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# SANS study of surfactant ordering in κ-carrageenan/cetylpyridinium chloride complexes

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**Abstract**

Small-angle neutron scattering using contrast variation by $H_2O/D_2O$ has been applied for the structural investigation of κ-carrageenan/cetylpyridinium chloride (CPC) complexes. Interaction of κ-carrageenan with an ionic surfactant involves self-assembly of the surfactant molecules in conjunction with the carrageenan molecules and the formation of an ordered structure. Contrast matching conditions for the polysaccharide (70% $H_2O$/30% $D_2O$) allowed to obtain the small-angle scattering pattern from the surfactant part of the complexes. The SANS curves reveal that the observed scattering heterogeneities represent regions with sharp phase boundaries. From the Guinier part of the scattering curves, the size of these regions is determined. The obtained values are in good agreement with the structural characteristics of the κ-carrageenan/CPC complexes determined independently by SAXS and SANS from the position and the half-width of the Braggs peaks of the scattering patterns. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Carrageenan gels; Gel–surfactant complexes; Small-angle neutron scattering

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## 1. Introduction

An increasing interest is directed today towards polymer–surfactant systems, both for potential industrial applications, for the relevance of polymer–surfactant interactions in biology, and for understanding the fundamental features of the interactions in such systems [1–3]. Of special interest are the complexes formed by polyelectrolyte networks and surfactants. Complexes of chemically cross-linked polyelectrolyte gels with ionic surfactants have been studied extensively in recent years [4–15] and it is now well established that such systems can give rise to well ordered mesoscopic structures as revealed by small-angle X-ray scattering (SAXS) [6–15]. The structure of the known gel–surfactant complexes show either a lamellar ordering [9,13], or a cubic system [8], or a hexagonal arrangement [10,12,15]. The formation of ordered structures is due to a combination of hydrophobic interactions of the surfactant molecules and of the electrostatic interactions between the polymeric gel and the surfactant [16]. It is known that for polyelectrolyte/ionic surfactant systems the polymer charge density parameter, as determined by the average linear charge density along the polymer backbone, is one of the decisive factors governing the binding process [17]. In addition, there appears to be no simple relationship between the amount of binding and the polyion linear charge density. From previous work it was concluded that other factors such as the hydrophobic character, the flexibility, and the detailed local structure of the polymer also strongly influence the binding process [18]. The strong interactions induce already a complex formation at very low surfactant concentrations, commonly known as the critical aggregation concentration (cac), which is usually some orders of magnitude lower than the critical micelle concentration (cmc) of the free surfactant. The aggregation of surfactant in conjunction with the polyelectrolyte molecules in the gel network changes the osmotic pressure inside the network and causes the gel to shrink and finally to collapse. The resulting polymer–surfactant complexes were shown to be a new class of polymer colloids.

At the same time, the interaction between thermoreversible gels (physical networks) and surfactants remains a completely unexplored research field. From this viewpoint the biopolymeric polyelectrolyte gels, on the basis of polysaccharides, can be of special interest for non-toxic natural materials of potential application in medicine and food industry. Over the last 15 years considerable effort was

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devoted to study the solution behavior of the well-known biopolymeric polyelectrolyte series with increasing linear charge density: kappa-, iota- and lambda-carrageenan [19–32]. Carrageenans are water-soluble, sulfated polysaccharides extracted from different species of marine red algae of the class Rhodophyceae [33]. Comprehensive light scattering and SAXS studies revealed that, in contrast to common knowledge in the literature, the gelation of the carrageenans (kappa and iota) is a two-step process involving a conformational transition of the type: coil-to-single helix, followed by a side-by-side association of the single helices to form a three-dimensional network immobilizing the solvent and resulting in a weakly elastic gel. This gelation is ion-induced and thermoreversible. Even though physical networks, including carrageenan systems, are extremely complex materials with spatial heterogeneities on a variety of length scales [34], the existing knowledge on the polyelectrolyte behavior of the carrageenans promotes them to a model system. In this work, results are reported on the supermolecular structure of κ-carrageenan–surfactant complexes by small-angle neutron scattering (SANS).

