Colloid Polym Sci (2005) 284: 334–339
DOI 10.1007/s00396-005-1376-4

SHORT COMMUNICATION

Verica J. Sovilj
Lidija B. Petrović

Influence of molecular characteristics of nonionic cellulose ethers on their interaction with ionic surfactant investigated by conductometry

Received: 19 May 2005
Accepted: 13 July 2005
Published online: 27 August 2005
© Springer-Verlag 2005

V. J. Sovilj (✉) · L. B. Petrović
Faculty of Technology, Department of Applied and Engineering Chemistry,
University of Novi Sad, Bul. cara Lazara 1,
21000 Novi Sad, Serbia and Montenegro
E-mail: miso@uns.ns.ac.yu
Tel.: +381-21-6350122
Fax: +381-21-450413

Abstract The interaction between nonionic derivatives of cellulose, hydroxypropylmethyl cellulose (HPMC) and methyl cellulose (MC), and ionic surfactant, sodium dodecylsulfate (SDS) were investigated by conductometric titration method, at 30°C. Obtained titration curves show two break points: critical aggregation concentration (cac) defined as the concentration of SDS at which interaction starts, and polymer saturation concentration (psp) as the concentration at which interaction finishes. Changes of characteristic concentration breaks were determined in dependence on concentration and molecular characteristics of cellulose derivatives (degree of substitution (DS) and molecular mass, i.e. intrinsic viscosity). It was shown that the first break point, cac, is independent of polymer concentration; while the second break point, psp, increases as polymer concentration increases, as described by a linear correlation. The slopes of linear relationship justify the DS on the intensity of the cellulose derivatives–SDS interaction. Changes in the intrinsic viscosity of cellulose derivatives do not exhibit influence on the interaction with SDS.

Keywords Polymer-surfactant interaction · Conductometric titration · Hydroxypropylmethyl cellulose · Methyl cellulose · Sodium dodecyl sulfate

Introduction

Polymer and surfactants are very commonly included in many products relevant for food, pharmaceutical and chemical industries, such as emulsions, suspensions and other colloidal systems, generally with the aim of obtaining thickening or stabilizing effects. Mixture of certain polymers and surfactants can exhibit molecular interactions that might affect physicochemical properties of the system. Because of that, the nature of these interactions has been the subject of investigation for several decades and the effects of polymer–surfactant interactions are useful in practice for modifying the properties of the systems [1, 2]. Depending on the particular system, there are two mechanisms of interaction of different intensity between polymer and surfactant: electrostatic and hydrophobic, although other mechanisms of interaction may also have a secondary role. As the polymer–surfactant interaction takes place, the properties of the systems change, and they can be detected by various techniques like conductometry [3, 4], tensiometry [5, 6], viscometry [7], rheometry [8, 9], equilibrium dialysis [10], NMR [11] and fluorescence [12, 13], among others.

Water soluble nonionic derivatives of cellulose, like hydroxypropylmethyl cellulose (HPMC), and methyl cellulose (MC) are physiologically harmless and hence are preferred for use in foodstuffs and pharmaceutical industry [14]. The introduction of methyl and hydroxypropyl groups renders the cellulose molecule hydrophobic [15]. In the presence of low molar mass surfactant, such as sodium dodecylsulfate (SDS), the hydrophobic centers on the HPMC and the MC molecules represent potential adsorption sites for surfactant molecules [8] i.e., for interaction with surfactant. The mechanisms of molecular interactions are still the subject of controversy, but the classical profile of the nonionic polymer–ionic surfactant interaction in the solution is surfactant adsorbtion onto the polymer in the form of smaller or larger aggregates forming mixed micelles with hydrophobic polymer segments. At sufficiently high surfactant concentrations, the polymer is saturated with surfactant and only free surfactant micelles are formed in the solution [16, 17]. When the polymer concentration and polymer hydrophobicity increases, the interactions become stronger and intermolecular in nature; so the properties of the system change in different ways [18, 19]. Because of that, the interaction between cellulose derivatives various kind of substituents and degree of substitution (DS), and SDS has to be studied.

