

INFLUENCE OF IONIC STRENGTH ON THE RHEOLOGICAL PROPERTIES OF HYDROXYPROPYLMETHYL CELLULOSE–SODIUM DODECYLSULFATE MIXTURES

Jaroslav M. Katona*, Alena Tomšik, Sandra Dj. Bučko and Lidija B. Petrović

University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

Mixtures of polymers and surfactants are commonly found in a range of products of pharmaceutical, cosmetic, and food industry. Interaction between polymers and surfactants influences different properties of these products, e.g. stability, flow properties, phase behavior, etc. It is known from previous work that an interaction in binary mixtures of hydroxypropylmethyl cellulose (HPMC) and sodium dodecylsulfate (SDS) takes place when SDS concentration (C_{SDS}) is higher than the critical association concentration (CAC) and lower than the polymer saturation point (PSP). The interaction results in the formation of an HPMC–SDS complex. The objective of this work was to study the effect of the ionic strength on the HPMC–SDS complex formation by rheological investigation. The HPMC/SDS mixtures composed of 0.70 % wt. HPMC, and 0.00 % to 2.50 % wt. SDS were prepared in deionized water, 0.01M and 0.05M NaCl solution. It was found that an increase in the ionic strength influences the HPMC–SDS complex formation by increasing the zero shear viscosity of the mixtures in the interaction region ($CAC < C_{SDS} < PSP$), while a decrease in the viscosity is observed for $C_{SDS} > PSP$. The HPMC/SDS mixtures showed a shear thinning or a shear thickening flow properties depending on C_{SDS} . The flow properties were influenced by the ionic strength of the mixtures.

KEY WORDS: polymer–surfactant interaction, nonionic cellulose ethers, hydroxypropylmethyl cellulose, ionic strength

INTRODUCTION

Polymers and surfactants are commonly found in many food, pharmaceutical and chemical industry products. An interaction between a polymer and a surfactant often takes place when they are jointly found in a solution. The polymer–surfactant interaction influences physico–chemical properties of the solutions and is often employed to achieve different effects such as emulsification, colloidal stability, viscosity enhancement, gel formation, solubilization, phase separation, etc. Details of polymer–surfactant interaction depend on molecular characteristics and concentration of both polymer and surfactant (1, 2, 3).

* Corresponding author: Jaroslav M. Katona, University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia, jkatona@uns.ac.rs

Hydroxypropylmethyl cellulose (HPMC) is a nonionic water-soluble cellulose ether. It is obtained by partial substitution of hydroxyl groups of cellulose with hydrophobic hydroxypropyl and methyl groups. The substituents make HPMC a typical amphiphilic polymer with properties such as ability to adsorb at air-water and oil-water interface, emulsification, self-assembly, and association with other amphiphilic molecules (4, 5). In this regard, the addition of low molar mass surfactants, especially anionics such as sodium dodecylsulfate (SDS), to HPMC solution may result in a polymer-surfactant interaction. The HPMC-SDS interaction takes place when the SDS concentration (C_{SDS}) exceeds the critical association concentration (CAC), which is a minimal surfactant concentration required for the onset of association of the surfactant and the polymer (6). The HPMC-SDS interaction takes place via hydrophobic moieties of the components, where SDS binds to HPMC chains and thereby brings about formation of the HPMC-SDS complex. The binding and complex formation support physical cross-links between entangled HPMC chains, which result in an increase in the viscosity of the HPMC/SDS mixtures. At the same time, formation of negatively charged SDS micelles along HPMC chains progressively converts the nonionic polymer into a polyanion. As C_{SDS} is further increased, the electrostatic repulsive forces between the neighboring HPMC chains start to dominate, the network structure is gradually lost, and consequently, the viscosity of the HPMC/SDS mixture drops. Individual HPMC chains become fully solubilized with SDS when C_{SDS} reaches the polymer saturation point (PSP). The increase in C_{SDS} above PSP causes only a slight decrease in the viscosity of the HPMC/SDS mixtures as a result of formation of free SDS micelles in the solution, which brings about slight conformational changes of the SDS-solubilized HPMC chains (7, 8, 9).