## 2. Experimental

### 2.1. Materials

The κ-carrageenan sample used is a commercial product of Sigma Chemical Co, Type III from Eucheuma Cottonii (code 37 050). It was dissolved in highly purified water (Millipore) by heating to 70°C and continuous stirring, and fractionated by drop-wise addition of isopropanol (C.ERBA P.A. product) under vigorous stirring. The filtrate was rinsed thoroughly with ultra-pure water (Milli-Q-Reagent Grade Water Systems, Millipore) and again dissolved in water afterwards. It was first dialyzed against 0.20 M NaCl to have κ-carrageenan as a sodium salt solution and then extensively against water before freeze-drying. KCl salts were products of analytical grade from Carlo Erba S.p.A. The weight average molar mass $M_w = 48\,000$ of κ-carrageenan was determined by wide-angle laser light scattering as described elsewhere [30,31]. The surfactant, *N*-cetylpyridinium chloride monohydrate 98% (CPC) was obtained from Aldrich and was used without additional purification. The Krafft point of CPC in water is around 11°C [35]. Heavy water of 99.8 at.% Deuterium was purchased from ACROS ORGANICS. Ultra pure water was obtained from Milli Q-Reagent Water System, Millipore.

### 2.2. Preparation of κ-carrageenan/surfactant systems for SANS measurements

Firstly, the solutions of 4% κ-carrageenan in pure water were heated till ~70°C under stirring. Then, after one night in the refrigerator, the solutions of κ-carrageenan were heated to 70°C and mixed with an equal amount of a 0.20 M KCl solution at 70°C. These solutions of κ-carrageenan in 0.10 M KCl were stirred during 10 min at 70°C and the calculated amount of the surfactant cetylpyridinium chloride (CPC) solution in 0.10 M KCl (after brief heating at 70°C) was added under continuous stirring. Afterwards, the solutions were allowed to cool down to room temperature. For the SANS measurements mixtures of different composition of $H_2O$ and $D_2O$ were used as solvent. The concentration of κ-carrageenan in the polysaccharide–surfactant complexes was 1 vol%, corresponding to 0.023 moles of ionic polymer sites per volume. The ratio [CPC]/[Car] is the molar relationship between polysaccharide and surfactant content at the level of the experiments.

### 2.3. SANS measurements

The SANS measurements were carried out using the SANS facility at the Risø National Laboratory in Denmark. The covered scattering vectors, defined as $|\mathbf{q}| = q = (4\pi/\lambda)\sin\theta$, vary between 0.01 and 0.5 Å$^{-1}$ with a neutron wavelength resolution $\Delta\lambda/\lambda = 0.18$ ($\lambda$ is the neutron wavelength, $2\theta$ is the scattering angle, and $\Delta\lambda$ is the value of the full width at half-maximum of the neutron flux vs. wavelength distribution). For each sample, the scattering patterns were obtained using three different spectrometer configurations ($\lambda = 3$ Å, $D = 3$ m, and $L = 3$ *m*; $\lambda = 3$ Å, $D = 1$ *m*, and $L = 1$ m, and $\lambda = 6$ Å, $D = 3$ m, and $L = 3$ m; where $L$ is the collimation length and $D$ is the sample-detector distance) corresponding to three partially overlapping ranges of the scattering vectors. The samples were measured in quartz cuvettes (Helma) with path lengths of 1 or 2 mm. All measurements were done at room temperature and the data were radially averaged to reduce the statistical error. The scattering due to the empty cell and the solvent, as well as the calculated incoherent background caused by the protons, was subtracted according to standard procedures.

### 2.4. Diffraction of X-rays and neutrons by polymer systems

Small-angle (X-ray or neutron) scattering analysis is an important tool for obtaining structural information in the field of condensed matter. In comparison to the ideally ordered structure, two types of disorder may coexist in a real, 'ordered' polymer system, the difference between them being most prominent when one considers large scattering volumes (i.e. large numbers of scattering centers), when it is reasonable to speak of long-range order [36]. There is little practical difference between these two types when the number of centers is small; diffraction calculations then give similar results.