In this work, the interaction between cellulose derivatives (HPMC samples various DS and molar mass and MC sample) with ionic SDS was studied by conductometric measurements. The SDS concentrations were well above the critical micelle concentration (CMC), and the HPMC and MC concentrations were above the critical overlap concentration (C*). The objective was to use the obtained results to determine the characteristic SDS concentrations at which properties of solutions caused by interaction are changed, as well as the influence of molecular characteristics of polymer on the interaction.

Experimental

Materials

Hydroxypropylmethyl cellulose, (trade names Methocel K100, Methocel K100M and Methocel E3) and MC (trade name Methocel A15), obtained from Colorcon Ltd., England, was used without any further purification. SDS, purity >99%, was obtained from Merck, Germany. Bidistilled water was used as a solvent.

Stock solution of polymers was prepared by dispersing the proper amount of polymer in water at 80°C (above the gel point which is approximately 70°C and 50°C for 2% aqueous solution of HPMC and MC, respectively), by gentle stirring. The stock solution was left for 24 h at room temperature before further use. Stock solution of SDS, 3.0% (w/v), was used after preparation. The molecular characteristics of the samples are given in Table 1. DS are from manufacturers specification. The Huggins extrapolation procedure was employed to determine intrinsic viscosities [η] at 30°C. The intrinsic viscosity is a measure of the aqueous volume that a given polymer mass fills up. If a container is imagined as full of polymers not entangling with each other, the inverse of [η] thus gives the maximum concentration of polymer that can be kept in solution without intermolecular entanglement. This concentration is usually referred to as the critical overlap concentration or C* [6, 20, 21].

Conductivity

Conductivity measurements were carried out at 30°C in a jacketed beaker by adding the proper volume of 3.0% SDS solution to 50 cm^3 of polymer solution of the following concentrations: 0.05, 0.1, 0.15, 0.2, 0.35 and 0.5% (w/v). After adding each portion of the surfactant, the solution was stirred with magnetic stirrer until a steady conductance value was attained [4]. Specific conductance of the solution was measured on a microprocessor conductivity meter Model MA 5964 (Iskra, Slovenia), using cell with the cell constant of 1,000. All solutions were prepared with bidistilled water of a specific conductance between 2 and 3 μS/cm at 30°C.

Results and discussion

Influence of SDS on the conductivity of cellulose ethers solution

The conductometric titration method is one of the most often used techniques to determine cmc of ionic surfactant, as well as to examine the nonionic polymer–ionic surfactant interaction in dilute solution [3, 4, 13].

The addition of surfactant to the water caused a linear increase of specific conductance up to the surfactant concentration at which micelle formation began, i.e. up to the cmc. After the cmc, the conductance increased further linearly, but with a smaller slope than before. The break on the conductance–concentration titration curve gives the cmc of the surfactant. For the SDS, the cmc determined by conductometric titration was 0.252 g/100 cm^3 at 30°C (Fig. 1).

Table 1 Characteristics of METHOCEL brand of cellulose ethers

METHOCEL	Methoxy (%)	Hydroxypropyl (%)	DS(%)	[η], (100 cm^3/g)	C* (%)
E3	28.9	8.9	37.8	0.49	2.024
K100M	23.0	10.7	33.7	9.19	0.109
K100	22.3	9.7	32.0	2.68	0.372
A15	30.0	–	30.0	1.58	0.633

The addition of SDS to the cellulose ether solution, is presented in Fig. 1 on example of HPMC K100M solution. The relationship between conductance and SDS concentration show two break points like most of ionic surfactant–nonionic polymer systems [3, 17]. In the classical profiles of conductivity investigation of ionic surfactant–nonionic polymer interaction, the breaks are related to the beginning of surfactant binding to the polymer, the so-called critical aggregation concentration, cac, and saturation point of the polymer by the surfactant, psp [22]. In the ionic surfactant–nonionic polymer solutions there are no interactions until the surfactant concentration reaches cac value. The cac is always lower than the cmc of the surfactant [23], implying that the surfactant concentration in the vicinity of polymer is higher and reach cmc at lower total surfactant concentration.

