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Approach to hydrodynamic equilibrium and its time dependence in the system EHEC/SDS/Water

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Abstract: The properties of the system EHEC/SDS/water in solution show considerable time dependence during several hours after preparation. The paper discusses various reasons for this time dependence. Similar time dependence in polymer solutions has been observed elsewhere. It is found that although the system properties vary, a true equilibrium is finally attained for all compositions. The most pronounced time dependence is shown in a region close to and above the CMC of a pure surfactant solution and for polymer concentrations at least equal to the critical overlap concentration. It is proposed that part of the explanation resides in the fact that in the solution preparation there appears intermediate states corresponding to high local polymer concentrations. Some quantitative aspects of the time dependence are also discussed.

Key words: Time dependence – viscosity – ethyl hydroxyethyl cellulose – sodium dodecyl sulphate – overlap concentration

Introduction

Recent investigations on the interaction between low molecular weight anionic surfactants and polymers in water solution, in particular the system ethylhydroxyethyl cellulose (EHEC)/ sodium dodecylsulphate (SDS)/water [1, 2], have indicated a very complex behavior. The properties of the EHEC/SDS/water system depend on the concentration of the surfactant as well as on that of the polymer in a very sensitive way which indicates clustering of the surfactant to the polymer backbone in the dilute polymer regime. For higher polymer concentrations intermolecular interaction between the polymer molecules become pronounced and there are signs of aggregation and even of gel formation.

Obviously, the properties of such a system could depend on its prehistory, especially if metastable states are being formed. However, extensive investigations presented here support the view that a true equilibrium is attained by a time-dependent process that may extend over several hours. Already at an early stage of our investigations of the system EHEC/SDS/water experiments indicated [1] that the system properties, for instance the viscosity, were strongly time dependent and ample time had to be allowed for the system to attain stable (equilibrium) properties. Some possible explanations were also presented based on the fact that in the solution preparation the composition change was such that states with considerable intermolecular interaction had to be "passed" before the final state was reached. Very precise surface tension studies performed in this laboratory by Nahringbauer [3] according to the pending drop technique support the view that considerable molecular changes take place in the SDS/EHEC/water system over a time scale comparable to the one we have observed. It was even possible for Nahringbauer to indicate changes that very likely refer to conformational rearrangements. The time scale of these rearrangements was of the same order of magnitude as other rearrangements observed in polymers on surfaces.

The previous publication [1] discusses equilibrium properties of the system SDS/EHEC/water. Some time-dependent effects have earlier been described for the dissolution process of EHEC in water [4]. However, in the characterization of EHEC and its interaction with certain additives in solution no such effects were described earlier [2, 5, 6]. Nevertheless, such 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.

Recently, time-dependent effects of a similar nature have been discussed for other important polymer systems [7, 8].

The present paper aims at a more extensive discussion of the origin of the time-dependent effects observed in the hydrodynamic studies. Three issues might thereby identified: a) to find unambiguous schemes to prepare well defined solutions showing equilibrium properties; b) to establish whether or not long lived metastable states are present, and if so, their relation to true equilibrium; c) to try to gain further insight into the system properties by a detailed investigation of the time evolution of system properties. Obviously, long-lived initial non-equilibrium properties of the type observed could be of practical importance.

Experimental

Ethyl hydroxyethyl cellulose (EHEC, fraction CST-103) with a weight average molecular weight (M_w) of approximately 480 000 was obtained from Berol Kemi AB, Stenungsund, Sweden. The cloud point (CP) of aqueous EHEC solutions was determined by visual observation in glass tubes and taken as the temperature when the last visible sign of clouding in the solution disappeared upon cooling. The CP of EHEC/CST-103 was observed in the interval 28–37° depending on the polymer concentration (see Fig. 1). If SDS is added to aqueous, salt free EHEC-solutions the CP is raised (see Fig. 2). Both these observations (Figs. 1 and 2) can be explained as effects of the hydrophobic properties of the system and their changes with polymer and additive concentration.

Time-dependent viscosity effects have also been found in some other EHEC/SDS/water systems for fractions with low CP (approx. 30–40 °C) but not found in other fractions with a high CP (approx. 60–80 °C) [9]. This fact indicated that the mechanism which is operating in the system is closely related to phase separation (or its incipient stage) and to the hydrophobic/hydrophilic balance in the system, cf. Figs. 1 and 2 concerning the cloud point variation.

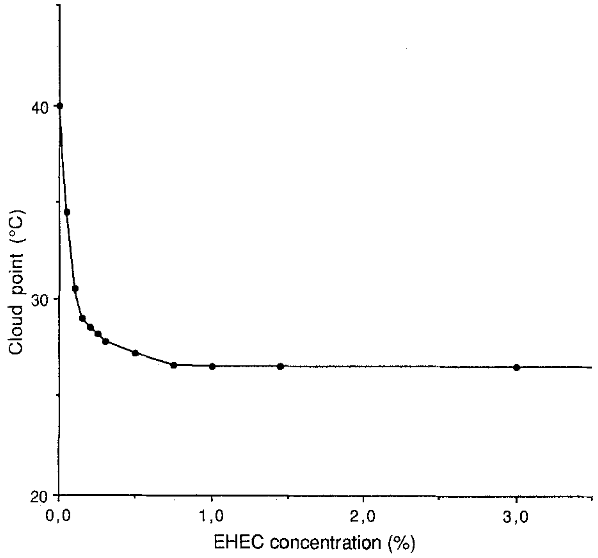

Fig. 1. Cloud point as a function of the EHEC concentration in the absence of SDS