Distortions in periodicity of the first kind are the ones in which the long-range order is retained. Such distortions in a lattice or in a chain molecule arise from thermal motion, which causes the atoms to deviate from their ideal positions. Scherrer showed [37] that the mean long-range order dimension, $L$, is related to the pure X-ray diffraction broadening and can be estimated from the Bragg peaks of the scattering

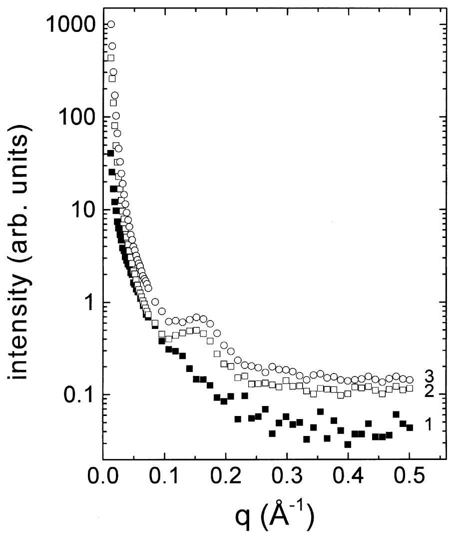

Fig. 1. SANS patterns of 1% κ-carrageenan/CPC complexes in 0.10 M KCl in $D_2O$: 1-physical gel; 2-[CPC]/[Car] = 0.5; 3-[CPC]/[Car] = 1.0.

patterns by the equation:

$$L = \frac{\lambda}{\beta_s \cos\theta}, \tag{1}$$

where $\beta_s$ is the full width at a half-maximum intensity of the Bragg peak observed at a mean scattering angle of $2\theta$.

For distortions of the second kind the peaks in the diffraction pattern broaden as their ordinal number increases. In the case a mean distance between first neighbors can be stated, but where there are no ideal fixed equilibrium positions throughout the object. Such distortions are characteristic for objects lacking strict periodicity such as liquids and assemblies of chain molecules. Inhomogeneity in the system is at the basis of the origin of the peaks in the diffraction pattern, the existence of separate maxima resulting from a region of interactions, which is bounded by an "interaction radius", $r_m$, outside which the density distribution function becomes practically smooth and approaches the mean value. The parameter defining the height of the interference maxima is then $\Delta/\bar{a}$, the ratio of the width of the fluctuations of the distance between first neighbors to the mean distance between them. The height of the peaks is inversely proportional to the square to this ratio and to the square of the order of reflection.

From the scattering curves a radius of interaction, $r_m$, and a degree of disorder in the system $\Delta/\bar{a}$, can then be calculated [36]:

$$r_m = \left(\frac{\pi}{2.5}\right)^2 \frac{\lambda}{\beta_s}, \tag{2}$$

$$\Delta/\bar{a} = \frac{1}{\pi}\sqrt{\frac{\beta_s \bar{a}}{\lambda}}. \tag{3}$$

Here, $\bar{a} = 2\pi/q_m$ is the characteristic size of the longest periodicity in the system under study and $\Delta$ is the mean-square deviation of the distances between the scattering neighbors.

SANS has several advantages as compared to X-ray scattering. The major ones are the possibility of isotope contrast and very little radiation damage to the sample under investigation [38,39]. With respect to the former point, SANS is an efficient tool to study multicomponent systems with dimensions in the range 10–1000 Å. Using contrast variation, one can selectively suppress the scattering from any component by matching the scattering length density of that component to that of the solvent. This can be achieved by deuterium labeling or the substitution of hydrogen by deuterium. At the present time, SANS is used extensively to the study of polymer–surfactant interaction [40]; for example, through selective deuteration of the solvent, the different components, either the poly(*N*-isopropyl acrylamide) gel or the sodium dodecyl sulfate (SDS), were rendered "invisible" to the neutrons, which allowed to receive structural information about the separate components of gel–surfactant aggregates [41,42]. Recently, investigations of the temperature-induced gelation and structures of physical gels in the ethyl(hydroxyethyl) cellulose–SDS–water system by SANS have been reported [43]. By contrast matching it was shown that the reversible gel formation in this system is defined by the competition between polymer–polymer interactions, which are temperature dependent, and the polymer–surfactant interactions.

