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Rheological investigation on dynamic and structure of separated phases in polymer mixture–ionic surfactant ternary system

Jaroslav M. Katona *, Verica J. Sovilj, Lidija B. Petrović

Department of Applied and Engineering Chemistry, Faculty of Technology, Bul. cara Lazara 1, 21000 Novi Sad, Serbia

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Abstract

Ternary systems composed of 0.30% sodium carboxymethyl cellulose (NaCMC), 0.70% hydroxypropylmethyl cellulose (HPMC), and sodium dodecylsulfate (SDS) of various concentrations (0.00–2.00%), were investigated by oscillatory and flow shear rheometry. The investigation on binary mixtures of HPMC/SDS (0.7% HPMC, 0.00–2.00% SDS) and HPMC/NaCMC (1.00% polymer mixtures with HPMC/NaCMC mass ratio ranging from 1/0 to 0/1) was also carried out. In the examined systems, various interactions between HPMC–NaCMC, HPMC–SDS and NaCMC–(HPMC–SDS) take place. The interactions may bring about phase separation in the ternary system into HPMC–SDS complex rich phase (coacervate), and NaCMC rich phase (supernatant). The possibility of employing the interactions in the ternary system to vary structural properties of the coacervate, in terms of viscoelasticity and shear rate influence, was investigated. Rheological properties of the ternary system, as well as of the separated coacervate and the supernatant were tested. Influence of shear rate on the interactions taking place in both the binary and the ternary mixtures was examined. It was found that the applied shear rate can influence the interactions. Molecular mechanisms determining the rheological properties of the coacervate were suggested. It was found that complex intermolecular interactions in the ternary system can be employed to attain control over the structural properties of the coacervate phase.

Keywords: Phase separation; Coacervation; Polymer–surfactant interaction; Rheology; Microstructure

1. Introduction

A macromolecule can remain in equilibrium with its solvent in three physically distinct states i.e. solution, gel and coacervate (Mohanty & Bohidar, 2005). To reach the latter state, a phase separation in a macromolecular system is to be involved. Simple coacervation is referred to phase separation brought about by reducing a macromolecule's solubility (Baken & Anderson, 1976; Weib, Knoch, Laicher, Stanislaus, & Daniels, 1995). Typically, simple coacervation is induced by the change in temperature, addition of inorganic salts or non-solvent addition. On the other hand, when phase separation is caused by addition of another macromolecule either complex coacervation (de Kruiff, Weinbreck, & de Vries, 2004; Turgeon, Beaulieu, Schmitt, & Sanchez, 2003) or thermodynamic incompatibility (Tolstoguzov, 2003; Norton & Frith, 2001) take place. During complex coacervation an (in)soluble complex of two associative macromolecules (e.g. polycation and polyanion) is formed (Ball et al., 2002; Girard, Turgeon, & Gauthier, 2003). The coacervate phase predominantly consists of the complex formed, while the equilibrium solution is more or less pure solvent. Thermodynamic incompatibility takes place if two macromolecules are mixed under repulsive conditions, and has been related to the classical Flory–Huggins's theory or to the depletion interaction theories, depending on the characteristics of the two macromolecules (Doublier, Garnier, Renard, & Sanchez, 2000; Tuinier, ten Grotenhuis, Holt, Timmins, & de Kruif, 1999). Both of the two phases formed are rich in just one of the two macromolecules involved.

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* Corresponding author. Tel.: +381 21 4853683; fax: +381 21 450413.
E-mail address: jkatona@uns.ns.ac.yu (J.M. Katona).

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Phase separation is involved in a number of practical situations. Coacervation is of special interest to the food and cosmetics industries, where macromolecules are found in the coacervate state in a wide range of products, and thereby define the properties of a product i.e. texture, taste, stability etc. (Tolstoguzov, 2003). In recent years, interest in complex coacervation taking place in biological systems has increased considerably (de Kruiff et al., 2004). In addition, due to a number of advances over conventional separation techniques, the aqueous two-phase systems are being successfully used for separation of various biomolecules, as well as for separation of different products of biotechnological processes (Antov, 2006). On the other hand, one of the earliest and the most important applications of phase separation is in microencapsulation technology (Baken & Anderson, 1976). By inducing phase separation and depositing a formed coacervate phase on a dispersed particles' surface (e.g. surface of emulsified oil droplets) microencapsulation is achieved. Not only is the encapsulated substance protected from the physico-chemical effects of the surrounding medium (e.g. oxidation processes), but, by devising desirable microstructural properties of the encapsulating layer, a control over diffusion kinetic of an encapsulated substance through the layer can be attained.

