POLYCATION-SURFACTANT INTERACTIONS AND THE FORMATION OF HYDROGELS WITH INTERNAL NANOSTRUCTURE

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Abstract

Oppositely charged polyelectrolytes and surfactants can form under specific conditions hydrogels containing micelle-like nanostructures. Due to its hydrophobic core, these structures are capable of solubilizing hydrophobic substances within hydrophilic soft solid matrix. Such hybrid materials can be subject of interest for medical applications. In this study, interactions between cationic dextran and sodium dodecylsulphate were studied and conditions of gel formation investigated. Using the technique of fluorescence probe, phase behaviour was analysed and region of the gel phase separation detected. Solubilisation of hydrophobic dyes confirmed the formation of micellar domains. The gel formation was affected by ionic strength of gelling solutions.

Keywords: Hydrogels, polyelectrolytes, surfactants, micelles, solubilisation

1. INTRODUCTION

Due to electrostatic interactions and electrostatic forces between polyelectrolytes and oppositely charged surfactants many types of colloids, nanocolloids or even bulk materials can be formed, see, e.g., the monograph by Holmberg et al. [1]. Hydrogels can be, under proper conditions, prepared by simple mixing of the polyelectrolyte and surfactant solutions, the surfactant micelles can act as crosslinking points and gelled material is formed. Dispersed phase in gels (colloidal “particles”) is in solid state and dispersion phase in gels is in liquid state. Surfactant micellar structures form hydrophobic domains which are in scale of nanometers and should be capable of solubilisation of hydrophobic substances (within the otherwise hydrophilic gel matrix). Hydrogels combine the behaviour of solids and liquids in a soft matter, which usually retains its shape, but is relatively easily deformable. Behaviour of these hydrogels depends on the density of its network or the density of crosslinks connecting the network.

In general, hydrogels are soft materials of significant interest for applications in various areas of industry. If there are no biocompatibility issues, hydrogels can have widespread applications in different fields related to human health, food industry, bioengineering, medicine, agriculture, cosmetics and so on. If hydrogels are prepared both from synthetic polymers and biopolymers, which are similar to biological tissues and compatible with them have been important materials for drug delivery and tissue engineering, wound healing, artificial implants, see, e.g., refs. [2,3] This work is focused on the preparation of hydrogels from positively charged polymers and negatively charged surfactants and on the study of their properties.

2. EXPERIMENTAL PART

Hydrogels were prepared from cationic polyelectrolyte dextran hydrochloride (DEAE) and anionic surfactant sodium dodecylsuphate (SDS). Dextran hydrochloride (powder prepared from dextran of average molecular weight 500,000) was purchased from Sigma Aldrich and used without further treatment. Sodium dodecylsulphate (≥ 99.0 %, Sigma Aldrich) was also used as received. Hydrogels were prepared by mixing polyelectrolyte and surfactant solutions. Solutions were prepared in deionized water (Purelab Flex, ELGA) or in 0.15 M NaCl. Stock solution of dextran was prepared at concentration of 0.5 % (weight) and stock solutions of sodium dodecylsulphate were prepared at wide range of concentrations (from 0.005 mmol·dm^{-3} to 100

mmol·dm^{-3}). Gels were prepared in vials by mixing equal volumes of stock solutions of polyelectrolyte and equal volumes of stock solutions of surfactant. To complete gelation process and separation of the gel phase the vials were left on a shaker overnight.

For the visualization of the solubilisation capabilities of the gel, Oil red O (Sigma Aldrich) was used as a hydrophobic dye. A small amount of the dye powder was added to the vial with freshly prepared gel and left to solubilize overnight on shaker.

Pyrene is fluorescent probe which reacts to polarity in its surroundings and due to that, it was used as fluorescence probe to further solubilisation properties of the hydrogels. Pyrene was purchased from Fluka. Stock solution of pyrene was prepared in acetone at concentration of $1 \cdot 10^{-4}$ mol·dm^{-3} and it was first added to the vials in such amounts to achieve its final concentration of $1 \cdot 10^{-6}$ mol·dm^{-3}, acetone was left to evaporate and then the gel preparation followed as described above. Fluorescence spectra were measured at laboratory temperature using AMINCO - Bowman Series 2. In the measurement of emission spectra, the excitation the monochrome was set to 335 nm and the spectrum was measured in the range from 360 nm to 530 nm. In the spectrum the main interest was the intensity of the first peak at 373 nm and the third peak at 383 nm. Their ratio is called emission polarity index (EmPi) and reacts to polarity. In the measurement of excitation spectra the monochrome was set to 392 nm and the spectrum was measured in the range from 310 nm to 340 nm. In the spectrum the main interest was the intensity of the first peak at 333 nm and the peak at 338 nm. Their ratio is called excitation polarity index (ExPi) and reacts to polarity too. The intensity ratio at 373 nm (monomer fluorescence) and 470 nm (maximum excimer fluorescence) is referred to as the excimer to the monomer (Ex:Mo) and indicates the pyrene content of the hydrophobic nuclei. Both emission and excitation polarities, as a function of concentration, show a decreasing sigmoid curve. This dependence is interleaved by the Boltzmann model. The Boltzmann curve has the following form:

