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## The time dependence of chitosan/ nonionic surfactant solution viscosity

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**Abstract** The measurement of the viscosity of semiconcentrated chitosan (0.08–0.14%) solutions in the system with octaethyleneglycol mono *n*-dodecylether ( $C_{12}E_8$ ) was carried out using Cannon–Fenske capillary viscometer. The interaction was – as expected – very weak, but when the time dependent hydrodynamic behaviour of the system was considered, the interaction has been established at particular surfactant concentrations. The most significant time dependence is shown in a form of sudden viscosity drop in a region close to and above CMC value of the surfactant, which implied existence of the interaction between chitosan and surfactant. At low surfactant concentrations viscosity values were constant with increasing surfactant concentration, but solution also showed time dependent decrease in the viscosity which has been connected with well known time

dependent viscosity of pure chitosan solution.

The viscometry enabled monitoring of the extent of chitosan/surfactant association by establishing the viscosity decrease rate constant. The rate constant was derived from the first order constant of the quadratic polynomial curves used for the approximation of experimental values when these are presented in the form of viscosity–time profiles. This method showed the existence of critical surfactant concentration values ( $C_1$ ,  $C_2$  and  $C_3$ ). These values are closely connected with the proposed interaction model which is based on the assumption that spherical surfactant micelles are bound by chitosan molecule.

**Key words** Chitosan – nonionic surfactant – interaction – viscosity – time-dependence

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### Introduction

Measurement of the viscosity of polymer solutions provides one of the most easily obtained and widely used items of information about the molecular structure of the polymer samples. As it is commonly known, a polymer molecule in solution is not a stationary piece of string, but instead is in a constantly coiling and uncoiling chain whose conforma-

tion in space is continuously changing [1]. Usually, water soluble polymers give rise to substantial viscosity increases when dissolved in water and when concentration of the polymer increases. Chitosan (poly (1,4–2-amino-2-deoxy-glucose)) is a hydrophilic cationic polymer produced by deacetylation of chitin. Due to the presence of protonated amino groups, chitosan in solution exhibits polyelectrolyte effect and its hydrodynamic behaviour in the solution is extremely complicated, even in the absence of electrolyte [2].

In the absence of electrolyte, the hydrodynamic behaviour of chitosan macromolecules in the solution depends primarily on chitosan concentration and pH of the solution. In very dilute solutions (below 0.001%) the reduced viscosity of the chitosan solution increases with a decrease in concentration below 0.001 g/l [3]. This increase is due to the increasing interactions among the polyions caused by greater Coulombic repulsion forces between the charged points, which expands the backbone of the macromolecule to perhaps nearly rodlike conformation in these electrolyte free highly diluted solutions. With concentration increasing to dilute regimes (over 0.001%), electrostatic screening (shielding) sets in among the polyions, neutralizing some of the charges and increasing flexibility of the local chain which causes macroion to shrink, consequently reducing the Debye length and decreasing the viscosity. Hence, the chitosan molecules in dilute solution (0.001–0.01%) behave as a worm-like non-draining polymer with a flexibility that can be controlled by both changing the degree of ionisation and changing the counterion concentration. Molecular configuration of chitosan becomes dictated by the electrostatic interactions between polyion and counterions [4].

In semiconcentrated (0.01–1.0%) and concentrated (over 1.0%) solutions, the structural organization of the solution is very dependent on the pH of the solution. The existence of extreme value (pH 5.2) could be connected with contraction of chitosan molecular coils due to electrostatic interactions as well as with forming of the associates with hydrogen bonds between nonprotonized amino groups [5]. Surfactants, as well as electrolytes, may influence the hydrodynamic behaviour of a chitosan solution.

In general, upon adding of surfactant drastic changes in the viscosity of most of the polymer solutions can be observed, and the measurement of the solution viscosity is the simplest method for monitoring the association between polymer and surfactant. The viscosity change implies the occurrence of interaction between solutes or some change in polymer conformation. However, it has been generally established that in case of ionic polymer (polyelectrolyte) and nonionic surfactant, interactions are weak and have been only considered in cases when hydrogen bonding between polymer and surfactant are effective, but structural and phase changes may be present and are highly probable [6].