Water-soluble nonionic derivatives of cellulose, such as hydroxypropylmethyl cellulose (HPMC) are physiologically harmless and suitable for use in food, cosmetic and pharmaceutical formulations (Zhang, 2001). Presence of hydroxypropyl and methyl groups in HPMC renders cellulose molecule hydrophobic and makes them surface active (Kulicke, Arendt, & Berger, 1998a). These groups represent potential adsorption sites for surfactant molecules which may lead to various inter/intra molecule interactions (Piculell, Guillemet, Thuresson, Shubin, & Ericsson, 1996; Kulicke, Arendt, & Berger, 1998b; Winnik & Regismond, 1996). It has been shown that HPMC forms complexes with sodium dodecylsulfate (SDS) through hydrophobic interactions, where, depending on the mass ratio of HPMC and SDS, the onset and the end of the interaction region can be identified (Sovilj & Petrović, 2005; Sovilj & Petrović, 2006). The interaction starts when the SDS concentration in the system reaches the critical aggregation concentration (CAC). At CAC an increase in viscosity of the binary mixture appears when compared to the pure HPMC solution. CAC is independent of HPMC concentration and is found to be lower than the critical micelle concentration (CMC) of SDS, indicating that the surfactant-polymer complex formation is energetically more favorable than the formation of SDS micelles. On increasing SDS concentration above CAC the interaction reaches a maximum at a certain concentration (CM). The interaction stops at concentration of the polymer saturation point (PSP). HPMC molecules are solubilized by SDS, which is indicated by a decreased viscosity of the binary mixture when compared to the viscosity of the pure HPMC solution. Further addition of SDS causes contraction of solubilized HPMC molecules and an additional, slight decrease in viscosity. Both CM and PSP depend on the HPMC content (Sovilj & Petrović, 2005; Šaletić, Sovilj, & Petrović, 2004). On the other hand, addition of sodium carboxymethyl cellulose (NaCMC) to the HPMC/SDS system may result in phase separation (Sovilj & Petrović, 2007). Namely, the formed HPMC/SDS complex behaves as a polyelectrolyte and bears a negative net charge which causes an electrostatic repulsion with NaCMC molecules. This leads to phase separation of the two incompatible polymers type. The ternary system separates in HPMC/SDS complex rich coacervate phase and NaCMC rich equilibrium solution (supernatant).

The main goal of the present paper was to investigate the possibility of obtaining coacervate phase of desirable and controlled structural properties, by employing complex intermolecular interactions in HPMC/SDS/NaCMC ternary system. Mass ratios of the components in the ternary system were varied and microstructural properties of thus obtained separated phases were examined by carrying out detailed rheological study. The results obtained were related to HPMC/SDS and NaCMC/HPMC interactions in the ternary system.

2. Experimental

2.1. Materials

HPMC, (trade name Methocel K4M CR, methoxyl content 22.7%, hydroxypropyl content 8.9%) was obtained from Colorcon Ltd., England. Viscosity average molecular mass (M_v) was $M_v = 91{,}500$ g/mol, determined at 20 °C, while the critical overlap concentration (c^*) of HPMC was $c^* = 0.1269\%$. As reported by the manufacturer, HPMC contained less than 0.1% of the residual salts, expressed on the dry matter. NaCMC, the degree of substitution (DS) DS = 0.77, purity >96%, was obtained from "Milan Blagojević", Serbia. Viscosity average molecular mass of NaCMC was $M_v = 121{,}000$ g/mol, determined at 25 °C, and the critical overlap concentration $c^* = 0.1927\%$. As reported by the manufacturer, NaCMC contained less than 1.5% of the residual salts, expressed on the dry matter. Details on HPMC and NaCMC samples characterization by viscosimetry can be found elsewhere (Alvarez-Lorenco et al., 2001). SDS, purity >99%, was obtained from Merck, Germany. The critical micelle concentration (cmc) was cmc = 0.244% at 20 °C, as determined by conductometric titration. According to the manufacturer, SDS contained no residual salts. All samples were used without any further purification.

2.2. Preparation of solutions

Stock solutions of 2.00% (w/w) HPMC and 1.00% (w/w) NaCMC were prepared by dispersing proper amount of HPMC and NaCMC in water at 80 °C (above the gel point of HPMC, which is approximately 70 °C for a 2% aqueous solution) and 20 °C, respectively, by gentle stirring. The stock solutions were left for 24 h at room temperature before further use. Stock solution of 7% (m/v) SDS was prepared by dispersing the required amount of SDS in bidistilled water at 20 °C.