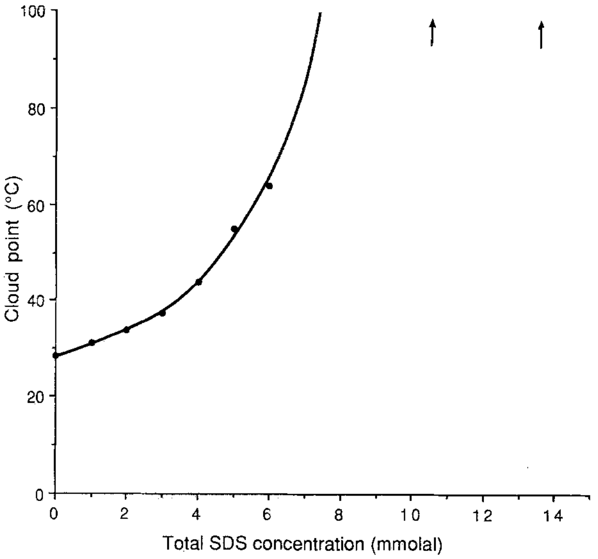

Fig. 2. Cloud point versus the total SDS concentration for 0.20% EHEC/water solutions

The procedure adopted to make an EHEC stock solution is described in a previous paper [1]. According to the manufacturer's recommendation [10] the stock solution was tested for degradation due to hydrolysis or action of microorganisms by measuring the viscosity at regular intervals (every second month). Analytical grade sodium dodecyl sulphate (SDS), supplied from Merck, was used without further purification. Both conductometric and surface tension measurements on the SDS/water system at 20 °C gave very smooth curves with a clear cut CMC breakpoint at 8.2 mM. The experiments were performed at pH ≈ 7 where SDS is stable [11]. Doubly distilled and filtered water was used as solvent in all experiments. All solutions were prepared by weight. EHEC and SDS concentrations are expressed in percent by weight (with good precision equal to grams per 100 ml; the corresponding concentration expressed as grams per ml is denoted c_P) and moles per kilogram of solvent (molal) respectively. For higher accuracy the following formula for the density variation of a water solution of EHEC and SDS can be used.

$$\rho = \rho_0 + a \cdot c_P + b \cdot [\mathrm{SDS}] \tag{1}$$

Here, ρ is the solution density, ρ_0 is the density of water, a and b are experimental parameters (density increments), and c_P is the polymer (EHEC) concentration. [SDS] is the surfactant concentration. The density determinations were performed in a digital densitometer DMA O2C Anton Paar K.G. [12]. The following values apply: At 20 °C $a = 0.30582$, $b = 4.4405 \cdot 10^{-2}\,\mathrm{g\,cm^{-3}\,M^{-1}}$; at 30 °C $a = 0.56463$, $b = 4.8410 \cdot 10^{-2}\,\mathrm{g\,cm^{-3}\,M^{-1}}$.

Solutions are normally prepared by mixing stock solutions – one containing EHEC in water and one containing SDS in water. A three component solution of given overall composition can be prepared from different concentrations of such stock solutions and by varying the order of mixing. However, different procedures lead to different initial viscosities and to a different time development towards the equilibrium value. This was observed early in our investigation and to avoid ambiguity the mixing order and stock solution concentration were standardized in our previous work [1]. To the appropriately diluted SDS stock solution a smaller volume of a concentrated (1.5% w/w) stock solution of EHEC was added, volumes and concentrations being selected to achieve the desired overall composition.

In the previous work all solutions were allowed to stand for about 12 h to make sure they had attained equilibrium. In the present paper, on the other hand, the dynamic process to attain equilibrium is studied and measurements have to be started very soon after solution preparation. The EHEC and SDS stock solutions and the doubly distilled water used for solution preparation were thermostated for about 14 h before mixing. The solution was transferred to the viscometer immediately after mixing. The starting time ($t = 0$) was taken to be the time when the EHEC solution was added to the diluted SDS-solution. Before any viscosity measurement could be performed a couple of minutes necessarily passed due to i) the need to mix the solutions, and ii) the time it takes for the liquid to flow through the viscometer. This time delay is sufficiently long to only allow measurements to be performed on the decaying part of the schematic curve in Fig. 12. The value $\eta(0)$, discussed later in connection with Eq. (4), has been obtained by extrapolation from this decaying part of the $\eta(t)$-curve.

Results will also be reported on the reversed mixing order, i.e., the EHEC stock solution appropriately diluted in water and concentrated (0.1 molal) SDS solution added as the last component into the solution. Similar results are obtained for solutions prepared by mixing three component solutions of various initial compositions.