In this work, the influence of the ionic strength on the formation of the HPMC-SDS complex was studied by a rheological investigation of HPMC/SDS mixtures of different SDS concentration and different ionic strength.

EXPERIMENTAL

Materials

Hydroxypropylmethyl cellulose (trade name Methocel K100M CR, methoxyl content 22.6 %, hydroxypropyl content 10.5 %) was obtained from Colorcon Ltd., England. The viscosity average molar mass was $M_v=717,490$ g/mol, and the overlap concentration was $c^*=0.072$ % w/v, as determined by capillary viscometry (10). Sodium dodecylsulfate purity >99 %, was obtained from Merck, Germany. The critical micelle concentration determined at 20°C by conductometric titration was CMC=0.244 % w/v. All samples were used without any further purification. Demineralized water was used as a solvent.

Preparation of solutions

The HPMC stock solutions of different ionic strength (0.00M, 0.01M and 0.05M NaCl) were prepared by dispersing HPMC powder in the corresponding NaCl solutions at 80–90°C by gentle stirring. The stock solutions were left for 24 h at room temperature before further use. Stock solutions of SDS of different ionic strength (0.00M, 0.01M and

0.05M NaCl) were prepared by dissolving SDS in the corresponding NaCl solutions at 20°C.

The HPMC/SDS mixtures of desired ionic strength (0.00M, 0.01M and 0.05M NaCl) were containing 0.7 % w/w HPMC and 0.00–2.50 % w/w SDS, and were prepared by mixing HPMC stock solutions with the SDS stock solutions and appropriate dilution with NaCl solutions. The mixtures were vigorously hand-mixed, and were left for 48 h prior to further use.

Rheological measurements

Rheological measurements were performed on a RheoStress 600HP rheometer (ThermoHAAKE, Germany), at 20°C. The cone and plate geometry was used ($d=60$ mm, $\theta=1^\circ$), and the steady-state controlled rate method was employed to measure apparent viscosity η at different shear rates (11). The apparent viscosity was normalized against the zero shear viscosity η_0 (i.e. η/η_0) when plotting the viscosity curves. The zero shear viscosity was determined at sufficiently low shear rates, where the apparent viscosity is shear rate independent and a Newtonian plateau is observed.

RESULTS AND DISCUSSION

The zero shear viscosity of HPMC/SDS mixtures of different ionic strength

The influence of C_{SDS} on the zero shear viscosity of HPMC/SDS mixtures of different ionic strength is shown in Figure 1.

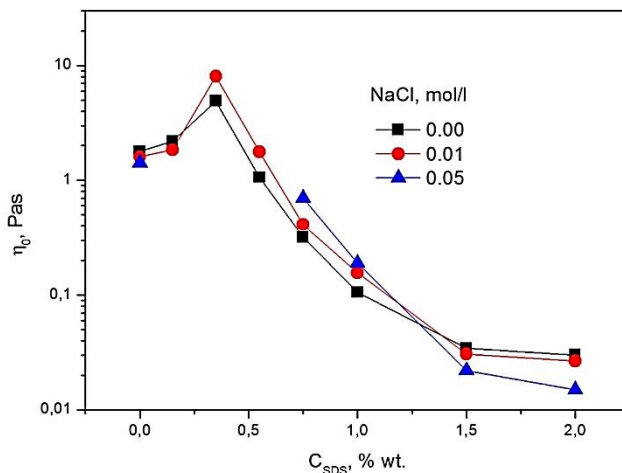


Figure 1. Influence of SDS concentration on the zero shear viscosity of the HPMC/SDS mixtures of different ionic strength