$$y = \frac{A_1 - A_2}{1 + e^{\frac{x - x_0}{\Delta x}}} + A_2$$

The variable y corresponds to EmPi or ExPi, the independent variable x denotes the total concentration of the surfactant, where x_0 is the inflection point and x indicates the slope of the curve drop. A_1 is the upper limit of the sigmoid curve and A_2 is the lower limit of the sigmoid curve.

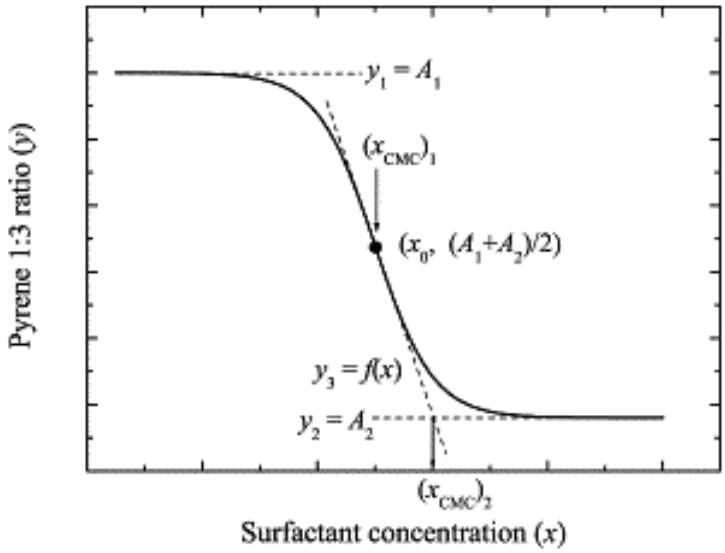

Figure 1 Boltzmann's curve fitting and its characteristic parameters [4]

3. RESULTS AND DISCUSSION

Sequences were prepared with a constant final concentration of dextran hydrochloride (0.25 wt. %) and varying concentrations of surfactant in water and 0.15 M NaCl. The system was investigated using both Oil red O (solubilisation experiments) and pyrene (fluorescence spectroscopy). Using the Oil red O the system was visually examined and using the pyrene and fluorescence spectroscopy only the supernatant formed over the hydrogel was examined.

Solubilisation experiments were conducted to familiarize with the system, to determine the area in which critical aggregation concentration (CAC) is and from which concentration the phase separation started. The most of the graphs contain the Boltzmann model curve, this model was used to determine CAC for individual systems.