The viscosity measurements were carried out in ordinary Ostwald capillary viscometers (approx. solvent flow time 100 s). Results are reported in terms of the dimensionless ratio $y = \eta(t)/\eta(0) = \eta_{\mathrm{rel}}(t)/\eta_{\mathrm{rel}}(0)$, where $\eta(t)$ denotes the viscosity (or rather the viscometer flow time) at time t after solution mixing (see above) and η_{rel} the relative viscosity with respect to solvent or some standard solution, see below. In some data presentations the results have been converted to reduced specific viscosities $\eta_{\mathrm{sp}}(t)/c$, where for simplicity $c = c_P$ and $\eta_{\mathrm{sp}}(t)$ is defined by

$$\eta_{\mathrm{sp}}(t) = [\eta(t) - \eta_r]/\eta_r\,, \tag{2}$$

and η_r is the viscosity of an SDS solution of the same composition.

All viscosity experiments were performed in a thermostated water bath. The data in this paper are obtained at 20 °C except for a few cases where the temperature was set to 30 °C, i.e. close to the CP of the EHEC fraction. Solutions allowed to attain time equilibrium were tested for possible non-Newtonian behavior over the entire composition range at 20 °C. However, up to $c_P = 0.4\%$ no such effect could be detected.

Experimental observations and results

One of the most conspicuous properties of the system EHEC/SDS/water in a temperature range below the cloud point is the strong viscosity maximum [1] (cf. Fig. 3) developed in an interval of the SDS concentration slightly below the normal CMC point for SDS in water ($[SDS]_{CMC} = 8.2$ mM at 20 °C, [11]). The present paper will deal almost exclusively with the time dependent effects observed for the viscosity measurements in an [SDS] interval from 0 to 14 mM, i.e. well below and above the normal CMC. It should then be recalled [1] that a viscosity increase with increasing [SDS] for constant polymer concentration, c_P, is only observed if $c_P > c_{crit}$, where $c_{crit} \approx 0.0015$ g/ml at 20 °C for EHEC fraction CST-103 used in this study. The polymer concentration corresponding to beginning of coil overlap is according to [1] for the same EHEC fraction given by $c^* \approx 1/[\eta] = 0.0023$ g/ml. The close agreement between c_{crit} and c^* indicates that the viscosity increase is connected with interpolymer interactions, possibly through SDS clusters [13–18]. An increase in temperature towards the cloud point makes the effects observed even more pronounced (cf. Fig. 4).

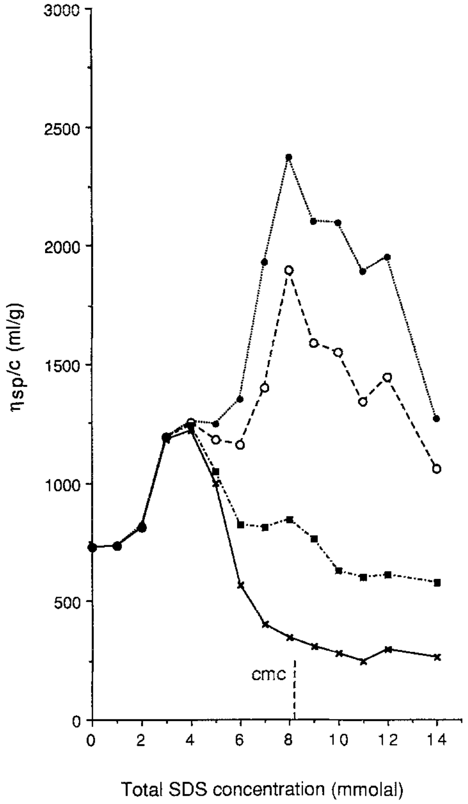

Fig. 3. Viscosity results at 20 °C based on the primary data in Fig. 6. η_{sp}/c as a function of the total SDS concentration at four different times after mixing of the EHEC/SDS/water solutions. The EHEC concentration (c) is 0.20% and CMC for the SDS/water system is indicated. ···●··· $t = 0$ min, --○-- $t = 5$ min, ---■--- $t = 30$ min, —×— $t = \infty$ min

A number of papers have described various aspects of surfactant/polymer interaction in solution [19–22] from a general physico-chemical point of view, but there has been no mention of any type of time dependence of solution properties. Furthermore, there is a general tendency for cluster formation in this interaction [13–18] which, according to our interpretation [1], is responsible for the pronounced viscosity effects observed.

The interpolymer interaction may extend over considerable distances in solution if c_P is high enough. The interaction is enhanced by the presence of SDS, possibly by the formation of clusters that may constitute tie points in three-dimensional network aggregates. Such "interaction aggregates" could be long lived. If this is the case the behavior of solutions becomes critically dependent upon the procedure adopted for their preparation. If, for instance, a composition $[SDS] > [SDS]_{max}$ (where $[SDS]_{max}$ denotes the concentration corresponding to viscosity maximum) should be achieved, the mixing of one solution containing only EHEC with one containing only SDS must ultimately "pass" the intermediate composition corresponding to the viscosity maximum. Thus, long-lived "interaction aggregates" may form and one has to wait for them to disintegrate before equilibrium is reached.