It would be expected that viscosity of the polymer solution generally increases when it forms complexes with surfactants, but the effect is proven to be anomalous [7]. The observation of increasing viscosity with increased surfactant concentration in the polymer/surfactant system, clearly implies a change in polymer conformation due to the expansion of polymer coils on association with the surfactant. This expansion of the macromolecule is easily

detectable by viscometry. A steady increase in the relative viscosity of PEO (poly(ethylene oxide)) solutions by adding increasing amounts of SDS (sodium dodecyl sulphate) is well-known [8–9], and has been recently reported [10] on HMPA (hydrophobically modified poly(sodium acrylate)) and a series of oligoethylene glycol monododecyl ether surfactants ( $C_{12}E_n$  with  $n = 4, 5$  and  $8$ ). On the other side, there is evidence that some coil collapse and viscosity decrease occur by adding surfactants to the polymer solution. The intrinsic and reduced viscosity of mildly hydrophobic polymer PVA (polyvinylalcohol) in water gradually decreases with the addition of nonionic surface active agent OP15 (polyethylene oxide octylphenyl ether) [11]. Also it has been established that in weak polyacid PAA (polyacrylic acid) solution the viscosity is decreased abruptly by addition of nonionic surfactants at a certain concentration, and this point is taken as  $T_1$  (critical surfactant concentration below CMC) [12]. Some other systems as PAAM (polyacrylamide) with DDBS (didodecyl benzoyl sulphate) [13] and EHEC B (ethyl(hydroxyethyl)cellulose) with SDS [14] also showed decrease in viscosity with increasing surfactant concentration, indicating that the surfactant micelles connect two or more parts of the single polymer chain.

The aim of our investigation was to present that even if only weak interaction between chitosan and nonionic surfactant has been expected, when the time dependent effects are considered it can clearly be seen that significant interaction exists. As it is known, the system properties (viscosity, surface tension, etc.) are in time dependent systems by no means linear functions of the composition, even though they are strongly dependent on composition. Such (time dependent) effects seem to play a role in most systems where amphiphilic systems interact with a polymer, although the effect can be more or less pronounced.

## Experimental

### Materials

Chitosan [2-amino-2-deoxy-(1 → 4)- $\beta$ -D-glucopyranan] (Fluka, Buchs, Switzerland) of low molecular weight ( $M_r \sim 70000$ ) with < 10% water and < 2% ash was used without further purification. Stock solution of 1% chitosan is made by dissolving in 1% acetic acid and filtered to remove any insolubles in the polymer concentration.

EMPILAN KBS8 (Teneco España S.A., Barcelona, Spain) was used as a commercially available technical grade nonionic surfactant without further purification. It is declared by the manufacturer as an octaethyleneglycol mono *n*-dodecyl ether ( $C_{12}E_8$ ), containing 100% of active

material, with HLB value 13 and pH 6–7 of 1% solution. CMC value is  $5.2 \cdot 10^{-5}$  mol/l.

NIKKOL BL-8 SY (Nikko Chemicals Co. Ltd., Tokyo, Japan) was used as guaranteed pure homogenous octa-ethyleneglycol mono *n*-dodecyl ether ( $C_{12}E_8$ ) with CMC value  $7.0 \cdot 10^{-5}$  mol/l.

Deionised water with conductivity less than  $1.5 \mu\text{S}/\text{cm}$  was used for all experiments.

## Methods

Viscosity measurements were carried out in ordinary Cannon–Fenske capillary viscometer after samples to be tested had been left in a temperature-controlled room at  $25^\circ\text{C}$  for defined time. The results were obtained at  $25^\circ\text{C}$  performing the experiments in a thermostated water bath.

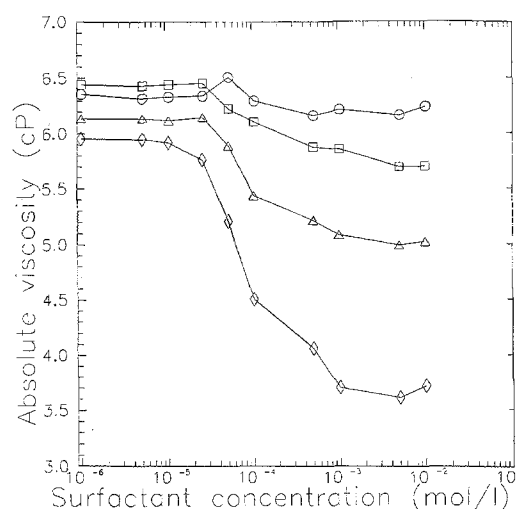
For each examined chitosan concentration ten solutions of different surfactant concentrations ranging from  $10^{-6}$  to  $10^{-2}$  mol/l were prepared by mixing the required amounts of chitosan and surfactant stock solutions in a measuring flask, and diluting with water. pH value of all solutions was 4 and they could be considered as semiconcentrated chitosan solutions.

## Results and discussion

### Viscosity time dependence

Even though the viscosity close to time zero was difficult to judge, it has been observed that solutions of the same chitosan concentration immediately after mixing showed similar viscosity not dependent on the surfactant concentration. On the contrary, after allowing some time to pass, the above solutions showed a noticeable decrease in the viscosity. Fig. 1 shows the absolute viscosity of the solutions containing 0.12% chitosan and different concentrations of EMPILAN, measured 4, 48, 96 and 216 h after mixing the solutions. The most significant time dependence is shown in a form of sudden viscosity drop in a region close to and above CMC. The existence of such critical concentration suggests some critical intramolecular micelle composition of the polymer in the presence of surfactant. When surfactant concentration is small enough (below CMC) – the viscosity is almost constant which indicates extended random coil conformations due to intramolecular repulsion between charged groups of the polymer.