It can be seen that the increase in C_{SDS} increased the viscosity of the 0.00M NaCl HPMC/SDS mixture, to reach a maximum at $C_{SDS}=0.35$ % wt. The increase in the viscosity is due to the formation of the HPMC–SDS complex, which takes place when C_{SDS} is higher than the critical association concentration $CAC=0.15$ % wt. The complex formation takes place via hydrophobic interactions, where SDS molecules bind to the HPMC chains. SDS forms micelles around the hydrophobic moieties of the neighboring HPMC chains, which strengthens the network of entangled HPMC chains and results in an increase in viscosity (12, 13). Further increase in C_{SDS} brings about a decrease in the viscosity of the HPMC/SDS mixture. The binding of SDS causes an increase in the negative net charge of HPMC chains and thus electrostatic repulsion between neighboring HPMC chains takes place, which results in gradual disentanglement of chains, network looseness, and consequently, in a drop in the viscosity of the mixtures (14). The changes in the viscosity of the HPMC/SDS mixtures take place no more, and a constant value is reached at the C_{SDS} of 1.50 % wt. This indicates that the HPMC–SDS interaction is finished, and that C_{SDS} reached the polymer saturation point (*PSP*). At the *PSP*, all hydrophobic moieties of the HPMC chains are fully solubilized with SDS micelles, the intermolecular links between the neighboring HPMC chains are broken, and the 3D network structure is completely lost (8, 9).

The same trends in the change of the zero shear viscosity as a function of C_{SDS} are observed when the ionic strength of the HPMC/SDS mixtures is increased, indicating the same HPMC–SDS interaction mechanism. However, at increased ionic strength, the viscosity in the interaction region is higher when compared to the zero ionic strength mixture, Figure 1. This is especially true for the 0.05 % wt. NaCl mixtures (data not shown), where for the C_{SDS} ranging from 0.15 to 0.55 % wt., the viscosity was so high that it was not possible to prepare homogeneous samples for rheological measurements. The increased viscosity comes from the pronounced charge screening effect of Na^+ ions, which enables formation of SDS micelles with higher aggregation number around the hydrophobic moieties of HPMC chains (1, 15). This strengthens the network and results in an increase in the viscosity. At $C_{SDS}>PSP$, an increase in the ionic strength of the HPMC/SDS mixtures leads to a decrease in the viscosity. Namely, the charge screening makes HPMC chains solubilized by SDS effectively less charged, which makes them smaller, and this consequently brings about a decrease in the viscosity of the mixtures.

Influence of shear rate on the viscosity of HPMC/SDS mixtures of different ionic strength

The viscosity curves of the HPMC/SDS mixtures having different concentration of SDS and 0.00M NaCl ionic strength are shown in Figure 2. The mixtures with $C_{SDS} < 0.35$ % wt. and >1.50 % wt. show a typical shear thinning flow behavior, where viscosity decreases on the increase in the shear rate. However, when $C_{SDS}=0.55–1.00$ % wt. shear thinning is observed only at lower shear rates. When a critical shear rate is reached, the viscosity of the mixtures sharply increases, flow profile changes from shear thinning to shear thickening, indicating a shear–induced structure formation (16).

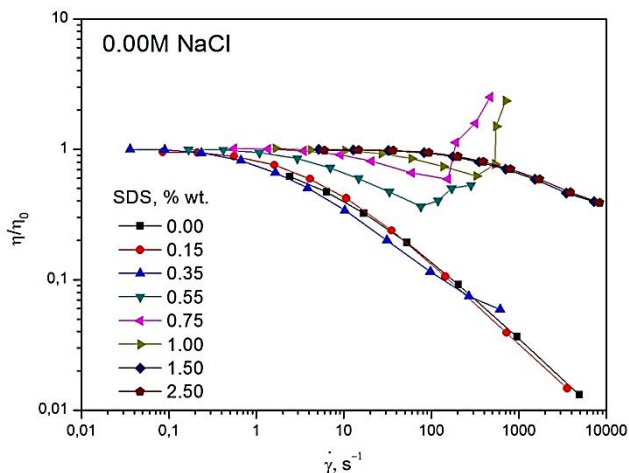


Figure 2. Viscosity curves of the HPMC/SDS mixtures containing 0.7 % wt. HPMC, 0–2.50 % wt. SDS, and 0.00M NaCl

The shear thickening flow is also observed when ionic strength of HPMC/SDS mixtures is increased, Figure 3 and Figure 4, where the shear thickening region extends to higher SDS concentrations. In the 0.01M NaCl mixtures the shear thickening flow is observed up to $C_{SDS}=1.50$ % wt., while in the 0.05% wt. NaCl mixtures the shear thickening flow is observed up to $C_{SDS}=2.00$ % wt., indicating that an increase in ionic strength of HPMC/SDS mixtures supports the shear-induced structure formation.