The experiments have agreed qualitatively with this picture. It has been observed that in certain

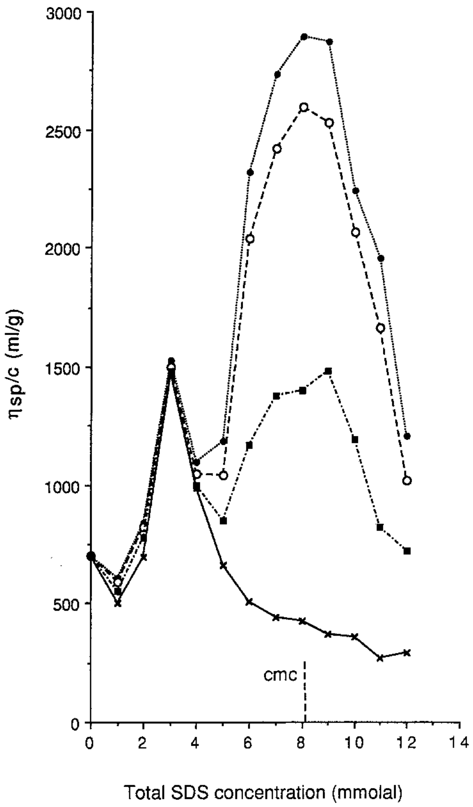

Fig. 4. Viscosity results at 30 °C based on the primary data in Fig. 7. η_{sp}/c versus the total SDS concentration at different times after mixing of the solutions. The EHEC concentration (c) is 0.20% and CMC for the SDS/water system is indicated. ···●··· $t = 0$ min, --○-- $t = 5$ ---■--- $t = 30$ min, —×— $t = \infty$ min

composition regions a blurring of the solutions resembling phase separation sometimes occurs. If the above interpretation is correct the microscopic composition of the solution could vary considerably from point to point and those parts corresponding to the viscosity maximum would dominate the hydrodynamic properties.

Assuming that this interpretation is correct, certain features of the viscosity behavior could be anticipated. One would be that the viscosity time dependence should depend strongly on composition, this dependence being most pronounced for those compositions that correspond to an [SDS] value somewhat higher than the viscosity maximum. A second feature would be that during the approach to equilibrium the viscosity would never attain a value higher than the maximum for the equilibrium situation corresponding to some intermediate polymer and SDS composition. A third feature would be that if the initial solutions from which the final solution is prepared are varied, at least the amplitude of the time dependence could be expected to change. For instance, mixing two solutions both with compositions on the high [SDS] side of the maximum should give a decreased time dependence. The time dependence should likewise be reduced if first the EHEC/water system is diluted and then SDS is added (cf. Fig. 5). All these features are compatible with the experimental observations.

An important question is if the analytical form of the time dependence can be reconciled with a specific physical model, possibly allowing rate constant estimates to be extracted from the numerical analysis.

Figure 6 gives the primary data for the time dependence of the viscosity ratio $y = \eta(t)/\eta(0)$ at 20 °C for a set of SDS concentrations already shown in Fig. 3. The general feature of the $y(t)$-curves in Fig. 6 with a steep drop at short times followed by a flattening out to an asymptotic constant value for long times is common to all experiments. However, the "amplitude" of the drop varies with the conditions of the experiment. A more detailed analysis of the $y(t)$-curves is

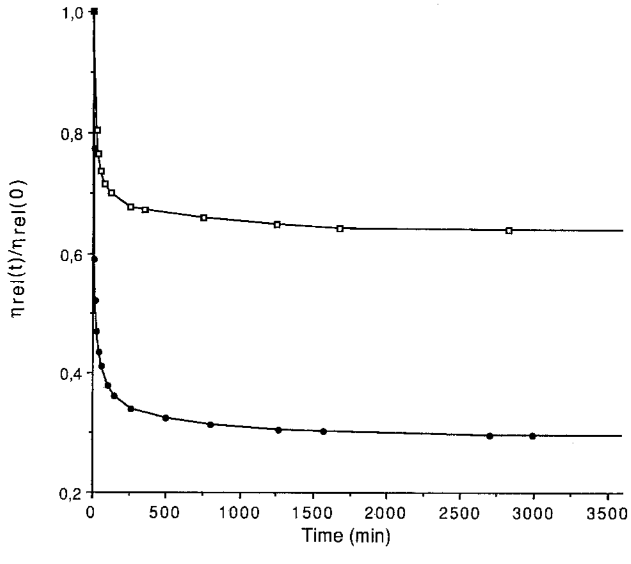

Fig. 5. Viscosity ratio, $\eta_{rel}(t)/\eta_{rel}(0)$, as a function of time for two 0.20% EHEC/8 mm SDS/water solutions with different order of mixing of the components at 20 °C. □ 1) EHEC, 2) water, 3) SDS, ● 1) SDS, 2) water, 3) EHEC. (1–3 indicates the order of adding each component)