Addition of SDS to HPMC K100M solution causes a linear increase in conductivity, with the same slope as for SDS without polymer up to the SDS concentration after which there is an evident decrease in the slope. This concentration is cac and can be explained by the depletion of free ions of the surfactant from solution, either by adsorption on, or by cluster formation with the polymer. This binding continues until saturation of HPMC molecules with SDS, which is determined by the second breaking point, i.e. psp. With the further addition of SDS conductivity dependence is again linear, with the same slope as for SDS without the polymer, after reaching the cmc value. All the plots show two linear regions, below the cac and above the psp, whose slopes are independent of polymer concentration and they are identical to the one in its absence [3, 24, 25]. Between cac and psp, is the region of interaction, i.e. of binding SDS molecules to HPMC, observed as a nonlinear dependence. It has been suggested [3] that this nonlinearity could be related to a step in the binding process that corresponds to a saturation of the available sites of the polymer with monomeric surfactants or micelles of low aggregation number; after that micelles with larger aggregation number begin to form. After the psp, only normal SDS micelles begin to form [3, 17], but this fact does not exclude the possibility of the SDS micelles forming below this break point [16, 24, 26]. The nonlinearity changes its form in dependence on critical overlap concentrations for HPMC solutions. At the HPMC concentrations below the critical overlap concentration, for the HPMC K100M in Fig. 1 the C^* $= 0.109\%$, a break at psp is more pronounced, whereas at the concentrations exceeding C^* there is a break at cac.

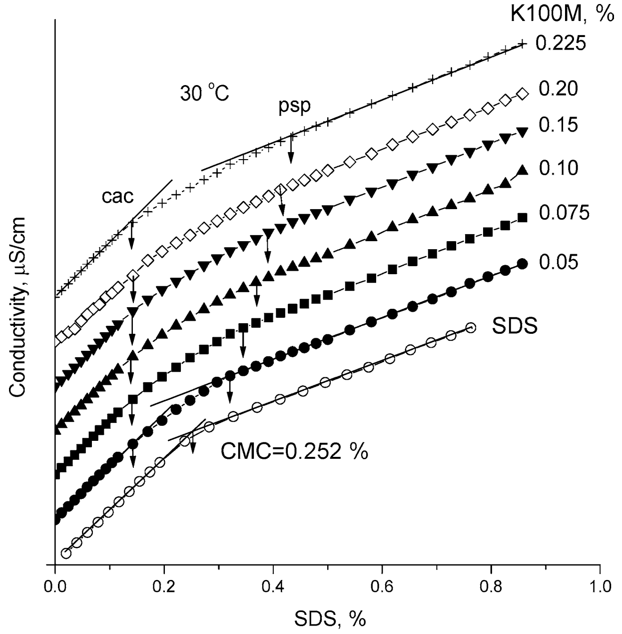

Fig. 1 Plots of conductivity (relative scale units) versus sodium dodecylsulfate (SDS) concentration for water, and for various concentrations of HPMC K100M

At HPMC concentrations $< C^*$, interactions take place at the molecular level, i.e. there is no intermolecular binding of the adjacent polymeric chains. When cac is reached, SDS molecules begin to bind to HPMC molecules, thus forming smaller or bigger micellar structures around the substituent of each individual polymer molecule, which are in equilibrium with SDS molecules in the solution. Mobility of the surfactant ions in the solution has not decreased significantly, and so neither has the measured conductivity. Further addition of SDS yields formation of bigger micellar structures [3], whereby the ion mobilities are significantly lowered, and the second break point (i.e. psp) is more pronounced.