The single component solutions of HPMC and NaCMC were prepared by suitable dilution of the stock solutions. The binary mixtures of HPMC/NaCMC were prepared by mixing the required amounts of HPMC and NaCMC stock solutions to obtain a total polymer concentration of 1% and desired HPMC/NaCMC mass ratio (from 1/0 to 0/1). HPMC stock solution and diluted stock solutions of SDS were mixed together to obtain HPMC/SDS mixture containing 0.7% of HPMC and desired SDS concentration in the range from 0.00% to 2.00%. The ternary mixtures of HPMC/NaCMC/SDS were prepared by adding appropriately diluted stock solution of SDS to 24 h old HPMC/NaCMC binary mixture to obtain the three-component system containing 0.7% HPMC, 0.3% NaCMC and desired SDS concentration (from 0.00% to 2.00%). All ternary mixtures were left for 24 h at room temperature prior further use. Concentration of the residual salts in the ternary systems was small (less than 0.0052%), and was assumed not to have a considerable influence on interactions in the system. Even if there was some effect of the residual salts, it was always the same. Namely, concentration of the residual salts in the system was constant due to constant concentration of HPMC and NaCMC. Therefore, a plausible effect of the residual salts on the investigated system was not specifically considered.

2.3. Phase separation

Phase separation in the ternary system consisting of 0.7% HPMC, 0.3% NaCMC and different SDS concentrations was visually followed in 10 ml measuring cylinders. Relative volume, 100 h/H, occupied by the coacervate in the ternary mixtures of various SDS concentrations was calculated, where h stands for volume of the coacervate and H for the volume of the whole ternary system in the measuring cylinder.

2.4. Rheometry

Rheological measurements were carried out by means of RS600 (Thermo Electron (Karlsruhe), GmbH, Germany) rheometer at 20 °C. The cone-and-plate geometry was used ($d = 60$ mm, $\theta = 1°$).

The steady-state and the continuous hysteresis loop methods were employed (Sovilj & Dokić, 1996) to obtain viscosity curves. The viscosity curves of HPMC and NaCMC solutions, the HPMC/SDS and HPMC/NaCMC binary mixtures, and the supernatant were found to be of shear thinning type and no time effects were observed (the upflow and downflow curves overlap). The obtained experimental data were fitted to Ostwald de Waele Eq. (1) to obtain the apparent viscosity (η_a) at a given shear rate ($\dot{\gamma}$). The K stands for the consistency constant, and n for the degree of pseudoplasticity.

$$\eta_a = K\dot{\gamma}^{n-1} \tag{1}$$

When examining the ternary HPMC/NaCMC/SDS systems the antithixotropy with complex time evolution was observed. The obtained viscosity curves are used for qualitative explanations.

Synergistic viscosity effects in binary HPMC/NaCMC mixtures were expressed as the relative positive deviation (RPD), defined as follows, Eq. (2):

$$\mathrm{RPD} = 1 - \frac{\eta_{a,\mathrm{HPMC+NaCMC}}}{\eta_{a,\mathrm{HPMC/NaCMC}}} \tag{2}$$

where $\eta_{a,\mathrm{HPMC+NaCMC}}$ is a sum of the apparent viscosities of single component solutions of HPMC and NaCMC of given concentrations, where the sum of HPMC and NaCMC concentrations is always 1%; $\eta_{a,\mathrm{HPMC/NaCMC}}$ is the apparent viscosity of 1% binary HPMC/NaCMC mixture of the same concentrations of HPMC and NaCMC as used for $\eta_{a,\mathrm{HPMC+NaCMC}}$.

The oscillatory measurements were carried out to investigate visco-elastic properties of binary HPMC/SDS mixtures, as well as of the separated coacervate phase in ternary HPMC/NaCMC/SDS systems. The amplitude sweep method was used. The oscillating frequency was 1 Hz. Plateau values of elastic, G', and viscous modulus, G'', were determined from the linear visco-elastic region with the confidence band of 95%. Relative contribution of the viscous to the elastic component of the investigated systems was evaluated by means of the tanδ value, Eq. (3):

$$\tan\delta = \frac{G''}{G'} \tag{3}$$

3. Results and discussion

3.1. Binary mixtures of HPMC/SDS and HPMC/NaCMC

Influence of SDS concentration on viscoelastic properties of 0.7% HPMC solution was investigated (Fig. 1). In the solution containing no SDS, the elastic modulus, G', is detected. It indicates existence of weak 3D network structure in the system (Tirrel, 1993). The network is established as a result of weak self-association of the hydrophobe-modified polymer molecules by crosslinking via hydrophobic HPMC substituents (Lindman et al. 1993). With addition of SDS to the system, the characteristic dependence of G' on SDS concentration is observed and CAC, CM and PSP can be identified (Fig. 1). At SDS concentration of 0.15% (CAC) and higher, molecules of the surfactant form micellar aggregates around the substituents of the adjacent hydrophobe modified polymer chains and thus support the 3D network formation (Lindman et al., 1993). This is evidenced by the increase in G' of the system when compared to the pure HPMC solution. The maximum of G' value is observed at CM = 0.35%. It indi-