Four hours after mixing the solutions the viscosity drop could still not be observed. However, slight increase of the viscosity was observed at surfactant concentration



**Fig. 1** Viscosity dependence of 0.12% chitosan solution at  $25^\circ\text{C}$  as a function of EMPILAN K8S8 concentration at different (4, 48, 96 and 216 h) times after mixing of the solutions (non aged chitosan stock solution).  $\circ$  – 4 h ample time;  $\square$  – 48 h ample time;  $\triangle$  – 96 h ample time;  $\diamond$  – 216 h ample time

near to CMC value, followed by a slight decrease in the viscosity with increasing surfactant concentration. After 48 h, the viscosity drop has been clearly observed, but it was still not as pronounced as after 96 and 216 h. At low surfactant concentrations viscosity values were constant with increasing surfactant concentration, but solutions showed time dependent decrease in the viscosity.

It is already known that the solution of chitosan in diluted acetic acid does not display a constant steady-state viscosity but strongly time dependent viscosity [15–16]. In this sense, time dependent decrease in the viscosity of pure chitosan solutions should be considered as expected behavior and it could be explained by structural rearrangement processes. In order to confirm this, we measured viscosity of pure chitosan solutions immediately after preparation and after 7 days. The results implied that there is a decrease of the viscosity of chitosan solutions after 7 days and that the magnitude of this change is comparable to the decrease observed with solutions containing low surfactant concentration. These results suggested that chitosan solutions containing low surfactant concentrations, behave similar to pure chitosan solutions and, hence, do not imply existence of any kind of interaction between chitosan and surfactant at this particular surfactant concentrations.

However, it has been recently reported that certain polymer/surfactant systems have time dependent properties. The time dependence of the surface tension is established for aqueous ethyl(hydroxyethyl)cellulose with sodium dodecyl sulphate (EHEC/SDS/water system) [17]

and similar observations were done for aqueous hydroxypropyl cellulose (HPC) solutions [18]. Other investigations of the system EHEC/SDS/water indicated that even viscosity of the system is strongly time dependent and ample time has to be allowed for the system to attain stable (equilibrium) properties [14, 19]. The most pronounced time dependence is shown in a region close to and above CMC of the pure surfactant solution and for polymer concentrations at least equal to the critical overlap concentration (polymer concentration corresponding to beginning of the coil overlap).

#### Derivation of the rate constants

The results presented on Fig. 1 can be presented for each surfactant concentration in the form of the viscosity–time profile. The shape of the curves obtained suggested that experimental values could be well enough approximated as straight lines (Eq. 1) (corresponding to the 1st degree polynomials) with different slopes (Fig. 2).

$$y = a + bx \quad (1)$$

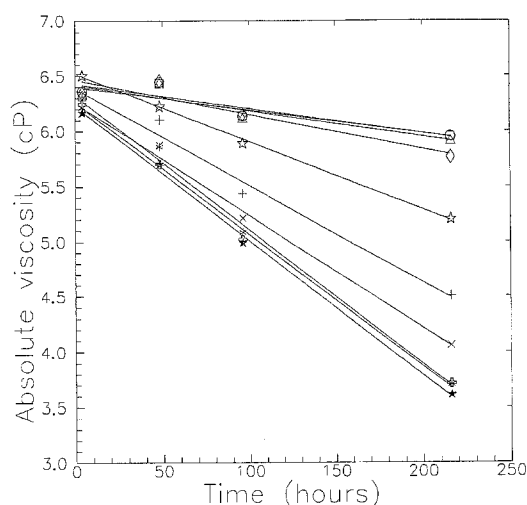
This kind of presentation seemed very convenient for further analysis as it clearly showed the existence of two distinct surfactant concentration ranges:

- diluted solutions (cca.  $1 \cdot 10^{-6}$  to  $2.5 \cdot 10^{-5}$  mol/l);
- highly concentrated solutions (cca.  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-2}$  mol/l)

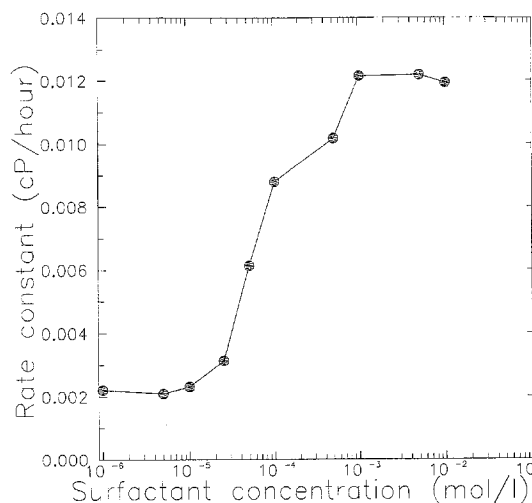
each consisted of similar or coincident values of a slope i.e. the first order constant  $b$ . Viscosity–time profiles of surfactant concentrations belonging to each of the ranges were almost coincident.