If the HPMC concentration is closer to C*, after reaching cac, intermolecular binding takes place via micellar aggregates that are formed around the substituents of the adjacent polymer chains, yielding the formation of network structures. As a consequence, mobility of dodecylsulfate ions was reduced, so the break on the conductivity curve at cac is more pronounced. With further increase in SDS concentration, micellar structures are formed around each individual substituent, the network structure is destroyed, ion mobility is not restricted, and the conductivity is almost proportional to the addition of SDS. Because of that, the second break point (i.e. psp) is less pronounced and it is often difficult to determine what is clearly shown on the MC sample, (Fig. 2) which is more hydrophobic than HPMC and this effect is exposed earlier [27]. Therefore, for higher polymer concentrations, other techniques are often used for their determination.

Dependence of cac and psp on molecular characteristics of Methocel samples

Conductometric titration curves for all cellulose ethers investigated show two break points and considering it,

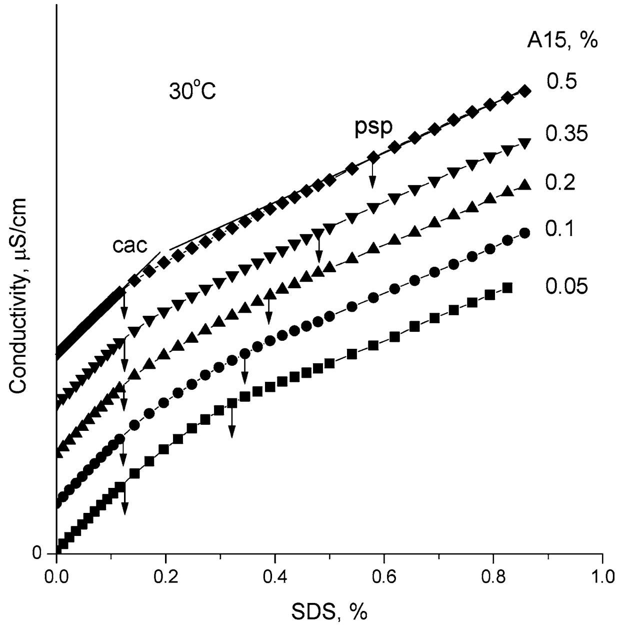

Fig. 2 Plots of conductivity (relative scale units) versus SDS concentration for various concentrations of MC A15

the characteristic concentrations of SDS, cac and psp are determined. Dependence of cac and psp on the cellulose ethers concentration is presented in Fig. 3. For Methocel K100M the maximum concentration investigated was 0.225%. At higher polymer concentrations, due to interaction, significant increases of solution viscosity [15], what reflects on very long time dependant equilibrium in SDS–polymer complexation. It can be seen that cac is independent of polymer concentration, and is lower than the cmc of SDS, while psp increases linearly with the polymer concentration. This behavior is characteristic of most nonionic polymer–ionic surfactant interactions [17, 25, 28]. The cac value and parameters of linear relationships for psp are shown in Table 2.

The cac values are almost constant for each Methocel sample and depend on molecular characteristics of polymers. Changes in cac value for various methocel samples can be explained by DS and the nature of substituents. HPMC samples K100 and K100M have DS and percent of hydroxyprophyl and methoxy substituents almost the same, which is shown in Table 1, and therefore the same cac values. Methocel E3 has higher DS contributed by a higher percent of methoxy content, thus, the hydrophobicity of molecules is increased and SDS molecules start to bind at a lower concentration. Methocel A15 with the lowest value of DS, which is 30, should have the cac value higher or the same as K100 sample, but it is not so. The cac value for Methocel A15 is between cac values obtained for K100 and E3. Methocel A15 has only methyl substituents and the molecule is more hydrophobic (has lower gel point), thus SDS starts to bind on it at lower concentration [20, 27]. Results show that not only DS value, but the hydrophobicity of substituents also affects cac.

