binding of surfactants by polyions.<sup>13</sup>

## 2. Experimental

### 2.1. Materials

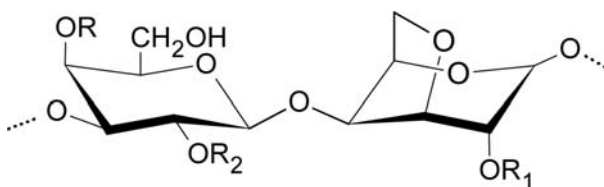
The  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan samples were commercial products from Sigma Chemicals Co. (Bornem, Belgium), Types III, (No. 127H-1222), V (No. 27F-0373), and IV (No. 58F-0604), respectively. They were purified

and transformed into sodium salts by the procedures reported in the literature.<sup>3–5</sup> 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. They were stored in a desiccator.

Polysaccharide stock solutions were prepared by carefully following the procedures reported in the literature.<sup>3–5</sup> A calculated amount of polymer was weighed into a volumetric flask and dissolved in triple distilled water at room temperature. Solution was heated to 75 °C and then a calculated amount of a concentrated NaCl solution was added drop-wise under continuous stirring. The solution was kept at 75 °C 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 and salt concentration. This procedure prevented any association between carrageenan chains.<sup>5,10,11</sup>

### 2.2. Potentiometry

The degree of binding,  $\beta$ ,<sup>1,2</sup> of DPC and CPC by carrageenans was determined by a commonly used potentiometric method utilizing surfactant-selective membrane electrodes for the determination of equilibrium concentration of free surfactant ions,  $c_s^f$ , in polyelectrolyte solutions.<sup>12–14</sup> The electrode and the setup were described elsewhere.<sup>12</sup> The binding of DPC and CPC by  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan was studied at a polymer concentration,  $c_p$ , equal to  $5 \times 10^{-4}$  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. All measurements were performed at 25 °C.



**Scheme 1.** Idealized disaccharide repeating unit of carrageenans:  $\kappa$ -carrageenan:  $R = \text{SO}_3^-$ ;  $R_1, R_2 = \text{H}$ ;  $t$ -carrageenan:  $R, R_1 = \text{SO}_3^-$ ;  $R_2 = \text{H}$ ;  $\lambda$ -carrageenan:  $R, R_1, R_2 = \text{SO}_3^-$ . Some hydrogen atoms are not explicitly shown.

## 3. Model Treatment of Binding Isotherms

Binding isotherms (*i.e.* plots of the degree of binding  $\beta$  as a function of  $c_s^f$ ) were treated by the Satake-Yang model,<sup>13</sup> which is the most frequently employed model in the treatment of surfactant binding by polyelec-

trolytes. The authors considered nearest neighbor-interactions in a linear lattice between bound surfactant molecules and arrived at an exact solution for the degree of binding as a function of  $c_s^f$ :

$$\beta = \frac{1}{2} \left\{ 1 + \left[ \frac{(Kuc_s^f - 1)}{\left[ (1 - Kuc_s^f)^2 + 4Kc_s^f \right]^{\frac{1}{2}}} \right] \right\} \quad (1)$$

In this equation,  $K$  is the constant of surfactant binding to an isolated site on the polymer and  $u$  is the so-called cooperativity parameter, which expresses the extra binding term included when binding occurs at a site adjacent to an already occupied site on the polyion and thus reflects hydrophobic interactions between surfactant hydrocarbon tails. The product  $Ku$  is the combined contribution of electrostatic and hydrophobic interactions to surfactant binding by polyelectrolytes. Both,  $u$  and  $Ku$  can be obtained from the experimental isotherms: the measure for  $u$  is the slope of the isotherm at the half-bound point where  $\beta = 0.5$  (Eq. 2), while  $Ku$  is proportional to the inverse of the free surfactant concentration when half of the sites on the polyion are occupied, designated as  $(c_s^f)_{\beta=0.5}$  (Eq. 3):

$$\left( \frac{d\beta}{d \ln c_s^f} \right)_{\beta=0.5} = \frac{u^2}{4} \quad (2)$$

or

$$\left( \frac{d\beta}{d \ln c_s^f} \right)_{\beta=0.5} = \frac{N-1}{4} \quad (3)$$

Although simple, the Satake-Yang model presents a convenient formalism when one wants to compare surfactant binding to various polyelectrolytes.