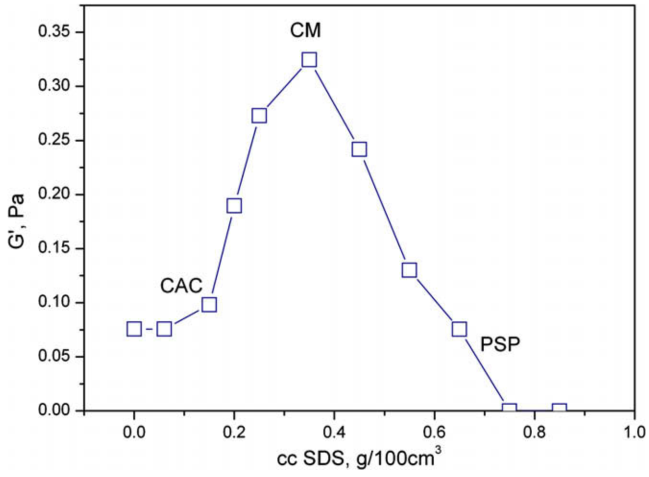

Fig. 1. Elastic modulus (G') of 0.7% HPMC solution as a function of SDS concentration (cc SDS).

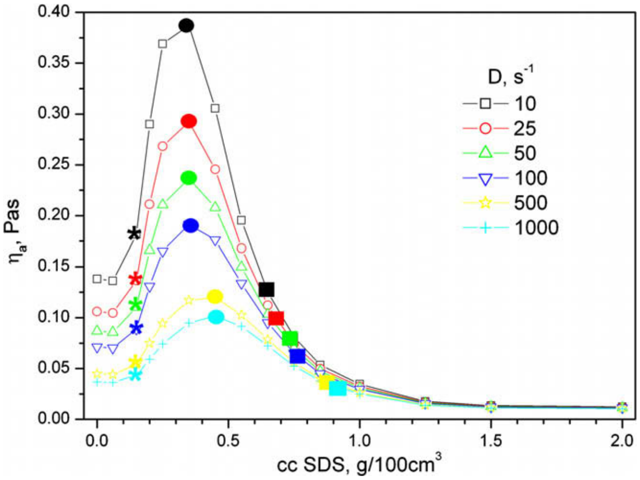

Fig. 2. Dependence of the apparent viscosity (η_a) of 0,7% HPMC solution on SDS concentration (cc SDS) at different shear rates. CAC, CM, and PSP are denoted as suitably colored stars and filled circles and rectangles, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cates the maximum of HPMC/SDS interaction. Further addition of SDS causes the decrease in G'. Namely, the more SDS in the system, the more SDS is bound to HPMC substituents, which increases negative charge of HPMC/SDS complex. Above CM the electrostatic effects start to predominate over the hydrophobic ones, leading to conformational changes of HPMC molecules and net repulsion of charged HPMC/SDS complexes (Sovilj & Petrović, 2006). This causes gradual breakup of the 3D structure and the decrease in G'. At SDS concentration higher than 0.65% (PSP), G' of the binary HPMC/SDS system is lower than G' of the pure HPMC solution. At this stage, individual HPMC molecules are solubilized by SDS. With further addition of SDS, G' is not detectable anymore, which indicates that the network structure is completely broken, and that all HPMC molecules are fully solubilized by SDS. Thus formed HPMC/NaCMC complex is an individual microstructural element and no intercomplex links exist.

Influence of SDS concentration on microstructural and dynamic properties of HPMC/SDS complex has been investigated. Dependence of apparent viscosity of 0.7% HPMC solution on SDS concentration, at different shear rates applied, is shown in Fig. 2. The obtained curves clearly indicate the characteristic concentrations of the interaction region i.e. CAC, CM and PSP. At CAC an increase in the viscosity of HPMC/SDS binary mixture appears when compared to the pure HPMC solution. CAC was found to be shear rate independent. Namely, an increase in the apparent viscosity at 0.15% SDS concentration is observed at all shear rates applied. This suggests the presence of SDS supported hydrophobic bounds among substituents of the adjacent HPMC chains even at shear rates as high as 1000 s^{-1}, though in a less extent. On the other hand, it has been observed that CM slightly increases, from 0.35% to 0.45%, with the increase in shear rate. In the vicinity of CM, the changes of η_a with change in SDS concentration are also less steep when higher shear rates are applied (Fig. 2). This implies that at higher shear rates the conformation of the complex is primarily determined by the applied shear rate and in less extent by SDS concentration. Therefore, it is assumed that the application of the shear rate leads to extension of HPMC chains in the HPMC/SDS complex which enables more SDS molecules to be bound to HPMC prior to the electrostatic repulsion starts to dominate hydrophobic interactions in the complex. As a consequence, a positive shift in CM occurs when the shear field is applied. In a similar way, PSP increases from 0.65% to 0.85% with increasing the applied shear rate. Namely, as shown in Fig. 2, the first SDS concentration at which η_a of the binary system is lower than one of the pure HPMC solution gradually shifts to higher values when the shear rate is increased. This is in agreement with the above explanations. Above 1.25% of SDS there is no influence of shear rate on η_a, and a conformation of HPMC/SDS complex is shear rate independent. The characteristic CAC, CM and PSP concentrations obtained from the oscillatory measurements are in agreement with their low shear rate η_a counterparts.