## 3. Results and discussion

In the present work, the ordering in the κ-carrageenan/CPC complex is studied by analyzing the small-angle scattering only due to the surfactant or polysaccharide part of the complexes. The scattering length densities $\rho$ can be calculated from the chemical composition of the polymer molecule according to equation:

$$\rho = \sum_i b_i d N_A / M. \tag{4}$$

Here $b_i$ is the coherent neutron scattering length for the $i$th atom (the summation is carried out over all atoms), $N_A$ is the Avogadro number, $M$ is the molar mass of the polymer, and $d$ is the volume density of substance (there is a definite uncertainty on the value of the density of the polymer in the solvent). The calculations show that for κ-carrageenan, $\rho_{car} = 1.39 \times 10^{10}\text{cm}^{-2}$, and for CPC, $\rho_{CPC} = 0.36 \times 10^{10}\text{cm}^{-2}$. These values mean that in the case of the aqueous solutions of κ-carrageenan in the presence of CPC, the contrast match point for κ-carrageenan is 70% $H_2O$/30% $D_2O$ (taking into account deutering exchange of some protons in the polymer molecule, and assuming that there is no internal structure in the CPC-molecules); hence for the latter conditions one only observes the small-angle scattering from the surfactant. The contrast match point for CPC is 86% $H_2O$/14% $D_2O$, and for this solvent the scattering is

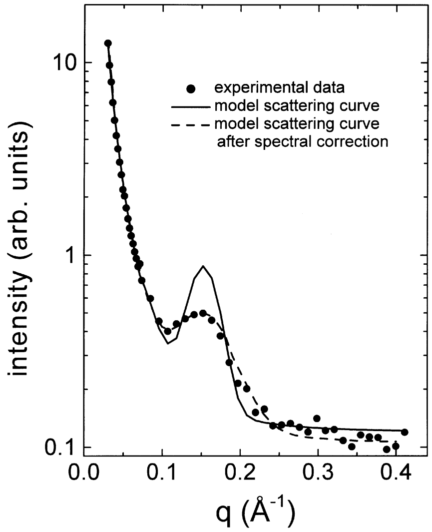

Fig. 2. Experimental and model SANS patterns of 1% κ-carrageenan/CPC complexes in 0.10 M KCl in $D_2O$, [CPC]/[Car] = 0.5.

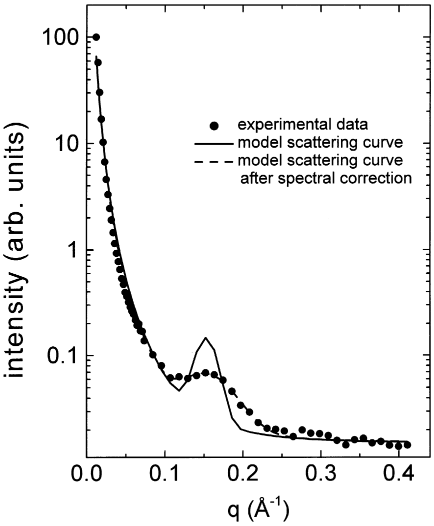

Fig. 3. Experimental and model SANS patterns of 1% κ-carrageenan/CPC complexes in 0.10 M KCl in $D_2O$, [CPC]/[Car] = 1.0.

solely due to the κ-carrageenan component. For κ-carrageenan/CPC complexes in $D_2O$ the scattering patterns are defined both by the polysaccharide and by surfactant molecules and consequently the scattering intensity in this case is essentially higher.