4. DEAE HYDROGELS PREPARED IN WATER

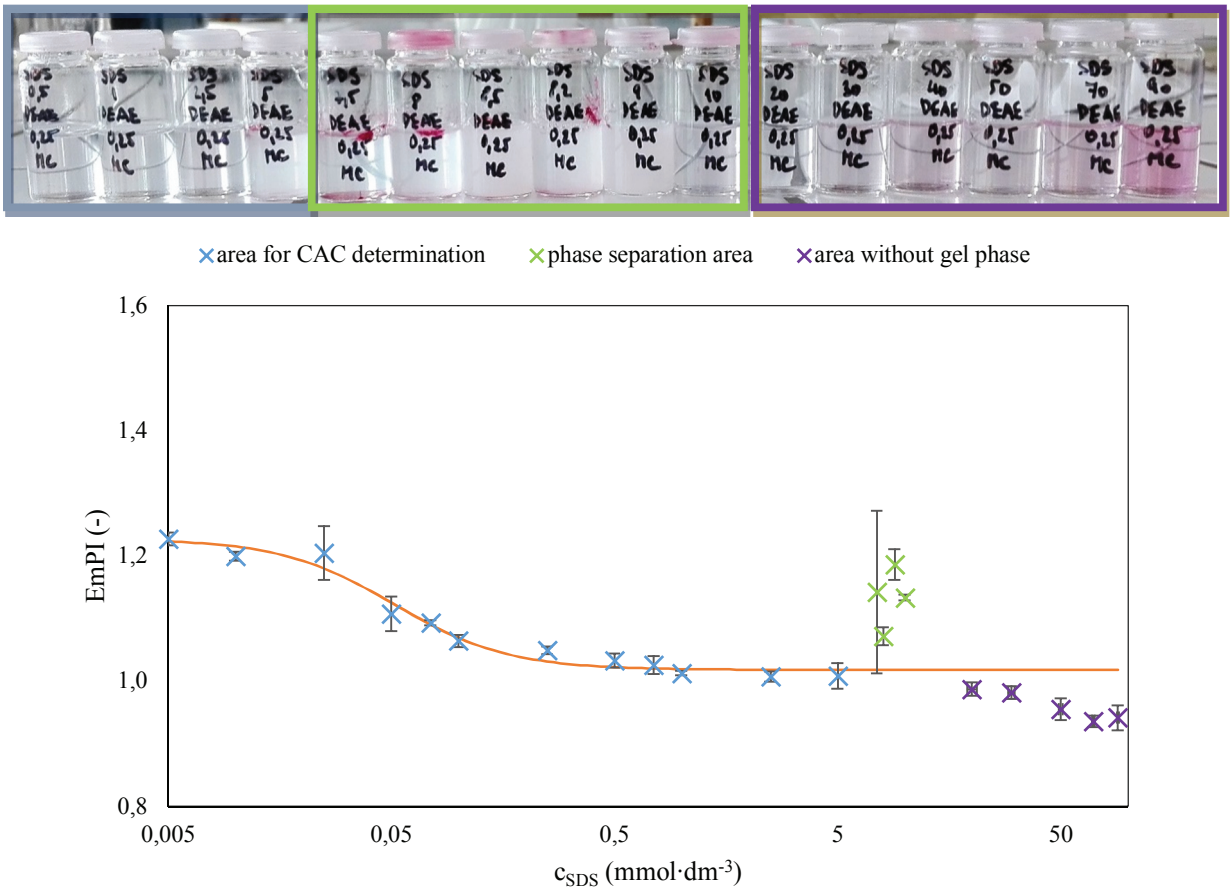

Figure 2 Concentration line with a constant DEAE concentration (0.25 wt. %) and the varying SDS concentration prepared by the wet way in water. In the first part of the figure, the concentration line with Oil red O is divided into three areas by behaviour, in the second part of the figure it can be seen the dependence of EmPi on increasing concentration of SDS with colour bounded areas according to the behaviour of the system

In **Figure 2** there is a concentration line with a constant concentration of dextran hydrochloride and varying concentrations of surfactant prepared by wet way in water. In the first part of the figure the solubilisation experiments are seen. Samples are divided into three areas depending on the interaction. From the concentration of 0.005 mmol·dm^{-3} to the concentration of 4.5 mmol·dm^{-3} of the surfactant phase-separated gel is not formed and in this part of the concentration range we are able to determine the CAC system. The final

value of the critical aggregation concentration in water in this system was determined at 0.05 mmol·dm^{-3}. The table value of critical micellar concentration for the sodium dodecylsulphate is 8.3 mmol·dm^{-3} so in our system there is a decrease due to addition of polymer.

In a further region (from 7.5 mmol·dm^{-3} SDS) phase separation and substantial clouding of the supernatant are already occurring. The gel which is formed is relatively incoherent but red coloured. That indicates the presence of surfactant in the gel as well. After examining EmPi dependence on surfactant concentration, the increase of polarity index in this area can be seen. This is due to the fact that even if the surfactant concentration increased and the intensity should remain at the same level, the system stabilizes due to the exclusion of the gel phase. Pyrene is bonded in the gel phase not in the supernatant. In the supernatant occurred pyrene which was not solubilized in micelles in the gel phase. The concentration of the surfactant in the supernatant is not so high so the micelles are not formed, and therefore the pyrene shows a signal from the aqueous medium.

In the last region (from 15 mmol·dm^{-3}) no gel is present in any of the samples. Only staining of the supernatant occurs due to a sufficient concentration of surfactant to form micelles. Even from the EmPi dependence on the concentration of the surfactant there can be seen the signal from the hydrophobic region.