In Fig. 3 RPD in 1% HPMC/NaCMC blends of various polymer mass ratios is presented. It is shown that the maximum in synergy is observed in blends consisting of 0.4% of HPMC and 0.6% of NaCMC, no matter what the applied shear rate. Namely, mixture of ionic and nonionic cellulose ethers in solutions are known to show synergistic viscosity effects (Walker & Wells, 1982; Zhang, 1999). The synergy is determined by molecular mass and the substitution characteristics of polymers. In general, maximum synergism is observed at a mass ratio of the polymers which provides same number of interacting groups. Detailed interaction mechanism between HPMC and NaCMC is given elsewhere (Alvarez-Lorenco et al., 2001).

Though we found maximum of the synergy to appear when HPMC/NaCMC ratio is 0.4/0.6, in this work we investigate systems where the ratio is 0.7/0.3. Namely, by

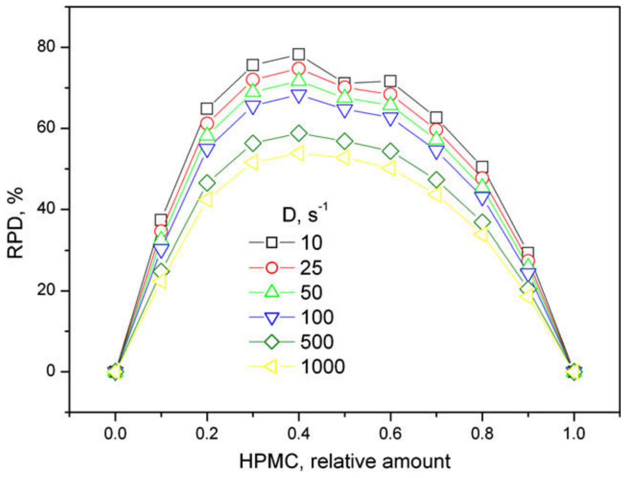

Fig. 3. Synergistic effect of HPMC/NaCMC blends. Relative positive deviation (RPD) in 1% polymers solution as a function of relative amount of HPMC in the blend. Influence of shear rate.

increasing HPMC content larger amounts of the coacervate in ternary HPMC/NaCMC/SDS system are obtained (Sovilj & Petrović, 2007).

3.2. Ternary mixture of HPMC/NaCMC/SDS

It was recently shown that a ternary mixture of HPMC/NaCMC/SDS phase separate when the SDS concentration is higher than CAC (Sovilj & Petrović, 2007).

Visco-elastic properties of the separated coacervate phase as a function of SDS concentration in the ternary HPMC/NaCMC/SDS system are investigated (Fig. 4). The shape of the obtained curve strongly resembles the one shown in Fig. 1, indicating that viscoelastic properties of the coacervate phase are largely influenced by HPMC/SDS interaction. It can be seen (Fig. 4) that G' reaches maximum value at 0.25% SDS. tanδ value is smaller than 1 at this concentration of SDS only, and the elastic properties dominate the viscous ones. The coacervate phase is compact and HPMC/SDS complex forms a firm 3D network throughout the separated phase. Further increase in SDS concentration brings about the decrease in G' and the increase in tanδ values. Namely, more SDS is bound to HPMC chains and an increase in charge of HPMC/SDS complex takes place. As a consequence, electrostatic repulsion among HPMC/SDS complexes occurs. The intercomplex links are gradually being broken and the separated phase looses the space-spanning network properties. Finally, at 1.25% SDS, no phase separation is observed. HPMC is fully solubilized and the HPMC/SDS complex bears enough charge to become completely soluble even in the presence of NaCMC.