The SANS profiles of the pure 1% κ-carrageenan gel (without CPC) and two 1% polysaccharide/surfactant complexes in $D_2O$ are shown in Fig. 1. The pure physical gel displays no characteristic peak, hence pointing to the absence of ordering in the gel structure. In this case, the scattering curves can be well described by the following scattering function, which is valid for physical networks of carrageenan [44]:

$$I(q) = I_G(0)\exp(-q^2\Xi^2/2) + I_L(0)/(1 + q^2\xi^2), \qquad (5)$$

here $I_L(0)$ and $I_G(0)$ are, respectively, the linear coefficients of the Lorentzian and Gaussian terms, describing the different components of scattering from polysaccharide solutions; $\Xi$ is the characteristic mean size of the static heterogeneities in the system under study and $\xi$ is the correlation length of polymer–polymer interactions between the fluctuating chains of polymer. Analysis of small-angle scattering data in terms of Eq. (5) has shown to be efficient for fitting the scattering information of several types of gels and other heterogeneous systems [15,25,26,43–50]. The fit of the experimental data according to this equation makes clear that the structure of the κ-carrageenan gel represents a network with characteristic sizes of heterogeneities in the system: $\Xi \sim 80$–100 Å and $\xi \sim 30$–40 Å. These values are in good agreement with the parameters of the supermolecular structure of carrageenan gels investigated by X-ray scattering and which are reported elsewhere [44,50].

The data obtained by SAXS for the gel–surfactant systems show that for the studied contents of surfactant in the gel phase ordered structures are formed [50]. In the case of SANS similar SANS curves are observed for the κ-carrageenan/CPC complexes. After addition of CPC to the systems under investigation a characteristic peak at about $q = 0.15$ Å$^{-1}$ emerges due to surfactant ordering within the gel (curves 2 and 3, Fig. 1).

Since in this study a non-monochromatic neutron beam (the wavelength resolution of the neutron beam was $\Delta\lambda/\lambda = 0.18$) has been used, it is not possible to extract the ordering parameters in the carrageenan/CPC complexes by direct use of Eqs. (1)–(3) for the high $q$-region.[1] One should apply a spectral correction to obtain the real scattering curve. A detailed description of the procedure used is reported in Ref. [38]. In the present case, the theoretical scattering function $I_{\text{theor}}(q)$ was modeled by various possible polynomials with a Gaussian-type maximum. If there is a wavelength spread, $F(\lambda)$, then this wavelength distribution in its analytical form is convoluted with the theoretical scattering function:

$$I_{\text{theor}} = \int_0^\infty F(\lambda) I_{\text{theor}}(q, \lambda)\, d\lambda,$$

where the function $F(\lambda)$ is normalized:

$$\int_0^\infty F(\lambda)\, d\lambda = 1.$$

The fitting procedure consists of finding the best agreement between the experimental scattering curves and $I_{\text{theor}}(q)$ by

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[1] It should be noted that for simplicity only the experimentally measured scattering data near the Bragg peak were corrected for the polychromatic nature of the beam, because the main contribution to the smearing of SANS data is defined by spectral distortions of the SANS instrument [38] and these distortions are significant in the region of peculiarities of the scattering pattern. Resolution effects are neglible in the Guinier part of the scattering curve [51]. In our case these effects are <3% and within the statistical uncertainties of the experiment.

Table 1
The structural parameters of the 1% κ-carrageenan/CPC complexes in 0.10 M KCl $D_2O$ solutions obtained from SANS curves

| [CPC]/[Car] | $q_{\max}$ (Å$^{-1}$) | $\bar{a}$ (Å) | $\beta_s$ (Å$^{-1}$) | $L$ (Å) | $r_m$ (Å) | $\Delta/\bar{a}$ |
|---|---|---|---|---|---|---|
| 0.5 | 0.153 | 41.1 | 0.036 | 174 | 275 | 0.15 |
| 1.0 | 0.153 | 41.1 | 0.026 | 240 | 379 | 0.13 |

varying the parameters of the width at half-maximum intensity of the peak and its position. The fitting of the experimental and model curves is estimated by the chi-square parameter in the region of the Bragg peak, since the most important task of this fit is to desmear the structural peak of the scattering curves. In Figs. 2 and 3 the corresponding data are presented for 1% κ-carrageenan/CPC complexes in $D_2O$ with different contents of surfactant. The structural characteristics of the gel–surfactant complexes obtained from the SANS data are given in Table 1.