The slope of straight lines was considered as a rate constant of the viscosity dependence on time, and, hence, indicating the extent of interaction between chitosan and surfactant. It could be noted that rate constant markedly differed for surfactant concentration values  $5 \cdot 10^{-5}$ ,  $1 \cdot 10^{-4}$  and  $5 \cdot 10^{-4}$  mol/l, which meant some kind of change of the state of polymer and surfactant in the solution at these surfactant concentrations. In order to define better a surfactant concentration range which corresponds to possible polymer–surfactant interaction, we plotted a rate constant (derived from the slope of the straight lines fitting the viscosity–time profiles) vs. log surfactant concentration (Fig. 3). As the diagram shows, the curve consists of three distinct parts:

- diluted solutions with no change in rate constant (1st plateau);
- mildly concentrated solutions showing gradual increase in rate constant;



**Fig. 2** Viscosity-time profiles of 0.12% chitosan solution at 25°C at different EMPILAN KBS8 concentrations.  $\circ$  – 0.000001 mol/l EMPILAN;  $\square$  – 0.000005 mol/l EMPILAN;  $\triangle$  – 0.00001 mol/l EMPILAN;  $\diamond$  – 0.000025 mol/l EMPILAN;  $\star$  – 0.00005 mol/l EMPILAN;  $+$  – 0.0001 mol/l EMPILAN;  $\times$  – 0.0005 mol/l EMPILAN;  $*$  – 0.001 mol/l EMPILAN;  $\star$  – 0.005 mol/l EMPILAN;  $\boxtimes$  – 0.01 mol/l EMPILAN



**Fig. 3** Viscosity decrease rate constant of 0.12% chitosan solutions as a function of log surfactant (EMPILAN KBS8) concentration

- highly concentrated solutions with no change in rate constant (2nd plateau), but indicating slight decrease at very high concentrated solutions.

The part of the curve between two plateaus is considered as the transitional region to the saturation binding of the surfactant. This kind of data presentation enables estimation of critical surfactant concentration values  $C_1$

and  $C_2$ , corresponding to surfactant concentration for “beginning of interaction” and “saturation of the polymer”. As estimated by graphical extrapolation, these concentrations are:  $C_1 = 1 \cdot 10^{-5}$  mol/l and  $C_2 = 9 \cdot 10^{-4}$  mol/l. It is interesting to note that  $C_1$  value is less than the critical micelle concentration (CMC) of the surfactant ( $5.2 \cdot 10^{-5}$  mol/l as estimated from surface tension measurements).

This concept is similar to  $T_1$  and  $T_2$  concept, introduced for polymer–surfactant interaction investigated by surface tension measurements [20], which implies that  $T_1$  value is in general less than the CMC of the surfactant since associated state of the surfactant with polymer represents a more favourable energy condition for the surfactant molecules than regular micelles.

Comparing viscosity–time dependence results (Fig. 1) to rate constant vs. concentration curve (Fig. 3), it can be seen that a sudden viscosity drop began at certain surfactant concentration between  $C_1$  and CMC. Decrease of the viscosity with time (Fig. 1) was mostly pronounced in the region of surfactant concentration coincident with the region of increasing rate constant (Fig. 3). The concentration range between  $C_1$  and  $C_2$  corresponds to increase of interaction. The concentrations bigger than  $C_2$  correspond to solutions over which interaction exists but the polymer is “saturated” and increase of surfactant interaction does not have any influence on the interaction.