Another approach to model binding isotherms has been presented by Hansson and Almgren,<sup>15,16</sup> who have introduced a simple law of mass action model for the interpretation of the cooperative binding of surfactant to a polyelectrolyte. Instead of the cooperativity parameter  $u$ , the aggregation number  $N$  is therein a measure of the degree of cooperativity. Interestingly, the Satake-Yang model and the mentioned approach<sup>15,16</sup> arrive at virtually the same result for the special case when  $\beta = 0.5$ , which can be seen by comparing Eq. 2 (the slope of the isotherm at the half bound point from the Satake-Yang model) with Eq. 4 (the slope of the isotherm as a function of  $N$  from the law of mass action model):

$$\left( \frac{d\beta}{d \ln c_s^f} \right)_{\beta=0.5} = \frac{N}{4} \quad (4)$$

Obviously, the aggregation number correlates with the cooperativity of binding isotherms so that steep iso-

therms (large  $u$ ) correspond to large micelles or aggregates (large  $N$ ).

## 4. Results and Discussion

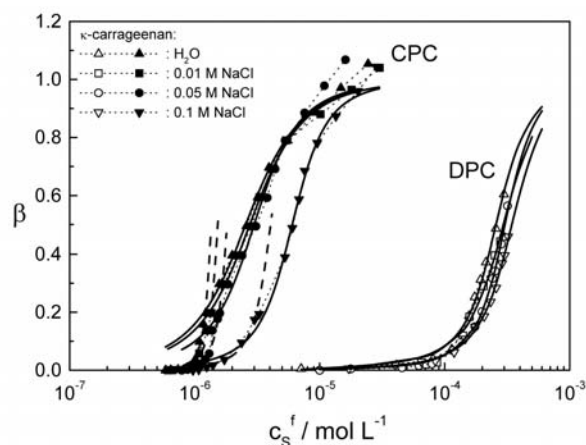
Figures 1–3 show binding isotherms for DPC and CPC binding to  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan at various NaCl concentrations. In these plots,  $\beta$  is defined as the number of moles of surfactant ions bound per mole of polyion charges. It is calculated from the relation

$$\beta = \frac{c_s^b}{nc_p} \quad (5)$$

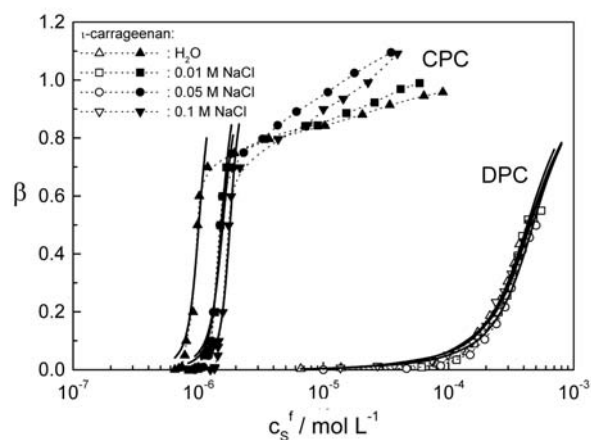
where  $c_s^b$  ( $= c_s^t - c_s^f$ , with  $c_s^t$  the total surfactant concentration) is the concentration of bound surfactant and  $n = 1, 2$ , or  $3$  for the idealized structures of  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan, respectively (see Scheme 1). The value of  $\beta$  equal to 1 signifies that all charges (*i.e.* potential binding sites) on the polyion are occupied by surfactant ions. The degree of binding was calculated up to a value of  $c_s^t$  around  $6 \times 10^{-4}$ ,  $12 \times 10^{-4}$ , and  $20 \times 10^{-4}$  mol/L for  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan, respectively, for both surfactants. This  $c_s^t$  value is close to the concentration of polyion charges in carrageenan solutions (see above). It was evident from the experimental potentiometric curves (not reported in the paper) that at higher  $c_s^t$  the difference between the calibration curve (no carrageenan present) and the curve in the presence of carrageenan becomes rather small, in particular for DPC, thus causing the calculation of  $\beta$  less reliable. It has, however, to be noted that the binding of DPC to  $\kappa$ - and  $t$ -carrageenan seems to proceed with the same trend also above  $\beta = 0.6$ , which is the highest  $\beta$  value reported for DPC in Figures 1 and 2.