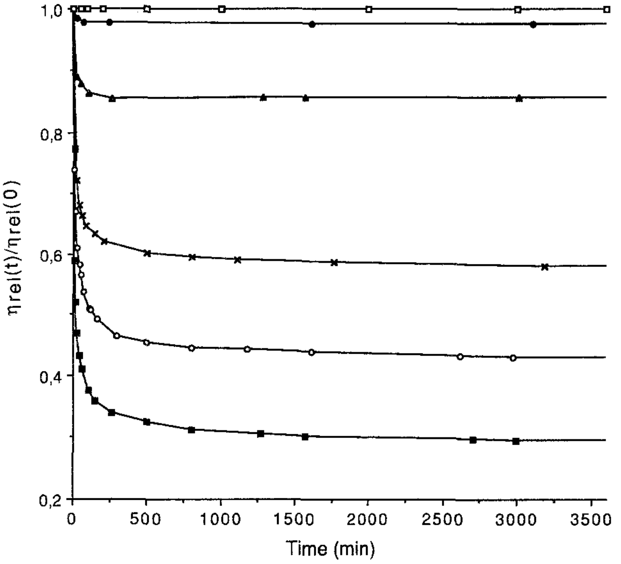

Fig 6. Hydrodynamic (viscosity) time dependence at 20 °C in the EHEC/SDS/water system presented as the viscosity ratio $\eta_{\mathrm{rel}}(t)/\eta_{\mathrm{rel}}(0)$ as a function of time for the following compositions: □ 0.20% EHEC + 1 m*m* SDS, ● 0.20% EHEC + 4 m*m* SDS, ▲ 0.20% EHEC + 5 m*m* SDS, × 0.20% EHEC + 6m*m* SDS, ■ 0.20% EHEC + 8m*m* SDS, ○ 0.20% EHEC + 14m*m* SDS

presented in section "Approach to equilibrium quantification" below. To get a "spectral" resolution of the time dependence along the [SDS]-axis, Fig. 6 has been used to construct Fig. 3, where y-values also have been transformed to reduced viscosity, $\eta_{\mathrm{sp}}(t)/c$, according to relation (3). At finite polymer concentrations the reduced viscosity can be written, if normal polymer theory applies,

$$\begin{aligned}\eta_{\mathrm{sp}}(t)/c &= f(t)\\ &= [\eta]_t + (\text{interpolymer interactions})_t\,,\end{aligned} \tag{3}$$

where $c = c_P$ and index t indicates the time dependence. If expression (3) is assumed to apply even in a non-equilibrium situation and in the presence of SDS, the experimentally accessible quantity $f(t)$ will give the time variation of the sum of the hydrodynamic coil volume and the interpolymer interaction. Our previous results [1] have shown that at the position of the viscosity maximum the equilibrium value of $[\eta]$ passes through a minimum and the interpolymer interaction through a maximum. The numerical variation of the interaction coefficient is almost twice as large as the variation of $[\eta]$. Furthermore, the interaction term is strongly dependent on the polymer concentration c. Inhomogeneities in the solution with c much larger than the average might therefore contribute to the overall viscosity with very large interaction terms. The life time of these inhomogeneities would then determine the change in viscosity with time, It is clear from Fig. 6 that at least during the first 30 min there is a considerable time dependence in $f(t)$ for $[\mathrm{SDS}] > [\mathrm{SDS}]_{\max}$ (where $[\mathrm{SDS}]_{\max}$ denotes the concentration corresponding to viscosity maximum). For $[\mathrm{SDS}] < [\mathrm{SDS}]_{\max}$ no time dependence could be observed at 20 °C. It could also be noted that the maximum in the time dependence corresponds to the normal CMC for SDS (see Fig. 3).

If the same experiments are repeated at 30 °C, which is close to the cloud point, one obtains very similar curves (see Figs. 4 and 7). A few observations could be made directly, however. The time dependence of the reduced viscosity is even more pronounced and seems to cover a somewhat broader [SDS] interval. Furthermore, the strong

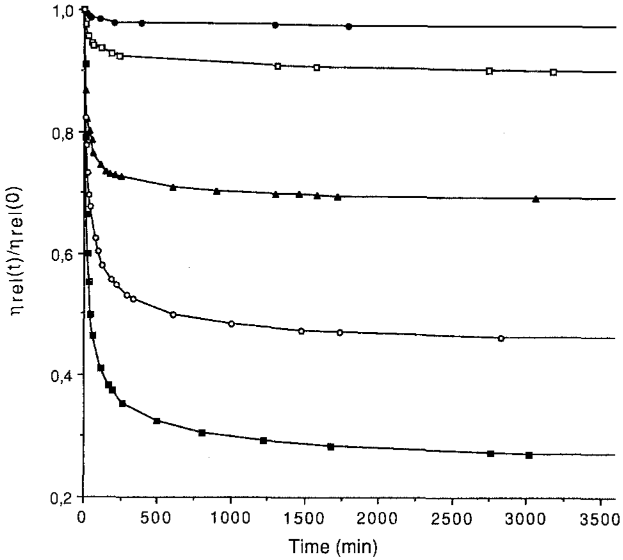

Fig. 7. Hydrodynamic (viscosity) time dependence at 30 °C. Viscosity ratio, $\eta_{\mathrm{rel}}(t)/\eta_{\mathrm{rel}}(0)$, as a function of time for the following compositions: □ 0.20% EHEC + 2m*m* SDS, ● 0.20% EHEC + 3m*m* SDS, ▲ 0.20% EHEC + 5m*m* SDS, ■ 0.20% EHEC + 8m*m* SDS, ○ 0.20% EHEC + 12m*m* SDS