#### The use of aged chitosan stock solution

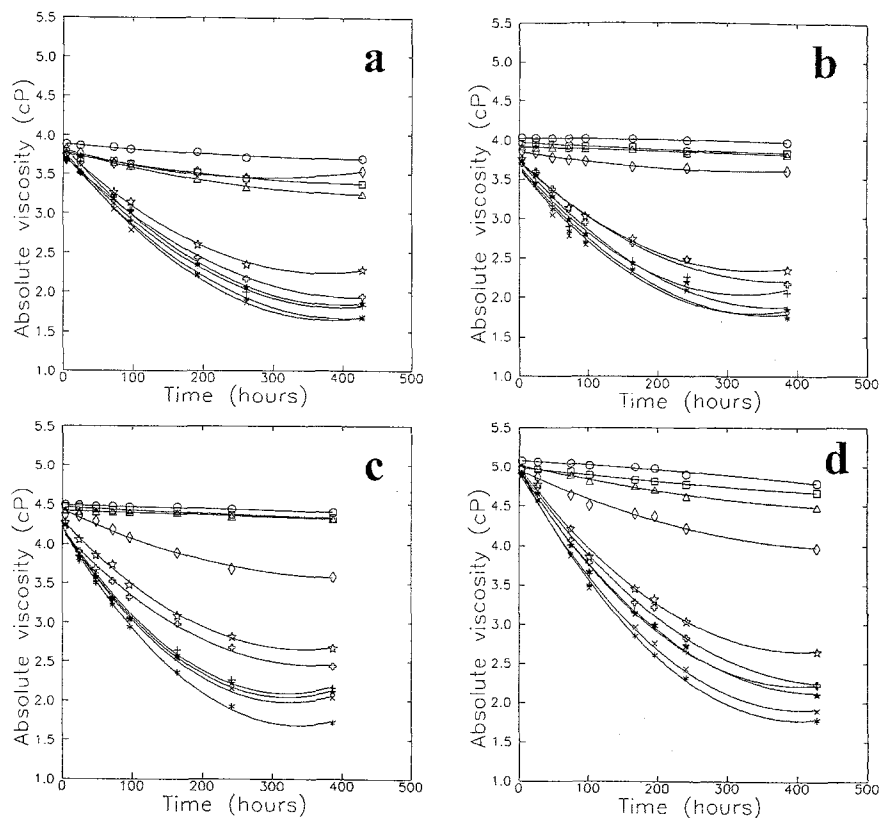
In order to follow only the influence of the surfactant and to avoid possible influence of the time dependence of the viscosity of chitosan solutions, for further experiments we used chitosan stock solution which had been prepared two months before the preparation of the chitosan/surfactant mixtures. The viscosity of this aged chitosan stock solution could be considered as stable in relation to time dependency. The surfactant solutions containing 0.08; 0.1; 0.12 and 0.14% chitosan have been prepared, and their viscosity measured – following time dependence of the viscosity over the longer period of time (up to 400 h after mixing). The obtained viscosity–time profiles for these solutions are presented at Fig. 4. It can be immediately seen that, in difference to Fig. 2 which presents viscosity–time profiles followed for a shorter period of time (about 200 h), the viscosity–time profiles of solution containing moderate and higher surfactant concentrations should not be considered as simple straight lines but as quadratic polynomial curves – parabolas (Eq. 2).

$$y = a + bx + cx^2 \quad (2)$$

Tables 1 to 4 show the values of coefficients for regression equation corresponding to investigated systems, and Fig. 5 presents corresponding rate constant vs. log surfactant concentration curves. It was expected that constant

**Fig. 4** Viscosity–time profiles of 0.08 (a), 0.1 (b), 0.12 (c) and 0.14% (d) chitosan solution at 25°C at different EMPILAN KBS8 concentrations (aged chitosan stock solution).

○ – 0.000001 mol/l EMPILAN;  
□ – 0.000005 mol/l EMPILAN;  
△ – 0.00001 mol/l EMPILAN;  
◇ – 0.000025 mol/l EMPILAN;  
☆ – 0.00005 mol/l EMPILAN;  
+ – 0.0001 mol/l EMPILAN;  
× – 0.0005 mol/l EMPILAN;  
\* – 0.001 mol/l EMPILAN;  
★ – 0.005 mol/l EMPILAN;  
⊕ – 0.01 mol/l EMPILAN



**Table 1** Coefficients for regression equation for chitosan 0.08% solution with EMPILAN

Surfactant conc. (mol/l)	Coefficients for regression equation			Correlation coefficient
	a	b	c	
0.000001	3.89	0.0008385	0.00000081	97%
0.000005	3.77	0.0016971	0.00000176	99%
0.00001	3.80	0.0024405	0.00000262	100%
0.000025	3.82	0.0025480	0.00000436	98%
0.00005	3.82	0.0085199	0.00001140	100%
0.0001	3.79	0.0100732	0.00001277	99%
0.0005	3.80	0.0113353	0.00001484	100%
0.001	3.76	0.010409	0.00001291	100%
0.005	3.86	0.0102596	0.00001296	99%
0.01	3.74	0.0086823	0.00001038	100%

**Table 2** Coefficients for regression equation for chitosan 0.1% solution with EMPILAN

Surfactant conc. (mol/l)	Coefficients for regression equation			Correlation coefficient
	a	b	c	
0.000001	4.03	0.0000457	0.00000031	96%
0.000005	3.98	0.0005443	0.00000043	97%
0.00001	3.92	0.0002374	0.00000015	96%
0.000025	3.86	0.0015113	0.00000220	98%
0.00005	3.73	0.0082822	0.00001221	99%
0.0001	3.67	0.010162	0.00001574	98%
0.0005	3.63	0.0108849	0.00001614	97%
0.001	3.65	0.0105079	0.00001471	98%
0.005	3.73	0.0101938	0.00001399	99%
0.01	3.72	0.0081019	0.00001077	99%

