

A thermoreversible double gel: Characterization of a methylcellulose and κ -carrageenan mixed system in water by SAXS, DSC and rheology

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Abstract

Sol–gel and gel–sol thermal transition of methylcellulose/water, κ -carrageenan/water and methylcellulose/ κ -carrageenan/water mixtures was investigated utilizing small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC) and oscillatory rheological experiments in temperature regime from 20 to 80 °C. Methylcellulose (E461) and κ -carrageenan (E407) are well-known additives used for gelation in various nutrition and other products. The formulation and characterization of a mixed thermoreversible methylcellulose/ κ -carrageenan/water gel with very interesting double thermal transition gel–sol–gel upon heating was possible. This specific thermal behavior provides a liquid state of the system between the low-temperature and high-temperature gel-state and at the same time allows for the easy temperature tuning of the system's state. As such this system is suggested to be further tested as potential carrier for various functional colloidal systems.

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1. Introduction

Polymers play a very important role in various natural processes and are nowadays very important also for numerous industrial applications. With modern polymerization and modification techniques it is possible to obtain a variety of different polymers with rather diverse properties depending on their chemical composition and structure [1–9]. One can of course find a variety of different polymers also in nature (proteins, carbohydrates, DNA, etc.).

Our study focuses on a natural polymer κ -carrageenan (E461; KC), an extraction product of red seaweed, and on hydrophobically modified cellulose—methylcellulose (E407, MC), which are both well-known food grade additives used in various nutrition and other products. We are especially interested in the thermal behavior of their water mixtures—their reversible sol–gel and gel–sol transitions. KC is known to form

a rather solid hydrogel at room temperatures (depending on KC concentration) that reversibly breaks/reforms with increasing/decreasing temperature. Similarly, but opposite, the MC shows in water a high-temperature gelation that reverses as the temperature is decreased again. Both polymers have already been extensively studied from various points of view [10–38]. Mechanisms of gelation are different in both polymers.

It is generally accepted that KC molecules first make a conformational change from coils to double-helices upon cooling. Further decrease of temperature results in the aggregation between the ordered double-helices and cross-linking leading to the formation of a large-scale network [10–12]. Since KC molecules carry charges due to the sulphate groups, the counter ions were found to play an important role in the gelation and corresponding gel characteristics [12–19]. Interestingly in the presence of K^+ counter ions KC molecules can form double helix domains much easier than in solutions without or with other counterions; hydrogels also appear stronger in the former case.

For the case of MC molecules in water three possible intermolecular interactions were reported: hydrogen bonding between (1) unmodified hydroxyl groups on cellulose chains or (2) between hydroxyl groups of cellulose and water molecules,

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and (3) intermolecular hydrophobic association between the methyl groups on the MC molecules [20]. The interplay of these interactions dictates the mechanism of thermoreversible gelation [20–38]. Hydrophobic association of MC becomes pronounced at elevated temperatures when the hydration cage-like structures [20–27] around hydrophobic parts of the MC molecules start to collapse yielding in considerable entropic contribution. This process of gelation was therefore found to be entropy-driven [20–22,28]. Recently also the scheme of thermogelation originally proposed by Haque and Morris [29] has been reported to be probable [30]. That is, the gelation of MC starts with the thermal disintegration of aggregated bundles of cellulosic structure, which is followed by the network formation due to the hydrophobic aggregation. Interestingly, also the process of MC gelation can be influenced by the presence of salts [21–24] or surfactants [26].

Our aim was to study the gel–sol and sol–gel thermal transitions of the two polymers in order to formulate a rather ‘tricky’ gel—a mixed KC/MC/water system that would behave as a gel at high and low temperatures with a narrow temperature regime in between where it would be a liquid solution facilitating the possible homogeneous incorporation of functional particles in such a system. Namely, our future interest lies in exploring these systems as possible entrapment media for various functional molecules, emulsion droplets or other colloidal nanostructured materials. In order to do that one of course needs to explore the plain systems first.