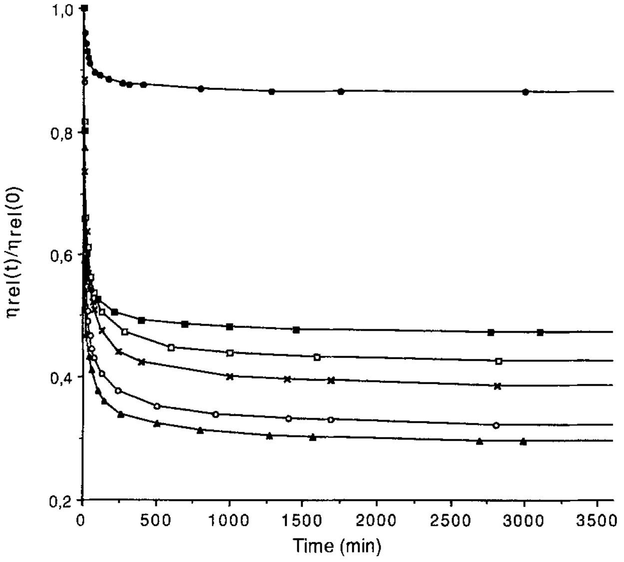

Fig. 8. Viscosity ratio, $\eta_{rel}(t)/\eta_{rel}(0)$, for 8 m*m* SDS/water solutions with different EHEC-concentrations at 20 °C as a function of time. ● 0.05% EHEC + 8m*m* SDS, ■ 0.10% EHEC + 8m*m* SDS, ▲ 0.20% EHEC + 8m*m* SDS, ○ 0.25% EHEC + 8m*m* SDS, × 0.30% EHEC + 8m*m* SDS, □ 0.32% EHEC + 8m*m* SDS

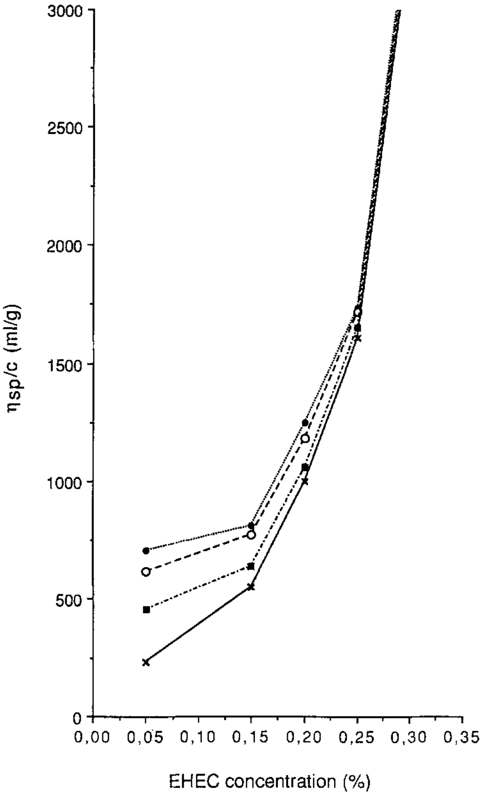

Fig. 9. η_{sp}/c for 5 m*m* SDS/water solutions versus the EHEC concentration at 20 °C and at different times after mixing of the solutions. ···●··· $t = 0$ min, --○-- $t = 5$ ----■--- $t =$ 30 min, —×— $t = \infty$ min

time dependence occurs for [SDS]-values where even in the equilibrium situation at elevated temperatures the reduced viscosity shows a second maximum [23]. The first equilibrium viscosity maximum is more narrow. There is also a slight time dependence for low values of [SDS]. Here, the system is very close to CP. Finally, the $y(t)$-curves in Fig. 7 seem to have a more extended decay, especially for those corresponding to the [SDS] values 8 and 12 mM.

The results in Figs. 3, 4, 6, 7 have been obtained for a constant polymer concentration of $c_P = 0.20\%$. Since the polymer interaction effect is very strong the variation of $\eta_{sp}(t)/c$ with time has been determined as a function of polymer concentration up to $c_P = 0.32\%$ and for [SDS] equal to 5, 8, and 14 mM, respectively. The basic data are given in terms of $y = \eta_{rel}(t)/\eta_{rel}(0)$. The results are collected in Figs. 8–11.

Figure 9 corresponds to [SDS] = 5 mM, which is close to the position of the equilibrium viscosity maximum and $\eta_{sp}(t)/c$ increases very steeply for $c_P > 0.2\%$. Furthermore, the steeper the curve the less becomes the time dependence. This result supports the view that the strong time dependence of viscosity resides in the formation of long-lived aggregates corresponding to, say, $c_P \approx 0.3\%$ and [SDS] $\approx$ 5 mM. There is a clear time dependence also in Figs. 10 and 11, but it decreases with increasing [SDS] and, for the highest values of c_P, it decreases (Fig. 10, [SDS] = 8 mM) or flattens out (Fig. 11, [SDS] = 14 mM). These last observations could be interpreted as a competition between the hydrophobic groups of the polymer to interact with themselves as compared to the interaction with SDS.