5. DEAE HYDROGELS PREPARED IN 0.15 M NaCl

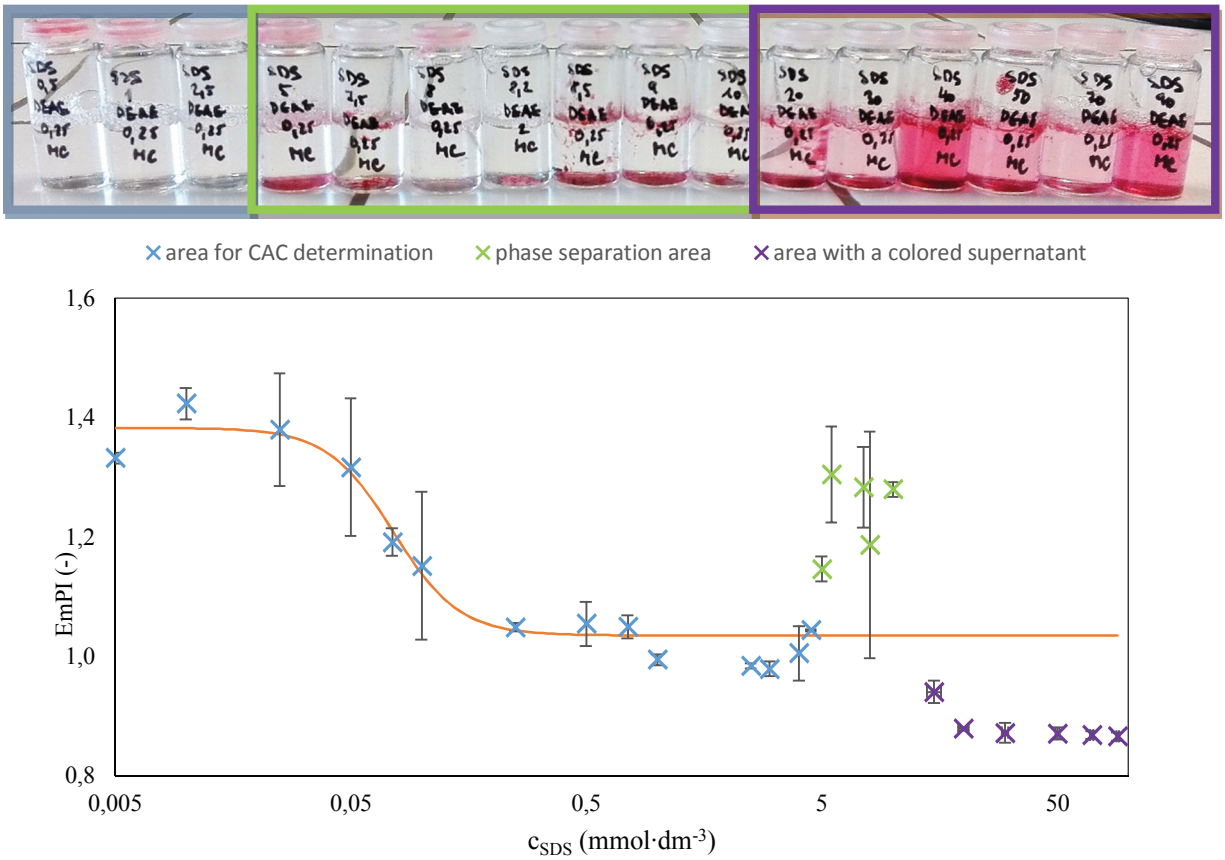

Figure 3 Concentration line with a constant DEAE concentration (0.25 wt. %) and varying concentrations of SDS prepared by the wet way in 0.15 M NaCl. In the first part of the figure the concentration line with Oil red O is divided into three areas by behaviour, in the second part of the figure there can be seen the dependence of EmPi on increasing concentration of SDS with colour bounded areas according to the behaviour of the system

In **Figure 3** there is a concentration line with constant concentration of dextran hydrochloride and varying concentrations of surfactant prepared by wet way in 0.15 M NaCl. In the first part of the **Figure 3** the solubilisation experiments can be seen. Samples are divided into three areas depending on the interaction. From 0.005 mmol·dm^{-3} to 4.5 mmol·dm^{-3} of the surfactant phase-separated gel is not formed and in this part of the concentration range we are able to determine the CAC of SDS in the system in the presence of NaCl and DEAE. This value was determined to 0.08 mmol·dm^{-3}. Without the addition of DEAE, the CMC in NaCl is determined at 1.1 mmol·dm^{-3}. Again, the influence of DEAE on the reduction of CMC value can be observed.

In the second part, the phase separation can be seen (from 5 mmol·dm^{-3} SDS). In contrast to the aqueous environment there is no turbidity. The turbidity was suppressed by the increasing ionic strength of the environment and the hydrogel formed. In this area various amounts of hydrogel were produced. The red colour and the change in EmPi confirm the presence of micelles of the surfactant in the gel.

In the last part (from 15 mmol·dm^{-3} SDS) of the concentration line hydrogels were formed but instead of the second area the colour of the supernatant can be observed. This phenomenon can be explained by the fact that the concentration of SDS which is not bound in the hydrogel is sufficient for the formation of micelles and solubilizing dyes. This is confirmed by the EmPi values which return back to the values typical for hydrophobic environment, again.

6. CONCLUSION

Under proper conditions cationic polyelectrolyte DEAE and anionic surfactant SDS can interact and form physically cross-linked hydrogels. Resulting hydrogels incorporate micellar hydrophobic nanocontainers which are able to solubilize hydrophobic compounds (molecules). Hydrophilic substances can be also entrapped within the hydrogel matrix. These hydrogels can be favourably employed in variety of applications, especially in the fields of biomaterials, (bio) medicine, cosmetics, drug delivery, and topical (skin or mucous membrane) treatments.

ACKNOWLEDGEMENTS

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