All isotherms have a sigmoid shape that is typical for cooperative binding of surfactants by polyelectrolytes.<sup>1,2,12–16</sup> The CAC values were determined from the steep increase of  $\beta$  above a well-defined free surfactant concentration by extrapolating the data points in the cooperative region (the steep part of the isotherms) to  $\beta = 0$ . CAC is plotted in Figure 4 as a function of the total concentration of sodium ions in solution,  $c_{Na}$  ( $= c_{NaCl} + nc_p$ ), originating from the simple salt (NaCl) and from the polyelectrolyte. The most evident, yet usual, result is that CAC values of DPC are around 2 orders of magnitude lower than those of CPC. This originates from a lower hydrophobic character of DPC. For both surfactants, CAC in  $\lambda$ -carrageenan solutions increases with  $c_{Na}$ , whereas it is practically independent of  $c_{Na}$  in solutions of  $\kappa$ - and  $t$ -carrageenan. The increase of CAC with ionic strength is in accordance with expectations and is attributed to the screening effect of the salt on attractive polyion-surfactant ion interactions,<sup>2</sup> whereas the relative constancy of CAC in  $\kappa$ - and  $t$ -carrageenan solutions may be related to a strong (side-by-side) association tendency of these chains

in the presence of suitable counterions. Different ions are known to have specific effects on association and potential gelation properties of  $\kappa$ - and  $\iota$ -carrageenan chains.<sup>5,10,11,17</sup> Although NaCl is supposed to be a non-gelling salt, the presence of surfactant may be favorable to induce side-by-side alignment of chains. This presumption is confirmed by the demonstrated lamellar type of ordering of surfactants in carrageenan solutions,<sup>8,9</sup> which leads either to vesicle formation<sup>8</sup> or to some other bilayer type of structure.<sup>9</sup> We presume that this specific feature leads to a less pronounced ionic strength dependence of CAC.



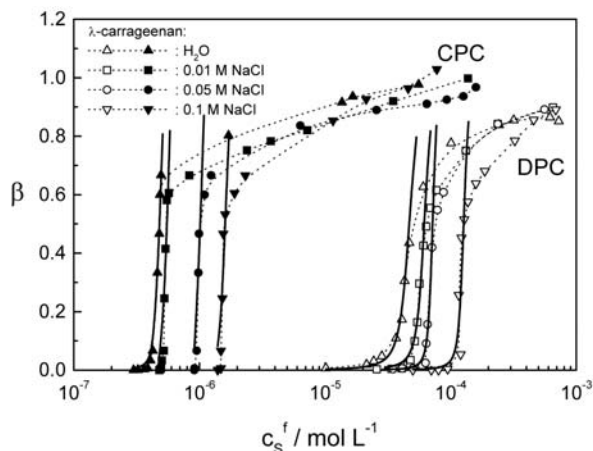
**Figure 1.** Binding isotherms for the DPC and CPC binding to  $\kappa$ -carrageenan in aqueous solutions with increasing NaCl concentration:  $c_{\text{NaCl}} = 0$  ( $\text{H}_2\text{O}$ ), 0.01, 0.05, and 0.1 mol/L (abbreviated as M).