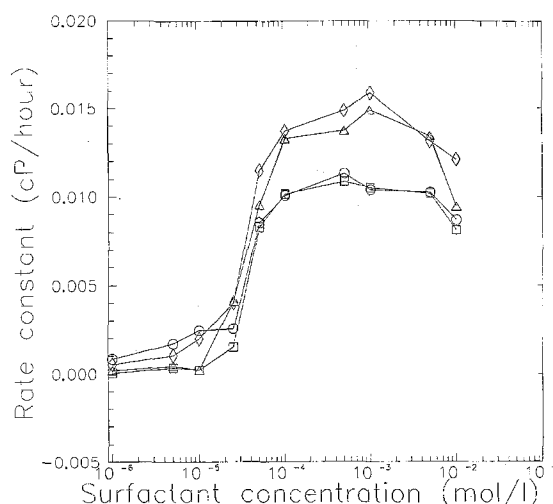
**Table 3** Coefficients for regression equation for chitosan 0.12% solution with EMPILAN

Surfactant conc. (mol/l)	Coefficients for regression equation			Correlation coefficient
	a	b	c	
0.000001	4.49	0.0001959	-0.00000007	96%
0.000005	4.47	0.0004490	+0.00000025	95%
0.00001	4.42	0.0002168	-0.00000015	95%
0.000025	4.43	0.0041138	-0.00000486	99%
0.00005	4.30	0.0095318	+0.00001385	100%
0.0001	4.21	0.0132806	+0.00002079	99%
0.0005	4.19	0.0137402	+0.00002131	100%
0.001	4.19	0.0149160	+0.00002214	100%
0.005	4.19	0.0134207	+0.00002094	100%
0.01	4.15	0.0094427	+0.00001311	99%

term *a* is independent on the surfactant concentration, but, however, a slight variation ( $\pm 5\%$ ) was obtained (Tables 1 to 4). As the second order constant *c* was small for all surfactant concentrations, and the first order constant *b* is considered as a measure of degree of viscosity decrease per

**Table 4** Coefficients for regression equation for chitosan 0.14% solution with EMPILAN

Surfactant conc. (mol/l)	Coefficients for regression equation			Correlation coefficient
	a	b	c	
0.000001	5.08	0.0005299	-0.00000039	97%
0.000005	4.99	0.0010317	+0.00000064	99%
0.00001	5.02	0.0019669	+0.00000168	99%
0.000025	4.95	0.0040392	+0.00000413	98%
0.00005	4.99	0.0114721	+0.00001412	100%
0.0001	4.97	0.0137160	+0.00001707	100%
0.0005	4.92	0.0148869	+0.00001833	100%
0.001	4.97	0.0158912	+0.00001975	100%
0.005	4.94	0.0131281	+0.00001527	100%
0.01	4.97	0.0120916	+0.00001387	99%

**Fig. 5** Viscosity decrease rate constant of 0.08, 0.1, 0.12 and 0.14% chitosan solutions as a function of log. surfactant (EMPILAN KBS8) concentration.  $\circ$  – 0.08% chitosan;  $\square$  – 0.1% chitosan;  $\triangle$  – 0.12% chitosan;  $\diamond$  – 0.14% chitosan

unit of surfactant applied, only the latter was used for formation of the rate constant vs. log surfactant concentration curves (Fig. 5). However, the contribution of the second order constant *c* to the viscosity decrease must be taken into account when estimating the chitosan/surfactant system viscosity – particularly at higher surfactant concentrations, in order to avoid errors in estimation.

Figure 5 clearly shows that with increasing surfactant concentration over certain limit independently on the chitosan concentration, the decrease in the rate constant was obvious – which implied lowering of interaction between chitosan and surfactant. This behaviour could be possibly attributed to the establishing of the factors opposing chitosan-surfactant interaction as well as solubilization properties of concentrated surfactant solution. The

surfactant concentration which corresponds to the beginning of the decrease of the rate constant (Fig. 5) could be marked as  $C_3$ , signifying the beginning of desintegration of the polymer-surfactant associate. The results presented in Fig. 5 also show that the values of the rate constant depend on chitosan concentration. It seems that more concentrated chitosan solutions show bigger values of the rate constant and hence faster lowering of the viscosity with time, but the surfactant ranges responsible for interaction seem unchanged.

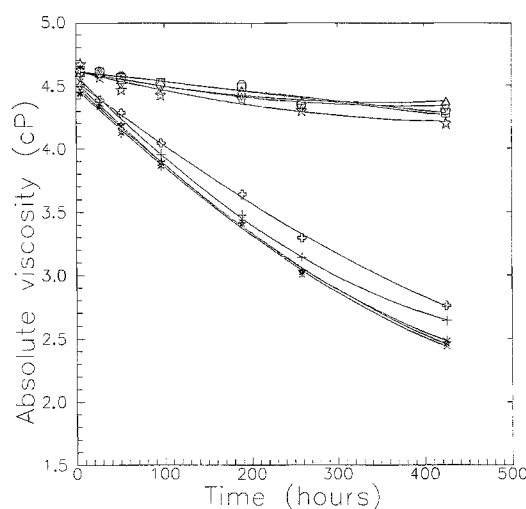
If the results obtained for shorter period of time (200 h) are compared with results obtained for longer period of time (400 h), the difference in viscosity-time curve shape, hence the difference in the degree of polynomial chosen for curve fitting, particularly for higher surfactant solutions, is obvious. Also, comparing the plots obtained for samples prepared from non-aged and aged chitosan stock solutions, the main difference is noticed at low surfactant concentrations where the rate constants of solutions prepared from aged stock solution are close to zero and almost coincident over the certain surfactant concentration range. This could be explained by the absence of any kind of interaction since chitosan viscosity was stabilized by the aging of chitosan stock solution. It confirms the fact that viscosity time dependence of the system could be considered as the consequence of the presence of surfactant.