The viscosity evolution

In order to better understand the change in properties of the system with time, one must somehow try to envisage the processes involved in the solution preparation. As already mentioned, two stock solutions are normally mixed. One (I) consists of a fairly concentrated (1.5%) EHEC

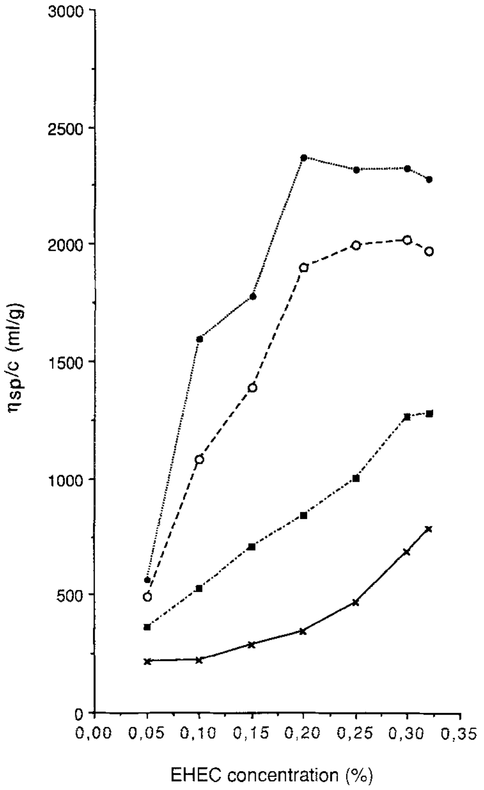

Fig. 10. η_{sp}/c for 8m*m* SDS/water solutions versus the EHEC concentration at 20 °C and at different times after mixing the solutions. ···●··· $t = 0$ min, --○-- $t = 5$ min, ----■--- $t = 30$ min, —×— $t = \infty$ min

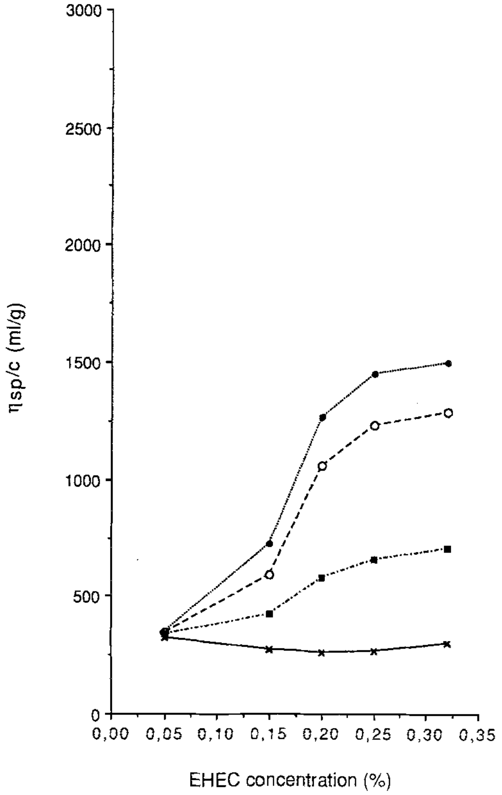

Fig. 11. η_{sp}/c for 14m*m* SDS/water solutions versus the EHEC concentration at 20 °C and at different times after mixing of the solutions.···●··· $t = 0$ min, --○-- $t = 5$ min, ----■--- $t = 30$ min, —×— $t = \infty$ min

solution. The other (II) is an SDS-solution with a surfactant content somewhat higher than that of the final combined solution. The combined solution will have a strongly increased viscosity, the more so the higher the content of EHEC.

We now imagine the first step of mixing as being a droplet of concentrated EHEC (solution I) being submerged into an SDS solution (solution II). When SDS begins to penetrate from II to I the viscosity increase in I will be very pronounced. This penetration process is mostly governed by the diffusion rate of SDS. After some time the mixing has gone farther in the sense that EHEC from I has diffused out into II and eventually the viscosity will begin to drop.

The overall time evolution of the average viscosity of the combined solutions could then in a qualitative way be described by Fig. 12. The first step in the mixing might well be dominantly convective. Soon, however, diffusion processes are likely to take over as rate-determining steps. It should then be observed that in the [SDS] interval investigated, the system properties (viscosity) are by no means linear functions of composition. In the initial part of the mixing process part of the bulk solution must pass through compositions of high EHEC concentration and with enough SDS to correspond to viscosities considerably higher than those of the overall system composition. Hence, one could expect difficulties in finding simple interpretations of the time dependence of system properties in terms of straight forward diffusion mechanisms. This is due to that parameters normally taken as constants in the diffusion expressions will vary with time since they depend heavily on composition.

The viscosity close to time zero is somewhat difficult to judge. However, from the considerations above, the viscosity is likely to first increase rapidly and then pass through a narrow

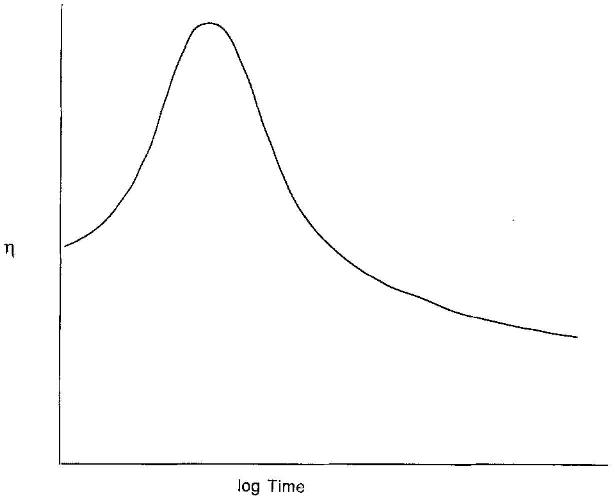

Fig. 12. Schematic viscosity-time profile in the EHEC/SDS/water system. $\eta(t)$ attains an asymptotic value, $\eta(\infty)$, when $t \to \infty$

maximum during a short initial period. This initial part is normally so fast that it is not picked up experimentally by capillary viscometry. All viscosity data is thus recorded on the declining part of the curve in Fig. 12.