Dependence of the relative volume occupied by the coacervate phase on SDS concentration in the ternary system is shown in Fig. 5. The coacervate phase occupies larger volumes at higher SDS concentrations due to increased hydrophilic properties of the HPMC/SDS complex (Sovilj & Petrović, 2007). At the same time, this implies that the effective concentration of the HPMC/SDS complex in the coacervate phase decreases with an increase in SDS content. Therefore, it is to be expected that the visco-elastic properties of the coacervate shown in Fig. 4, are determined not only by microstructural properties of HPMC/SDS complex, but also by the effective concentration of HPMC/SDS complex in the separated phase. The smaller the coacervate volume, the higher the concentration and larger values of G' are to be expected. The smallest volumes of the coacervate phase are observed at the onset of phase separation i.e. at 0.15% and 0.20% of SDS in the ternary system. However, the largest value of G' is observed at 0.25% SDS (Fig. 4). The reason for this may be twofold. Firstly, at the onset of the coacervation there is not enough SDS to support the hydrophobic intercomplex links and

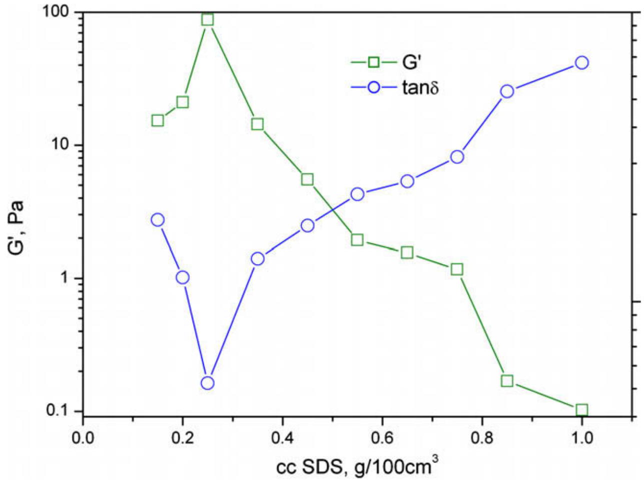

Fig. 4. Visco-elastic properties (G' and tanδ) of the coacervate phase as a function of SDS concentration (cc SDS) in the ternary HPMC/NaCMC/SDS system. Concentration of HPMC and NaCMC in the system is 0.7% and 0.3%, respectively.

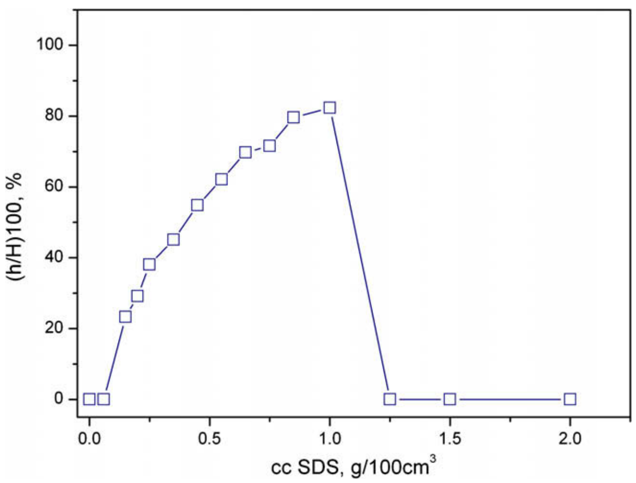

Fig. 5. Volume share, (h/H)100, of the coacervate phase in the ternary HPMC/NaCMC/SDS system as a function of SDS concentration, cc SDS. 1% polymer mixture where HPMC/NaCMC = 0.7/0.3.

form as firm network as with 0.25% of SDS. Secondly, not all of HPMC molecules of the ternary mixture are found in the coacervate but some of them remain in the supernatant. This makes the coacervate volume small but not necessarily compact. The second option is possible when not all HPMC molecules form the complex with SDS to be repulsed with NaCMC. We examine this possibility in more details. In the ternary system having 0.7% HPMC and 0.3% of NaCMC not all of HPMC molecules are actually able to interact with NaCMC. Namely, the synergism is decreased due to the lack of available NaCMC molecules to interact with the surplus of HPMC (Fig. 3). Therefore, it is to be expected that the free HPMC molecules and those interacting with NaCMC interact in a different manner with the added SDS. On the other hand, if one portion of HPMC indeed remains in the supernatant, then some synergistic HPMC–NaCMC viscosity effects are to be present, and an increase in the supernatant viscosity is to be observed. Viscosity curves of the supernatant obtained for different SDS concentrations in the ternary system are shown in Fig 6. Here, the supernatant volume decreases with an increase in the SDS concentration (Fig. 5), and an increase in viscosity is to be expected due to increased NaCMC concentration. Indeed, this is the case at all SDS concentrations apart from 0.15%. The viscosity of the supernatant of the 0.15% SDS is considerably higher than of the next few following SDS concentrations. This again implies the presence of some synergistic HPMC–NaCMC viscosity effects in the supernatant of 0.15% of SDS in the ternary mixtures. However, as suggested by the viscosity curves, at higher SDS concentrations all HPMC–NaCMC links are broken and no HPMC is expected to be present in the supernatant.