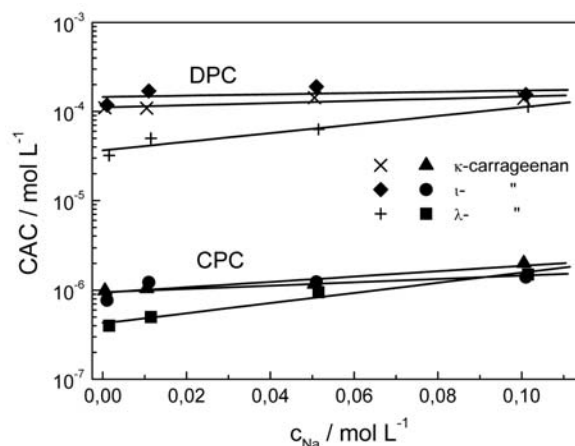
**Figure 2.** Binding isotherms for the DPC and CPC binding to  $\iota$ -carrageenan in aqueous solutions with increasing NaCl concentration:  $c_{\text{NaCl}} = 0$  ( $\text{H}_2\text{O}$ ), 0.01, 0.05, and 0.1 mol/L (abbreviated as M).

Beside CAC values, interactions between surfactants and polyelectrolytes are often appraised by the value of the degree of binding in the region where the isotherms level off (so-called  $\beta_{\text{sat}}$  values<sup>18</sup>). The saturation region can be clearly defined for the CPC binding to  $\iota$ - and  $\lambda$ -carrageenan (at  $\beta \geq 0.6$  and 0.7, respectively), but is only

slightly indicated in the  $\kappa$ -carrageenan case (above  $\beta \approx 0.8$ ). An almost continuous increase of  $\beta$  in CPC/ $\kappa$ -carrageenan (and also in DPC/ $\kappa$ -carrageenan) solutions may repeatedly be explained by some type of bilayer structure. Interestingly,  $\beta_{\text{sat}}$  values are the lowest for  $\lambda$ -carrageenan that has the highest charge density. Obviously, distribution of charges, chain stiffness, and steric effects play an important role. It is well known that  $\lambda$ -carrageenan is not capable of forming an ordered domain of aligned helices, as are  $\kappa$ - and  $\iota$ -carrageenan, due to a higher number of sulfate groups that enhance the rod-like conformation.<sup>17</sup> The par-



**Figure 3.** Binding isotherms for the DPC and CPC binding to  $\lambda$ -carrageenan in aqueous solutions with increasing NaCl concentration:  $c_{\text{NaCl}} = 0$  ( $\text{H}_2\text{O}$ ), 0.01, 0.05, and 0.1 mol/L (abbreviated as M).



**Figure 4.** Dependence of the critical aggregation concentration, CAC, values for the DPC and CPC binding to  $\kappa$ -,  $\iota$ - and  $\lambda$ -carrageenan on the total concentration of sodium ions,  $c_{\text{Na}}$ , in solution:  $c_{\text{Na}} (= c_{\text{NaCl}} + nc_p)$ .

ticular distribution of sulfate groups may also cause that charges are less accessible for surfactant cations due to steric hindrance. As a consequence,  $\beta_{\text{sat}}$  is lower in comparison with the other two carrageenans. In the case of DPC, the measurements were not performed up to concentration values where the saturation would be observed.

A two-parameter fit of binding isotherms was obtained by applying Eq. 1. The solid lines in Figures 1–3 are the best fits of the experimental data to Eq. 1 at lower degrees of binding.<sup>14</sup> The resulting binding parameters  $u$  and  $Ku$  are summarized in Table 1. Although both  $u$  and  $Ku$  can be determined in this way in majority of cases, the strong cooperativity exhibited by the isotherms in Figure 3 (DPC and CPC binding to  $\lambda$ -carrageenan) makes the precise determination of  $u$  difficult. However,  $Ku$ , which equals the reciprocal of the free surfactant concentration at  $\beta = 0.5$  (Eq. 3), can be determined accurately. Individual values of  $u$  in  $\lambda$ -carrageenan solutions varied between 120 and 660 and between 500 and 1000 for the DPC and CPC case, respectively. Due to great uncertainty, no particular trend of  $u$  on salt concentration could be deduced.

respectively. In agreement with the above discussion, the large difference in slope suggests that aggregation of surfactants in the presence of carrageenans is different from the usual micelle formation.