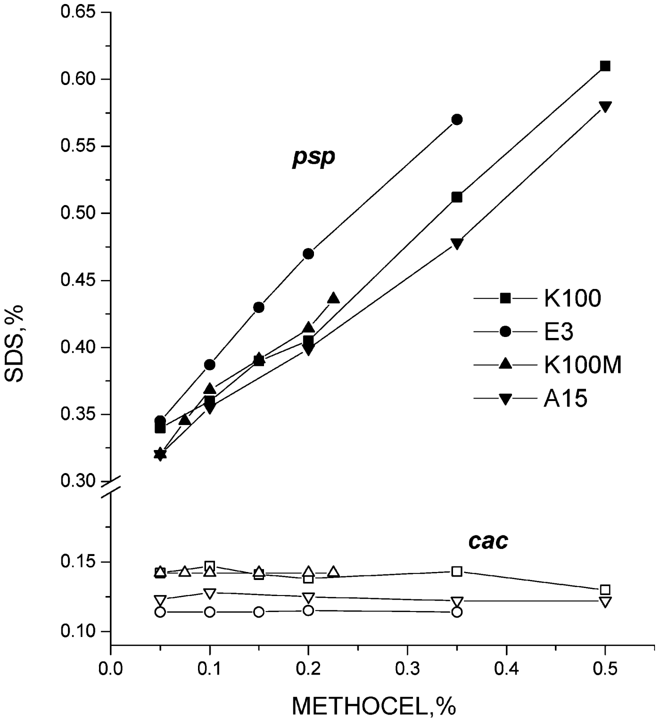

Fig. 3 Characteristic concentration breaks [critical aggregation concentration (cac) and polymer saturation concentration (psp)] on conductometric titration curves as a function of Methocel concentration

The psp values increase linearly with polymer concentration (Fig. 3) according to the parameters of linear relationship equation (Table 2). From this equation, it is possible to calculate the conductivity break point, psp, for any methocel concentration and predict the concentrations of SDS needed for the desired region of interaction. Thus, for any methocel concentration, interaction starts at cac and finishes at psp concentration of SDS calculated from the linear relationship. Between cac and psp is the region of interaction. The slope (parameter B) of the linear relationships represents grams of SDS bound per gram of methocel [4] i.e.,

Table 2 The cac values, parameters of linear relationships for psp ($\text{psp} = A + BC_{\text{polymer, \%}}$)obtained for cellulose ethers

Methocel	*cac* (%)	Parameters		
		A	*B*	r^a
E3	0.114	0.3133	0.7473	0.9978
K100M	0.142	0.2979	0.6091	0.9898
K100	0.145	0.2986	0.6113	0.9957
A15	0.126	0.2919	0.5626	0.9971

[a] *r* = coefficient of correlation

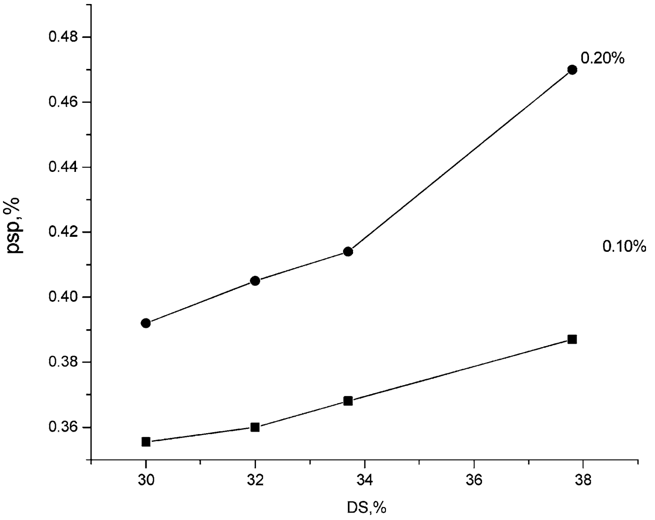

Fig. 4 Changes of polymer saturation point (psp) with degree of substitution (DS) of Methocel samples at concentrations 0.10% (*filled square*) and 0.20% (*filled circle*)