As indicated by the viscosity curves of the supernatant, when compared to the viscosity curves of the single component NaCMC solutions, NaCMC concentration in the supernatant is estimated to be in the range of 0.3% to 0.8% w/w, depending on SDS concentration in the ternary mixture.

The exact determination of the concentration of individual components in separated phases of the ternary system was out of the scope of this work.

3.3. Dynamic behavior of the ternary system

The rheological properties of the ternary system were tested. When present, the coacervate phases were gently redispersed and a set of rheological measurements on the ternary systems was carried out.

The viscosity curve of the ternary mixture containing 0.7% HPMC, 0.3% NaCMC and 0.06% SDS is compared to the viscosity curves of corresponding binary mixtures and single component solutions (Fig. 7). Addition of SDS to the HPMC/NaCMC mixture, even below CAC (0.15%) and before onset of macroscopically observable phase separation, decreases the synergistic effects between HPMC and NaCMC, as indicated by the decrease in viscosity. Evidently, some of links between HPMC and NaCMC chains are broken, which is evidenced by the decrease in viscosity of the ternary mixture when compared to the binary HPMC/NaCMC mixture. It seems that presence of NaCMC decreases CAC of SDS and that already at 0.06% SDS binds to HPMC molecules to form the complex incompatible with NaCMC. However, the viscosity of the ternary mixture is still considerably higher than the one of corresponding binary mixture consisting of 0.7% HPMC and 0.06% SDS, showing that most of HPMC–NaCMC links are still present. The viscosity curve of the ternary mixture is of shear thinning type and no time effects are observed.

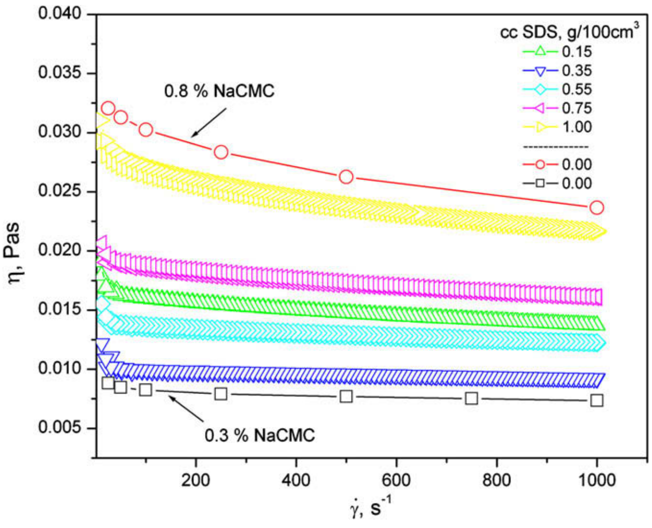

Fig. 6. Viscosity curves of supernatant in ternary HPMC/NaCMC/SDS system having 0.7% of HPMC, 0.3% NaCMC and different amounts of SDS in the system. Viscosity curves of 0.3% and 0.8% solutions of NaCMC are also shown.

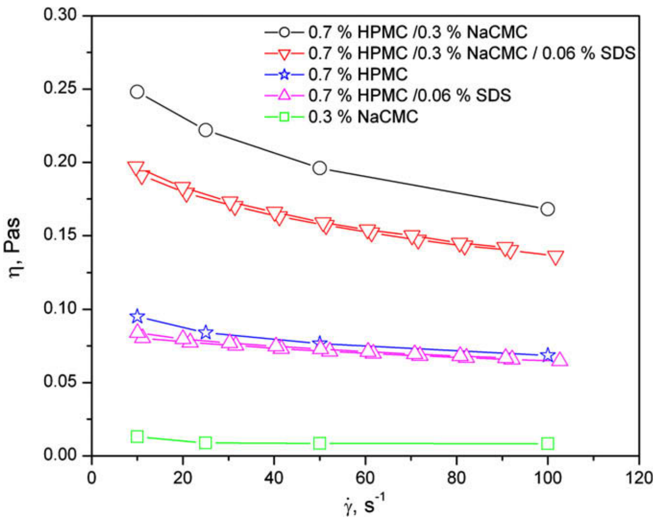

Fig. 7. Viscosity curves of following solutions: 0.7% HPMC/0.3% NaCMC/0.06% SDS; 0.7% HPMC/0.3% NaCMC; 0.7% HPMC/0.06% SDS; 0.3% NaCMC; 0.7% HPMC.