When one compares the scattering data obtained for the different CPC contents (Fig. 1 and Table 1), one observes an increase of ordering for systems with higher CPC concentration, at constant position of the main peak, which reveals CPC-induced ordering when compared to the pure κ-carrageenan. The characteristic size of the ordered elements in the κ-carrageenan/CPC complexes is $\bar{a} = 41.1$ Å on average. According to Tanford [52], the maximum length of one hydrocarbon chain with 16 C-atoms embedded in a micellar-like surfactant aggregate is 20.48 Å. Therefore the $\bar{a}$-spacings are very close to the largest possible extension of two cetylpyridinium hydrocarbon chains incorporated in a liquid hydrocarbon like environment. It is assumed that the most favorable orientation of the surfactant molecules inside the polymer–surfactant network should be in the form of highly ordered bilayers interconnecting carrageenan chains together into a three-dimensional network. This ordering gives the characteristic size of the bilayer, which equals exactly to two times the length of the surfactant chain. By increasing the [CPC]/[car] ratio, aggregates grow in one-dimension keeping a constant distance and successively increasing the ordering in the system ($L$ and $r_m$ increase with increasing [CPC]/[car], cf. Table 1). These “ladder-like” surfactant bilayers are interrupted by less ordered parts of “free-floating” chains, and that ultimately decreases the ordering throughout the system under investigation. Such a system can be defined as a partial bilayer structure. In the case of ι-carrageenan/CPC complexes a second order diffraction maximum is observed, which confirms the lamellar type of ordering in the carrageenan–surfactant system [50]. The appearance of this maximum was associated with the higher linear charge density of the κ-form of carrageenan in comparison with the κ-form. Higher charge density leads to stronger electrostatic interactions between the polyelectrolyte and the surfactant molecules, which favor the increased ordering of the complexes.

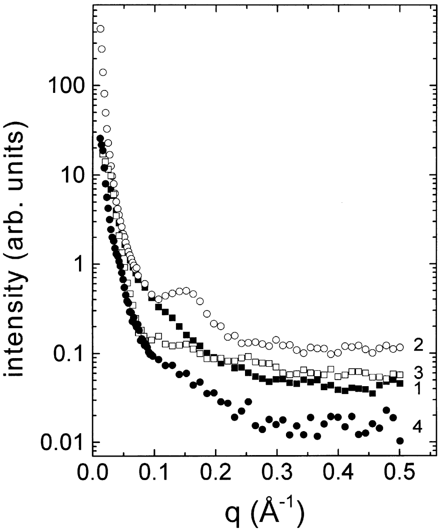

Fig. 4. SANS patterns of 1% κ-carrageenan/CPC complexes ([CPC]/[Car] = 0.5) in 0.10 M KCl in aqueous mixtures: 1-pure physical gel in $D_2O$; 2-polysaccharide/surfactant complex in $D_2O$; 3-in 70% $H_2O$/30% $D_2O$ mixture; 4-in 86% $H_2O$/14% $D_2O$ mixture.