Approach to equilibrium quantification

The hydrodynamic measurements provide numerical data for the viscosity, η, as a function of time, t. In order to try to evaluate these data in a more quantitative way some relationship has to be assumed for the decay to equilibrium conditions. The following procedure has proved to be illuminating.

Let us define the dimensionless quantity y according to (cf. the experimental section)

$$y(t) = \eta(t)/\eta(0)\ . \tag{4}$$

It must be understood that $\eta(0)$ is the earliest experimental value of the viscosity that is accessible and is not necessarily the *real* initial value, if such a value ever could be defined (cf. the remarks in section "Experimental"). Obviously, $y(0) = 1$ and when t tends to infinity the experiments have shown that $\eta(t)$ and hence $y(t)$ attain an asymptotic value y_a, i.e.,

$$\lim_{t \to \infty} y(t) = y_a\ . \tag{5}$$

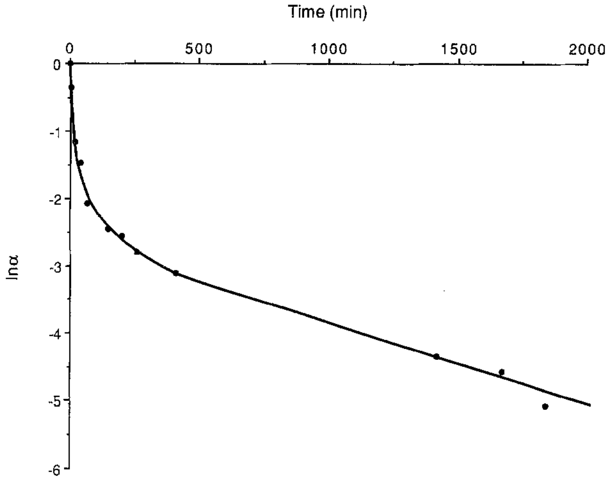

Fig. 13. ln α as a function of time for a 0.20% EHEC/8m*m* SDS/water solution

Furthermore, all experimental results indicate a similar time behavior of $y(t)$ although the asymptotic value y_a may differ. Hence, the data can for comparison purposes be normalized by defining a quantity, α, according to

$$\alpha(t) = [y(t) - y_a]/[1 - y_a]\ . \tag{6}$$

An elementary approach would be to assume the decay towards equilibrium ($\alpha = 0$) to be exponential, i.e., to correspond to ideal dissolution kinetics. Under these assumptions one may write

$$\alpha(t) = a\exp(-bt) \tag{7}$$

$$\ln\alpha = -bt + \ln a\ . \tag{8}$$

When (8) is applied to the experimental data (see Fig. 13), it is found that this relationship holds for longer times, whereas the initial part is much faster. This fact is most likely due to the non linear dependence of viscosity on concentration as discussed in the previous section.

In some way these nonlinear effects can be quantitatively understood from treatments of similar problems concerning heat conduction. In [24] the heat conduction from a sphere in contact with a well-stirred fluid is discussed. From the expressions given there it is found that if the ratio of the heat capacity of the fluid to that of the sphere would change during the process it should lead to a decay function which is fast at the beginning and gradually slows down to an exponential decay. Here, the sphere in a fluid is analogous to a droplet of concentrated EHEC solution being immersed into a pure SDS solution. Obviously, it is difficult to provide an exact theory but the analogous expressions for the heat conduction problem provides at least a qualitative explanation of the effects observed.

Various ways of analyzing the data in more detail have been tried, but no clearcut interpretation could be reached. Plotting various functions versus $\sqrt{t}$ does not give any obvious clue to a diffusion controlled model. It is found, however, that the process of attaining equilibrium is highly reproducible. For instance, a set of curves plotted according to Eq. (8) show only a small, continuous increase in slope with increasing c_P for constant [SDS]. Furthermore, the intercepts in such plots are both reproducible and almost constant. Characteristic times defining half times for attaining equilibrium are very consistent with the slopes. This very similar nature shows that it is basically the same mechanism that governs the process although the amplitude of the approach to equilibrium varies considerably (see Fig. 13).

Conclusions

It is found that although the properties of the system show considerable time dependence a true equilibrium is finally attained for all compositions. The approach to equilibrium begins with a rapid initial part followed by a slower and more extended one. However, the form of the time dependence is almost the same independent of the "amplitude" of the approach to equilibrium and the characteristic time constants vary but a little.

The most pronounced time dependence is shown in a region close to and above the CMC of the pure surfactant solution and for polymer concentrations at least equal to the critical overlap concentration. These properties of the time dependence can be explained in terms of the equilibrium properties when the procedure for solution preparation is taken into account.

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