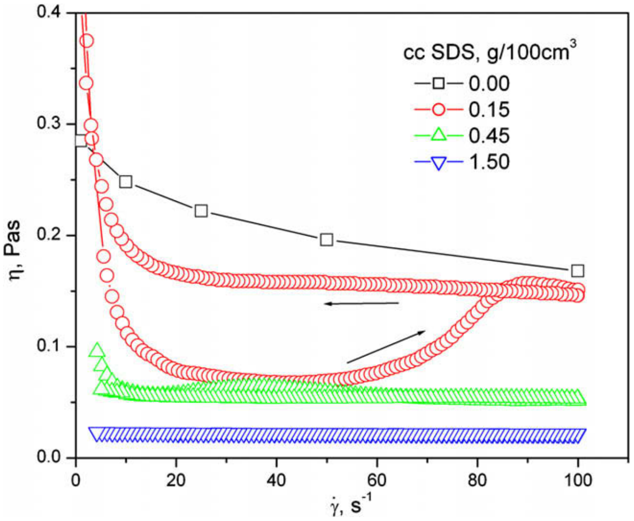

Fig. 8. Viscosity curves of ternary HPMC/NaCMC/SDS systems having 0.7% HPMC, 0.3% NaCMC and different amounts of SDS.

Viscosity curves of ternary HPMC/NaCMC/SDS systems having 0.7% HPMC, 0.3% NaCMC and different amounts of SDS are shown in Fig 8. The antitixotropic hysteresis loop is detected at 0.15% SDS. It is supposed that extension of HPMC chains in the HPMC/SDS complex takes place under the influence of shear rate. This decreases the electrostatic repulsion effects and enables reestablishment of some HPMC–NaCMC links which is followed by the viscosity increase. This is in agreement with the discussion that follows Fig. 2. Time effects are observed up to the 0.45% of SDS (not shown). Above this concentration the viscosity curves are of Newtonian type. The Newtonian flow properties show that the applied shear field has no influence on the microstructural elements in the ternary system. HPMC/SDS complex is solubilized to an extent where the applied shear filed has no influence on its conformation, and the electrostatic repulsion between the complex and NaCMC suppresses reestablishment of HPMC–NaCMC links. Further addition of SDS slightly decreases viscosity of the ternary mixture indicating further solubilization of HPMC and small conformational changes in HPMC/SDS complex (Kulicke et al. 1998b). Above 1.25% SDS there is no phase separation in the system. Influence of SDS concentration on viscosity of the ternary mixture is also absent, as represented by the viscosity curve of 1.50% SDS (Fig. 8). HPMC is fully solubilized and the complex bears enough charge to be completely soluble even in the presence of NaCMC.

4. Conclusion

Rheological investigations of HPMC/SDS mixture showed that an applied shear rate may have significant influence on the polymer–surfactant complex properties. It was shown that both CM and PSP increase when shear rate is applied. This is most likely due to extension of HPMC chains in the complex which enables more SDS to be bound prior to the electrostatic repulsion predominates the hydrophobic interactions. On the other hand, no dependence of CAC on shear rate was observed. CAC, CM and PSP determined by the oscillatory measurements were proved to be in agreement with the low shear rates viscosity measurements results. At high shear rates, it seems that a conformation of the complex is primarily determined by the applied shear field and in less extent by SDS concentration.

Study on synergistic effects in 1% HPMC/NaCMC blends demonstrated that maximum of the synergy takes place when blends consisting of 0.4% of HPMC and 0.6% of NaCMC are made. The maximum is shear rate independent. In 0.7% HPMC and 0.3% NaCMC blends, due to the lack of NaCMC, just one portion of HPMC is linked to NaCMC molecules.

Phase separation in the ternary HPMC/NaCMC/SDS system was observed at SDS concentrations ranging from 0.15% to 1.00%. Though, an influence of as small as 0.06% SDS on the HPMC/NaCMC synergy was observed. This implies that even at such low concentrations SDS binds to HPMC and decreases synergistic HPMC–NaCMC viscosity effects. The visco-elastic properties of the coacervate phase proved to be primarily determined by HPMC–SDS interactions. Maximum in G' was observed at 0.25% SDS. Only at this concentration the elastic properties of the coacervate phase dominates the viscous ones. At concentrations lower than 0.25% SDS, results suggest that one portion of HPMC molecules is still present in the supernatant, being in the synergy with NaCMC. Dynamic behavior of the ternary system for SDS concentrations ranging between 0.15% and 0.45% was largely influenced by the applied shear field. For these systems, antithixotropic flow behavior was observed. It suggests that the applied shear rate brings about HPMC chains extension in the complex, decrease in charge density of the complex, and reestablishment of some HPMC–NaCMC. At higher SDS concentrations Newtonian viscosity curves are obtained, indicative of more or less full solubilization of HPMC by SDS molecules. The results presented should help obtaining the coacervate of desirable structural and dynamic properties.

Finally, we show that by carrying out detailed rheological measurements molecular interactions in a complex system can be successively investigated.

In our current work we investigate deposition of the coacervate of the defined properties on the oil/water interface in emulsions. In this way, microencapsulation with controlled barrier properties of the encapsulating layer could be achieved.

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