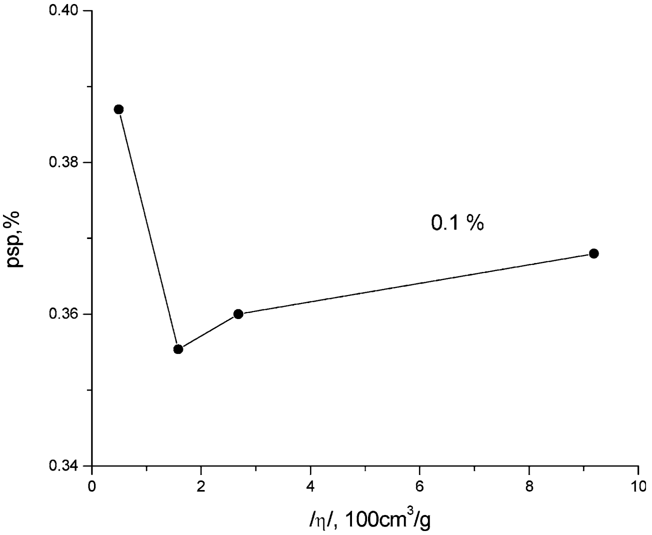

Fig. 5 Changes of psp with intrinsic viscosity [η] of Methocel samples

capacity of certain polymer to bind surfactant. From Fig. 3 and the values of slope B, it can be concluded that the sample with higher DS (Table 1) has higher B value, and of course, psp value for certain polymer concentration, because of more binding sites for SDS molecules. Dependence of psp on DS value for two methocel concentrations are presented in Fig. 4, which show that psp value changes according to the DS, so E3 sample with DS = 37.8 has the highest psp value. This behavior is more pronounced with increasing polymer concentration.

Dependence of psp on intrinsic viscosity [η] of the cellulose derivatives, which is proportional to molecular mass, is presented in Fig. 5. It can be seen that the HPMC samples K100 and K100M with great difference in intrinsic viscosity, have almost the same psp values, because their DS values are not very different. There is no relationship between psp and intrinsic viscosity, i.e. the molecular mass [25]. The diagram in Fig. 5 indicates that present substituents, i.e., DS value is a determining factor for SDS binding.

Conclusions

Investigations of the interaction of nonionic cellulose derivatives, HPMC and MC, with an ionic surfactant, SDS, show that the conductometric titration method is a useful and relatively simple technique for the determination of characteristic concentrations of SDS at which interaction starts and finishes, if the concentrations of polymer are not above the critical overlap concentrations. For all samples investigated, the cac is constant and independent of polymer concentration, but dependent on hydrophobicity of substituents. The psp values are dependent on polymer concentration and DS, but not on molecular mass. The psp values change linearly with polymer concentrations and from linear relationships it can be calculated the SDS concentrations necessary for reaching the desired degree of interaction, as well as the maximal amount of SDS bond to polymer.

This work is, thus, important regarding many practical applications where an understanding of the interaction mechanism is needed in order to control it fully and optimize the system. A problem that occurs particularly in food foams and emulsions, is that there is often a mixture of polymers and surfactants competing for the interface. In concentration regimes, where a mixture of polymer–surfactant interface exists, a reduction in stability is often observed [29, 30]. These investigations are also important for the microencapsulation process, where the interaction at the adsorption layer around the core material can change its permeability and influences the stability of microcapsules [31, 32].

Acknowledgements This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia (Grant Number 0426). The authors are thankful to Colorcon Ltd. (England) for their generous gift of the HPMC sample.