In order to describe the structure of the κ-carrageenan/CPC complexes in more detail SANS measurements of 1% ι-carrageenan/CPC with 0.10 M KCl for a ratio of [CPC]/[Car] = 0.5 in different mixtures of $H_2O$ and $D_2O$ are carried out. The corresponding SANS patterns are presented in Fig. 4. The SANS measurements of the κ-carrageenan gels in the presence of CPC in 0.10 M KCl for contrast matching conditions for the polysaccharide (70% $H_2O$/30% $D_2O$) allow to obtain the small-angle scattering solely due to the surfactant part of complexes (Fig. 5). From the scattering curve in the double logarithmic plot one observes 3 $q$-ranges of different intensity behavior. The high $q$-region with $I(q)$–$q^{-4}$ points to scattering entities, which have rather sharp boundaries (Porod’s law). The radius of gyration of the latter entities can be calculated from the Guinier part ($q < 0.03$ Å$^{-1}$) : $R_g = 52$ Å. This value is in good agreement with the radius of gyration that can be estimated from the parameters $\bar{a}$ and $L$, which were determined from the position and half-width of the Braggs peaks of the SANS patterns. While $L$ measures the range of correlation (the local order) of the system and accepting a cylinder model for the scattering entities; one calculates a value of $R_g = ((\bar{a}/2)^2/2 + L^2/12)^{1/2} = ((41.1/2)^2/2 + 174^2/12)^{1/2} = 52$ Å. It should be stated that the same result for $R_g$ is obtained in the case of a tetragonal prism with ribs; $\bar{a}$, $\bar{a}$ and $L$, which means that the exact shape of the scattering entities is not yet available, but that at least the system is fairly well characterized by $\bar{a}$ and $L$. The $q^{-0.65}$ slope of the tail part of SANS curve is close to the $q^{-1}$ dependence of the scattering intensity characteristic of a rod-like conformation of the scatters to be ascribed to single surfactant molecules inside of the scattering entities.

Analysis of the SANS data from the pure 1% κ-carrageenan gel in $D_2O$ (curve 1 in Fig. 4) and of the polysaccharide part of the complex in a 86% $H_2O$/14% $D_2O$ mixture (curve 4 in Fig. 4) shows that the scattering curves are similar and

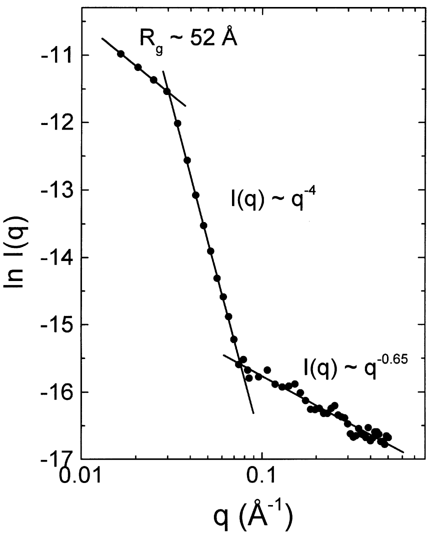

Fig. 5. Double logarithmic representation of SANS patterns for 1% κ-carrageenan/CPC complexes in 0.10 M KCl, [CPC]/[Car] = 0.5, 70% $H_2O$/30% $D_2O$.

have the same supermolecular parameters. No real difference was obtained, which could mean that charging a physical gel by surfactant does not crucially affect the network structure of the polysaccharide. This conclusion however needs further research because the scattering signal from the 1% κ-carrageenan gel in 86% $H_2O$/14% $D_2O$ mixture is small and because there might be some possible kinetic differences resulting from the preparation of these samples. The decrease of the scattering signal also explains the hardly pronounced Bragg maximum for the 1% κ-carrageenan/CPC complex in 70% $H_2O$/30% $D_2O$ mixture (curve 3 in Fig. 4). As the scattering intensity is proportional to the square of the contrast between the two phases — compound and the solvent — a simple calculation shows that changing the solvent from pure $D_2O$ to a 70% $H_2O$/30% $D_2O$ mixture results in a decrease of the scattering intensity by at least of a factor of 30.

## 4. Conclusions

Interaction of a physical κ-carrageenan gel with an ionic surfactant leads to the formation of an ordered structure. The ordering results from hydrophobic and electrostatic interactions in the polymer network/surfactant system. The surfactant molecules in conjunction with the carrageenan molecules self-assemble and result in a lamellar type of organization. The SANS measurements of the κ-carrageenan gels in the presence of CPC in 0.10 M KCl for contrast matching conditions for the polysaccharide (70% $H_2O$/30% $D_2O$) allow to observe the small-angle scattering solely due to the surfactant part of complexes. The surfactant molecules self-assemble in regions with well defined sharp boundaries. The size of these scattering formations is in good agreement with a value calculated independently for a cylinder model of scattering particles using the position and the half-width of the Bragg peaks in the SANS patterns. These results are additional evidence for and support the structural model of carrageenan/surfactant complexes reported elsewhere [50].

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