Finally, we turn our attention to the cooperativity parameter  $u$ . As outlined above, no particular trend of  $u$  with increasing ionic strength could be observed. Similar behavior of  $u$  was previously observed for the binding of dodecyltrimethylammonium bromide, DTAB, to sodium dextrane sulfate, NaDxS,<sup>14</sup> also a sulfated polysaccharide. Carrageenans and NaDxS all have hydrophilic backbones; consequently, the cooperative effect of binding of surfactants is due completely to the hydrophobic interaction between bound surfactant ions, *i.e.* no hydrophobic interaction between surfactant and the polyelectrolyte is invol-

**Table 1.** Binding parameters for the DPC and CPC binding to  $\kappa$ -,  $t$ -, and  $\lambda$ -carrageenan in aqueous solutions without or with added NaCl.

	DPC			CPC	
	$C_{\text{Na}}$ (mol L <sup>-1</sup> )	$u$	$Ku \times 10^3$ (mol L <sup>-1</sup> )	$u$	$Ku \times 10^3$ (mol L <sup>-1</sup> )
$\kappa$ -carr.	0	10 ± 1	3.90 ± 0.05	3.7 ± 0.7 (250 ± 60)	390 ± 14
	0.01	8 ± 2	3.4 ± 0.1	3.9 ± 0.6 (150 ± 40)	362 ± 11
	0.05	13 ± 1	3.3 ± 0.1	5.4 ± 1.5 (110 ± 40)	334 ± 16
	0.10	10 ± 1	2.9 ± 0.03	9 ± 2 (33 ± 9)	170 ± 4
$t$ -carr.	0	5.9 ± 0.7	2.35 ± 0.05	110 ± 70	990 ± 30
	0.01	5.5 ± 1	2.22 ± 0.06	110 ± 40	650 ± 12
	0.05	6.4 ± 1	2.11 ± 0.05	70 ± 30	640 ± 20
	0.10	5.2 ± 0.4	2.27 ± 0.03	130 ± 60	560 ± 13
$\lambda$ -carr.	0		18 ± 1		2100 ± 12
	0.01	340	15 ± 1	760	1820 ± 25
	0.05	±120	13 ± 7	±340	953 ± 27
	0.10		7.4 ± 0.4		583 ± 33

The dependence of the product  $Ku$  on  $c_{\text{NaCl}}$  is parallel to that of the reciprocal value of CAC because it reflects the position of the isotherm on the concentration axis (see Eq. 3). It can be seen that  $Ku$  decreases with increasing salt concentration in  $\lambda$ -carrageenan solutions, in accordance with the previously found increasing trend in CAC. In  $\kappa$ - and  $t$ -carrageenan solutions,  $Ku$  is more or less independent of salt concentration, again in accordance with the insensitivity of CAC to ionic strength. In comparison with other polyelectrolyte/surfactant systems, where the slopes of  $\log Ku$  vs.  $\log c_{\text{NaCl}}$  curves are around  $-0.7$  (*e.g.* in the DTAB/NaDxS case<sup>14</sup>), the slopes in the presence of carrageenans are between  $-0.01$  and  $-0.3$  in DPC/carrageenan and between  $-0.06$  and  $-0.5$  in CPC/carrageenan solutions. The slopes of the  $\log \text{CMC}$  vs.  $\log c_{\text{NaCl}}$  curves, obtained from the CMC data of DPC and CPC in aqueous NaCl solutions<sup>19</sup> are  $-0.55$  and  $-0.64$ ,

ved. This in turn implies that the variation of  $Ku$  with  $c_{\text{NaCl}}$  in these systems comes solely from the dependence of  $K$  on the ionic strength of the solution. Because the association between polyion and surfactant ions is favored by the release of polyion counterions, the main effect of salt on  $K$  should be attributed to the entropy of mixing of surfactant and simple ions.<sup>20</sup> This effect is the largest for the no added salt case.