The solutions containing guaranteed pure surfactant

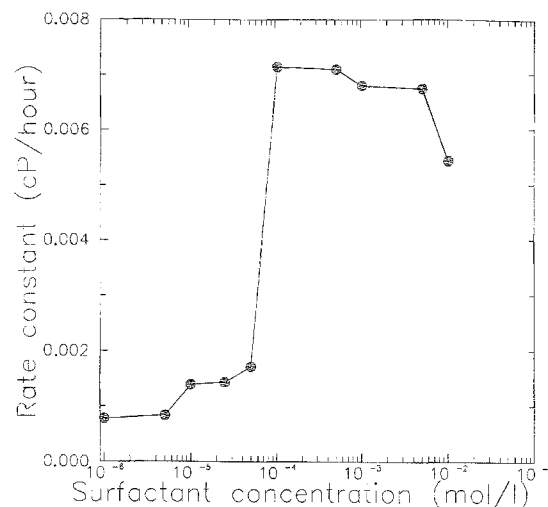
Since nonionic surfactant used is a technical grade product it could be assumed that it contains a certain amount of impurities. It is known that impurities usually present in nonylphenol ethoxylate adducts are free polyethylene glycol and normally very little phenol. The presence of electrolytes is not probable. In order to avoid very low but anyhow present possibility that impurities are responsible for chitosan-surfactant interaction, the guaranteed pure surfactant NIKKOL has been used for repeated measurements, and results are presented in Figs. 6 and 7, as well as in Table 5. These results imply the existence of the same kind of interaction, in the same surfactant concentration region, only with noticeable lower magnitude of rate constants and with a very clearly defined and sharp transitional part of the curve. The values  $C_1$ ,  $C_2$  and  $C_3$  are clearly defined.

The model proposed for the interaction

Obtained results show that viscosity curves for the chitosan- $C_{12}E_8$  system follow the suggestions given for



**Fig. 6** Viscosity-time profiles of 0.12% chitosan solution at 25 °C at different NIKKOL BL-8 SY concentrations.  $\circ$  – 0.000001 mol/l NIKKOL;  $\square$  – 0.000005 mol/l NIKKOL;  $\triangle$  – 0.00001 mol/l NIKKOL;  $\diamond$  – 0.000025 mol/l NIKKOL;  $\star$  – 0.00005 mol/l NIKKOL;  $+$  – 0.0001 mol/l NIKKOL;  $\times$  – 0.0005 mol/l NIKKOL;  $*$  – 0.001 mol/l NIKKOL;  $\star$  – 0.005 mol/l NIKKOL;  $\boxplus$  – 0.01 mol/l NIKKOL



**Fig. 7** Viscosity decrease rate constant of 0.12% chitosan solutions as a function of log. surfactant (NIKKOL BL-8 SY) concentration

other polymer/surfactant systems by other authors [19–20]. The investigated chitosan solutions (pH 4, semi-concentrated) contain acetic acid in excess and ionic strength of the solutions is very low since acetic acid is a weak electrolyte ( $pK_a$  4.76) whose increasing of concentration leads to nonsignificant increase of  $CH_3COO^-$  ions. In these circumstances amino groups of the chitosan are supposed to be protonated, and since increased protonation increases electrostatic repelling between charged