References

1. Goddard DE (1993) Application of polymer–surfactant systems. In: Goddard ED, Ananthapadmanabhan KP (eds) Interaction of surfactants with polymers and proteins. CRC, Boca Raton, pp 395–413
2. Goddard DE (2002) J Colloid Interface Sci 256:228
3. Minatti E, Zanette D (1996) Colloids Surf A Physicochem Eng Aspects 113:237
4. Sovilj V (1998) Colloid Polym Sci 276:328
5. Persson B, Nilsson S, Sundelöf O-L (1996) Carbohydr Polym 29:119
6. Alvarez-Lorenzo C, Gómez-Amoza LJ, Martínez-Pachero R, Souto C, Concheiro A (2001) Colloid Polym Sci 270:1045
7. Jiang HW, Han JS (2000) J Colloid Interface Sci 229:1
8. Kulicke MW, Arendt O, Berger M (1998) Colloid Polym Sci 276:617
9. Sovilj JV, Dokić PP, Petrović BL (2003) Acta Periodica Technologica 34:71
10. Arora SPJ, Singh PS, Singhal KV (1984) Tenside Detergents 21:197
11. Hammarström A, Sundelöf O-L (1993) Colloid Polym Sci 271:129
12. Winnik MF, Regismond ATS (1996) Colloids Surf A Physicochem Eng Aspects 118:1
13. García-Mateos I, Pérez S, Velázquez MM (1997) J Colloid Interface Sci 194:356
14. Zhang ML (2001) Carbohydr Polym 45:1
15. Kulicke MW, Arendt O, Berger M (1998) Colloid Polym Sci 276:1019
16. Smitter LM, Guédez JF, Müller AJ, Sáez AE (2001) J Colloid Interface Sci 236:343
17. Goddard DE (1993) Polymer–surfactant interaction. Part I. Uncharged water-soluble polymers and charged surfactants. In: Goddard ED, Ananthapadmanabhan KP (eds) Interaction of surfactants with polymers and proteins. CRC, Boca Raton, pp 123–169
18. Kientz E, Holl Y (1994) Colloid Polym Sci 272:141
19. Clasen C, Kulicke MW (2001) Progr Polym Sci 26:1839
20. Ridell A (2003) Characterisation of aqueous solution liquid crystals and solid state of non-ionic polymers in association with Amphiphiles and drugs. PhD Thesis, Faculty of Pharmacy, Uppsala
21. Hormnirum P, Sirivat A, Jamieson MA (2000) Polymer 41:2127
22. Zanette D, Soldi V, Romani PA, Gehlen HM (2002) J Colloid Interface Sci 246:387
23. Li Y, Dubin LP (1994) Polymer–surfactant complexes. In: Herb CA, Prud'homme RK (eds) Structure and flow in surfactant solutions, ACS Symposium Series 578. American Chemical Society, pp 320–336
24. Bo AD, Schweitzer B, Felippe AC, Zanette D, Lindman B (2005) Colloids Surf A Physicochem Eng Aspects 256:171
25. Müller JA, Garcés Y, Toress M, Scharifker B, Sáez AE (2003) Progr Colloid Polym Sci 122:73
26. Gjerde MI, Nerdl W, Hoiland H (1998) J Colloid Interface Sci 197:191
27. Ridell A, Evertsson H, Nilsson S (2002) J Colloid Interface Sci 247: 381
28. Froehner SJ, Balarmino A, Zanette D (1998) Colloids Surf A Physicochem Eng Aspects 137:131
29. Langevin D (2000) Adv Colloid Interface Sci 88:209
30. Wilde PJ (2000) Curr Opin Colloid Interface Sci 5:176
31. Sovilj V, Djaković LJ, Dokić P (1993) J Colloid Interface Sci 158: 483
32. Sovilj V, Dokić P, Sovilj M, Erdeljan A (1996) Progr Colloid Polym Sci 100:235