2. Experimental and methods

2.1. Materials

κ -Carrageenan is a linear sulphated polysaccharide extracted from red seaweeds. Its idealized structure is a repeating disaccharide sequence of β -D-galactopyranose-4-sulphate residues linked 1,3- and 3,6-anhydro- α -D-galactopyranose residues linked through positions 1,4 as shown in Fig. 1a. Methyl cellulose is a synthetic product and does not occur in nature. It is hydrophobically modified cellulose with a basic building block schematically depicted in Fig. 1b.

4 wt% stock solution of MC as also KC in water was prepared by weighing the MC (Methocel® A4C FG sample; Dow Chemical Company) or KC (Fluka BioChemika) and hot water into a glass vial, heating it up to approximately 70 °C and letting the samples to cool-down slowly during vigorous stirring. The samples were then kept to rest over the night in a fridge at 4 °C before further dilution and use. All water was deionized using Millipore Water systems. Samples of mixed MC/KC/water systems were prepared directly by weighting MC, KC and water into a glass vial and then proceeding in the same way as for pure binary mixtures. All samples were used without further purification.

2.2. Small-angle X-ray scattering measurements

Small-angle X-ray scattering spectra were measured with a SAXSess camera [39] (Anton-Paar, Graz, Austria), which was

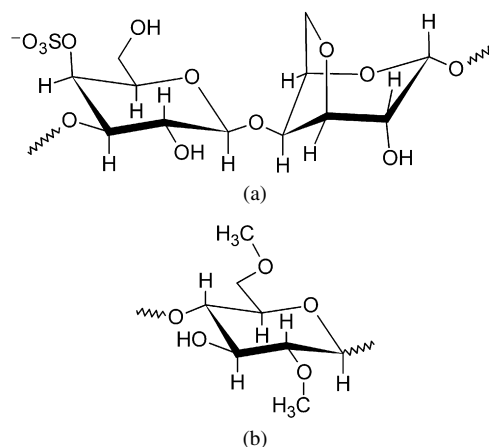


Fig. 1. Structural representation of (a) κ -carrageenan and (b) methylcellulose building blocks.

connected to an X-ray generator (Philips, PW 1730/10) operating at 40 kV and 50 mA with a sealed-tube Cu anode. A Göbel mirror was used to obtain a focused monochromatic line-shaped beam of $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm). The 2D scattering pattern was recorded by a PI-SCX fused fibre optic taper CCD Camera from Princeton Instruments, which is a division of Roper Scientific, Inc. (Trenton, NJ, USA). The used CCD detector has a chip of 50×50 mm, 2084×2084 array with a pixel size of 24×24 μm . The detector is operated at -30 °C to reduce the thermally generated charge. The samples were measured in a standard quartz capillary (outer diameter of 1 mm and wall thickness of 10 μm) that was centered in the X-ray beam and carefully thermostated (± 0.1 °C) using a Peltier element. Temperature was changed in a stepwise manner—the samples were equilibrated at a specific temperature for 30 min and then three subsequent 5 min measurements followed, which were averaged afterwards. Cosmic ray correction and CCD background subtraction was performed on the 2D image before further data processing. The 2D image was integrated into the one-dimensional scattering function $I(q)$, where q represents the length of the scattering vector:

$$q = \frac{4\pi}{\lambda} \sin(\vartheta/2), \quad (1)$$

with λ being the wavelength of the X-rays and ϑ the scattering angle. The SAXS measurements were obtained for the regime $0.07 < q < 6$ nm^{-1} . No corrections for the background scattering were made.

Arising from the scattering theory, the scattering vector is the basis of the so-called reciprocal space where the scattering function $I(q)$ is expressed. The name ‘reciprocal’ follows from the fact that the length of the scattering vector q is according to the well-known Bragg law

$$D = \frac{2\pi}{q} \quad (2)$$

inversely proportional to the distances D from the real space where one operates with the actual dimensions and particle shapes. The connection between these two spaces is the Fourier transformation. For the understanding of the SAXS results presented in the present paper it is, however, sufficient for the

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