The value of  $u$  in  $\kappa$ - and  $t$ -carrageenan solutions is rather low (between 3 and 10), except in the CPC/ $t$ -carrageenan system where  $u$  is around 100. Usually,  $u$  is higher for surfactants with longer hydrocarbon chains. However, in  $\kappa$ -carrageenan solutions the cooperativity of DPC binding is around 2-times higher than that of CPC. The values of  $u$ , reported in Table 1 for CPC/ $\kappa$ -carrageenan case, refer to the region of the isotherms with  $\beta \geq 0.2$  (see the solid lines in Figure 1). By fitting the data points to Eq. 1

in the region  $\beta < 0.2$ , a considerably higher cooperativity parameter is obtained (see the values reported in brackets in Table 1, from which the dashed curves in Figure 1 were calculated), suggesting that initially cooperativity is rather high for CPC binding to  $\kappa$ -carrageenan. This is consistent with a larger hydrophobic character of CPC in comparison with DPC. However, after some charges on the  $\kappa$ -carrageenan chain have been blocked by  $CP^+$  cations, the cooperativity decreases and becomes comparable with that of  $DP^+$  cations. We presume that the tendency of  $\kappa$ -carrageenan chains to form some type of aligned structure prevails over surfactant hydrophobicity in their mutual complexation. In addition, since binding isotherms do not show any explicit plateau region, this type of binding obviously proceeds above the charge neutralization point ( $\beta \geq 1$ ), in agreement with literature reports.<sup>9</sup> The reason why such behavior was not observed with  $\iota$ - and  $\lambda$ -carrageenans is not completely clear. It may be that the higher charge density of these chains favors first the saturation of the polyion and only after a sufficient excess of the surfactant has been added can a more widely extended bilayer structure be formed. In our study, cases with surfactant to polyelectrolyte molar ratios considerably larger than 1 were not investigated.

## 5. Conclusions

The binding of CPC and DPC to  $\kappa$ -,  $\iota$ -, and  $\lambda$ -carrageenan was studied in aqueous solutions in the presence of NaCl by using the potentiometric method based on surfactant-selective membrane electrodes. The major observation of this study is that interaction between cationic surfactants and carrageenans, as evaluated by parameters such as critical aggregation concentration CAC, cooperativity parameter  $u$ , and cooperativity binding constant  $Ku$ , does not depend considerably on salt concentration. Our findings can be explained by a lamellar type of ordering of surfactant in conjunction with carrageenan chains that is favored by the strong tendency of rigid polysaccharide chains towards side-by-side alignment. This specific feature weakens the usually very pronounced ionic strength dependence of CAC,  $u$ , and  $Ku$ , which is observed in other mixed polyelectrolyte/surfactant systems.

## 6. Acknowledgements

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## Povzetek

S potenciometrično metodo na osnovi surfaktantne ionoselektivne electrode smo določili izoterme vezanje dodecil- (DPC) in cetilpiridinijevega klorida (CPC) na  $\kappa$ -,  $i$ - in  $\lambda$ -karagene v vodnih raztopinah brez in z dodatkom NaCl s koncentracijami  $c_{\text{NaCl}} = 0,01; 0,05$  in  $0,1$  mol/L. Iz izoterm vezanja smo določili kritične koncentracije agregacije, CAC. Te so približno dva velikostna razreda nižje za CPC kot za DPC in skoraj neodvisne od koncentracije NaCl, v raztopinah  $\kappa$ - in  $i$ -karagena, medtem ko v raztopinah  $\lambda$ -karagena naraščajo z naraščajočo  $c_{\text{NaCl}}$ . Eksperimentalne izoterme smo obravnavali z modelom kooperativnega vezanja surfaktantov na polielektrolite. Odvisnost kooperativnostnih parametrov  $u$  and  $Ku$  od ionske moči raztopine je bila v skladu z dokaj neizrazito odvisnostjo CAC od koncentracije dodanega NaCl. Izoterme vezanja v primeru  $i$ - in  $\lambda$ -karagena kažejo močno kooperativen karakter z vrednostmi parametra  $u$  do skoraj 800, medtem ko je le-ta v prisotnosti  $\kappa$ -karagena precej manjši (med 3 in 10). Poleg tega izoterme za vezanje CPC na  $\kappa$ -karagen ne kažejo, da bi v tem sistemu prišlo do nasičenja verige poliiona z ioni surfaktanta, ampak se vezanje nadaljuje tudi za stopnjo vezanja nad 1. Naša opažanja smo razložili s predpostavko o lamelnarnem načinu urejanja surfaktanta v prisotnosti togih verig polisaharidov.