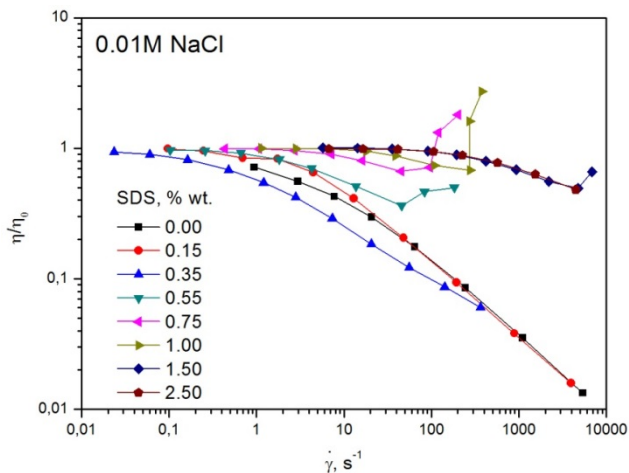


Figure 3. Viscosity curves of HPMC/SDS mixtures containing 0.7 % wt. HPMC, 0–2.50 % wt. SDS, and 0.01M NaCl

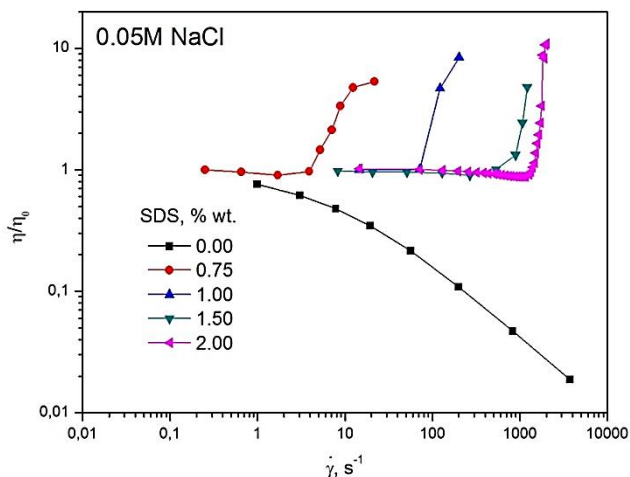


Figure 4. Viscosity curves of HPMC/SDS mixtures containing 0.7 % wt. HPMC, 0–2.50 % wt. SDS, and 0.05M NaCl.

The influence of the SDS concentration on the critical shear rate, i.e. the shear rate where the onset of shear thickening takes place, for the HPMC/SDS mixtures of different ionic strength is shown in Figure 5.

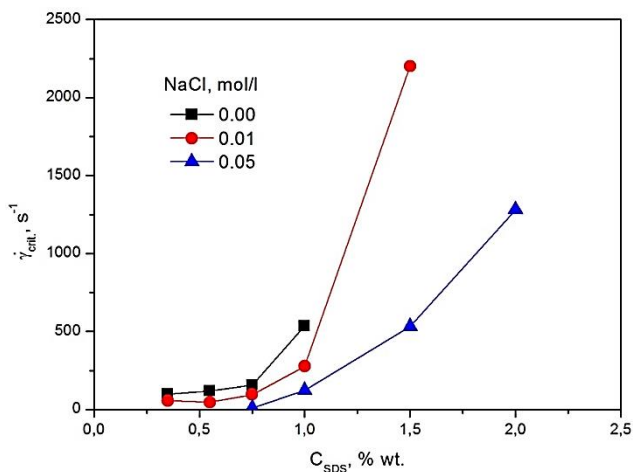


Figure 5. Influence of the SDS concentration on the critical shear rate for the HPMC/SDS mixtures of different ionic strength