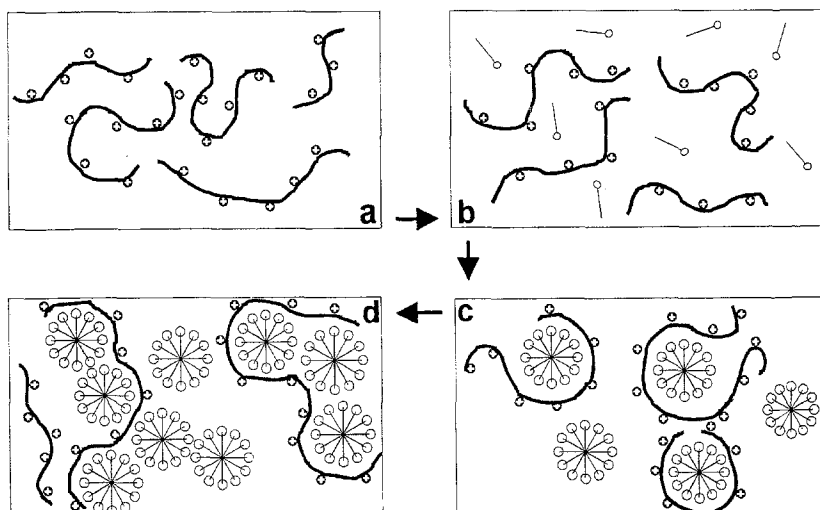
groups of the same sign, it leads to increased swelling of the macromolecules [6]. In difference to dilute chitosan solutions where only intramolecular and polyion-solvent interactions influence hydrodynamic behaviour, investigated systems show increased probability of intermolecular contacts and macromolecules tend to be linear which promotes viscosity of the system (Fig. 8a). When surfactant is added (Fig. 8b) there is no change in the conformation of chitosan molecules, until certain surfactant concentration  $C_1$  is reached. The existence of critical binding concentration ( $C_1$ ) implies that chitosan-surfactant association is a cooperative process and must involve a surfactant micelle. In order to explain the observed phenomena, it is important to note that at 25 °C the  $C_{12}E_8$  is believed to form small spherical micelles in the entire range of surfactant concentration studied, hence the aggregation number of  $C_{12}E_8$  is constant [21–22].

**Table 5** Coefficients for regression equation for chitosan 0.12% solution with NIKKOL

Surfactant conc. (mol/l)	Coefficients for regression equation			Correlation coefficient
	a	b	c	
0.000001	4.61	0.0007749		93%
0.000005	4.62	0.0008316		96%
0.00001	4.62	0.0014007	+ 0.00000196	95%
0.000025	4.62	0.0014372	+ 0.00000182	97%
0.00005	4.62	0.0017106	+ 0.00000177	92%
0.0001	4.58	0.0071404	+ 0.00000605	100%
0.0005	4.53	0.0070941	+ 0.00000508	100%
0.001	4.48	0.0067961	+ 0.00000490	100%
0.005	4.50	0.0067448	+ 0.00000453	100%
0.01	4.54	0.0054360	+ 0.00000289	100%

Formation of the chitosan-surfactant associate (Fig. 8c) gives rise to important conformational changes in the chitosan molecule, and could be supposed that chitosan molecules are adsorbed at the interface between the surfactant micellar core and water in order to minimize electrostatic interactions between chitosan molecules. The spherical surfactant micelles bound by chitosan molecule become positively charged and find themselves at a certain distance because of the charge repulsion effects. This process continues with increasing surfactant concentration until every available chitosan molecule has one micelle bound on it (a fraction of chitosan is free since there always exists a thermodynamical equilibrium between free and associated molecules). Once chitosan saturation with only one micelle has been reached ( $C_2$ ), with further increasing of surfactant concentration the rate constant does not increase until the total surfactant concentration required for forming bridges between neighbouring micelles ( $C_3$ ) is reached. At this concentration (Fig. 8d) chitosan presumably adsorbs onto more than one micelle. Chitosan-surfactant associates composed of a series of spherical micelles with their surfaces wrapped by chitosan segments and connected by chitosan strands belonging to the same chitosan molecule coexist with free chitosan molecules and free surfactant micelles. Steric repulsion within the chitosan layer surrounding micelle surface begin to be strong enough and this is the main factor opposing association. The proposed model fits well with the results obtained for chitosan/ $C_{12}E_8$  system and it is based on the fact that there is no important change in micellar size with surfactant concentration. However, it must be noted that conformation change of the chitosan molecules in the investigated systems is very slow and this is the main reason for the existence of time-dependence.

**Fig. 8** Simple model of association between chitosan and  $C_{12}E_8$ . Schematic representation of the effect of surfactant concentration. a) no surfactant added; b) a small amount of surfactant added (below  $C_1$ ); c) higher surfactant concentration (between  $C_1$  and  $C_2$ ); d) very high surfactant concentration (over  $C_3$ )





## Conclusion

The viscosity of chitosan/ $C_{12}E_8$  system shows considerable time dependence which suggested existence of the chitosan-surfactant interaction. The most pronounced time dependence is shown in the form of a viscosity drop in a region close to and above CMC of the pure surfactant solution.

The presentation of the viscosity time dependence in the form of the viscosity-time profiles made possible the calculation of the viscosity decrease rate constants and showed the existence of critical surfactant concentration

values ( $C_1$ ,  $C_2$  and  $C_3$ ) which could be closely connected with proposed chitosan/ $C_{12}E_8$  interaction model.

The observed change of the viscosity of chitosan solution upon addition of surfactant can be explained by the interplay between the chitosan polyelectrolyte effect and possible conformational changes related to the presence of the surfactant and association of the chitosan molecules with surfactant micelles.

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