It can be seen that the critical shear rate increases when the C_{SDS} of the HPMC/SDS mixture is increased, regardless of the ionic strength of the mixtures. This indicates that for a more solubilized HPMC–SDS complex a larger shear is needed to bring about conformational changes of the HPMC chains. The conformational changes make the new

hydrophobic moieties available for the establishment of the intermolecular link supported by SDS binding, and eventually lead to an increase in viscosity. On increasing the ionic strength of the HPMC/SDS mixtures the critical shear rate decreases. This is attributed to the charge of the screening effect of Na^+ ions, which makes the HPMC–SDS complex effectively less charged and thus more flexible and prone to conformational changes under the effect of shear, as opposed to highly charged polyanions having a rigid, rod-like conformation.

CONCLUSION

Interaction in the HPMC/SDS mixtures takes place when C_{SDS} is higher than the critical association concentration $\text{CAC}=0.15$ % wt. and ends at the polymer saturation point $\text{PSP}=1.50$ % wt. The increase in the ionic strength of the HPMC/SDS mixtures influence the interaction, as evidenced by an increase in the viscosity of the mixtures in the interaction region ($\text{CAC}<C_{\text{SDS}}<\text{PSP}$), and a decrease in viscosity for $C_{\text{SDS}}>\text{PSP}$. The HPMC/SDS mixtures show a shear thinning or shear thickening flow behavior, depending on C_{SDS} and ionic strength of the mixtures, indicating that a product design having desirable rheological properties can be achieved by careful tuning of polymer–surfactant interactions.

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grant No. III46010. It was done within COST MP1106 and CM1101 action framework.

REFERENCES

1. Lindman, B. Surfactant–Polymer Systems. In *Handbook of Applied Surface and Colloid Chemistry*; Holmberg, K., Ed.; John Wiley & Sons Ltd.: West Sussex, 2002; pp 445-463.
2. Antunes, F.E.; Marques, E.F.; Miguel, M.G.; Lindman, B. Polymer–vesicle association. *Adv. Colloid Interface Sci.* **2009**, *147-148*, 18-35.
3. Taylor, D.J.F.; Thomas, R.K.; Penfold, J. Polymer/surfactant interactions at the air/water interface. *Adv. Colloid Interface Sci.* **2007**, *132*, 69-110.
4. Camino, N. A.; Perez, O. E.; Sanchez, C. C.; Patino, J. M. R.; Pilosof, A. M. R. Hydroxypropylmethylcellulose surface activity at equilibrium and adsorption dynamics at the air–water and oil–water interfaces. *Food Hydrocolloids* **2009**, *23*, 2359-2368.
5. Futamura, T.; Kawaguchi, M. Characterization of paraffin oil emulsions stabilized by hydroxypropyl methylcellulose. *J. Colloid Interface Sci.* **2012**, *367*, 55-60.
6. Winnik, F. M.; Regismont, S. T. A. Fluorescence methods in the study of the interactions of surfactants with polymers. *Colloids Surf., A* **1996**, *118*, 1-39.
7. Nilsson, S. Interactions between Water-Soluble Cellulose Derivatives and Surfactants. 1. The HPMC/SDS/Water System. *Macromolecules* **1995**, *28*, 7837-7844.

8. Katona, J.; Sovilj, V.; Petrović, L. Rheological investigation on dynamic and structure of separated phases in polymer mixture–ionic surfactant ternary system. *Carbohydr. Polym.* **2008**, *74*, 193-200.
9. Picullel, L.; Egermayer, M.; Sjostrom, J. Rheology of Mixed Solutions of an Associating Polymer with a Surfactant. Why Are Different Surfactants Different? *Langmuir* **2003**, *19*, 3643-3649.
10. Tirrel, M. Fundamentals in Polymer Solutions. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, D. E.; Ananthapadmanabhan, K.P., Eds.; CRC Press: Florida, 1993; pp 203-269.
11. Schramm, G. A. *Practical Approach to Rheology and Rheometry*; Gebrueder HAAKE GmbH: Karlsruhe, 2000; pp 36-64.
12. Su, J.C.; Liu, S.Q.; Joshi, S.C.; Lam, Y.C. Effect of SDS on the gelation of hydroxypropylmethylcellulose hydrogels. *J. Therm. Anal. Calorim.* **2008**, *93*, 495-501.
13. Nilsson, S.; Thuresson, K.; Hansson, P.; Lindman, B. Mixed Solutions of Surfactant and Hydrophobically Modified Polymer. Controlling Viscosity with Micellar Size. *J. Phys. Chem. B* **1998**, *102*, 7099-7105.
14. Silva, S.M.C.; Antunes, F.E.; Sousab, J.J.S.; Valentea, A.J.M.; Pais, A.A.C.C. New insights on the interaction between hydroxypropylmethyl cellulose and sodium dodecyl sulfate. *Carbohydr. Polym.* **2011**, *86*, 35-44.
15. Nystrom, B.; Kjoniksen, A.-L.; Lindman, B. Effect of temperature, surfactant, and salt on the rheological behavior in semidilute aqueous systems of a nonionic cellulose ether. *Langmuir* **1996**, *12*, 3233-3240.
16. Clasen, C.; Kulicke, W. M. Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives. *Prog. Polym. Sci.* **2001**, *26*, 1839-1919.

УТИЦАЈ ЈОНСКЕ ЈАЧИНЕ НА РЕОЛОШКЕ ОСОБИНЕ СМЕША ХИДРОКСИПРОПИЛМЕТИЛ ЦЕЛУЛОЗЕ И НАТРИЈУМ ДОДЕЦИЛСУЛФАТА

*Јарослав М. Катона, Алена Томишиќ, Сандра Ђ. Бучко, Лидија Б. Петровић,
Јадранка Л. Фрај*

Универзитет у Новом Саду, Технолошки факултет, Булевар цара Лазара 1, 21000 Нови Сад, Србија

Производи фармацеутске, козметичке, прехранбене и хемијске индустрије врло често у свом саставу садрже смеше полимера и сурфактаната. Интеракција између полимера и сурфактаната утиче на низ особина тих производа као што су нпр. стабилност, реолошке особине, сепарација фаза и сл. Познато је да до интеракције између хидроксипропилметил целулозе (ХПМЦ) и натријум додецилсулфата (СДС) долази када је концентрација СДС $C_{СДС}$ већа од критичне концентрације асоцијације (ЦАЦ) а мања од концентрације засићења полимера (ПСП). Као последица дате интеракције долази до формирања ХПМЦ–СДС комплекса. Циљ овог рада је испитивање утицаја јонске јачине на формирање ХПМЦ–СДС комплекса путем рео-

лошких мерења. У том циљу, припремљене су ХПМЦ/СДС смеше које су садржале 0,70 % м/м ХПМЦ, 0,00 % м/м до 2,50 % м/м СДС у дејонизованој води, и 0,01М и 0,05М растворима NaCl. Добијени резултати указују да вискозитет при нултој брзини смицања смеша ХПМЦ/СДС расте са повећањем јонске јачине у опсегу ХПМЦ–СДС интеракције ($\zeta_{\text{АПЦ}} < \zeta_{\text{СДС}} < \text{ПСП}$), док опада за $\zeta_{\text{СДС}} > \text{ПСП}$. ХПМЦ/СДС смеше показују псеудопластично или дилатантно протицање у зависности од $\zeta_{\text{СДС}}$. Јонска јачина такође утиче на реолошке особине смеша.

Кључне речи: полимер–сурфактант интеракција, нејонски етри целулозе, хидроксипропилметил целулоза, јонска јачина

Received: 22 May 2015.

Accepted: 15 July 2015.