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# Influence of nonionic surfactant on aggregation state of scleroglucan in aqueous solution

**Tami El Ouriaghli, Jeanne François, Dominique Sarazin***

*Institut Charles Sadron, CNRS Université Louis Pasteur, 6 rue Boussingault, 67083 Strasbourg Cedex, France*

&

**Nguyen Truong Dinh**

*European Laboratory Rohm and Haas, Sophia Antipolis, 06565 Valbonne Cedex, France*

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The interactions between nonyl phenol polyethylene oxide and scleroglucan are investigated by turbidimetry, viscosimetry filterability tests and measurements of elastic modulus and adsorption. The phase diagrams of this ternary system have been established as a function of temperature and composition. It is shown that the surfactant molecules are adsorbed by the polymer at a low surfactant concentration, $c_s$; the adsorption induces a breaking down of the polymer aggregates and the filterability properties of the solutions are greatly improved. An excess of surfactant phase separation is observed by heating at a temperature that is a decreasing function of $c_s$. This is explained by the formation of a complex polymer-surfactant which has the same thermodynamic properties (lower critical solution temperature) as polyethylene oxide and the derived nonionic surfactants.

## INTRODUCTION

Scleroglucan seems to be a promising candidate for a thickening agent in Enhanced Oil Recovery processes. This polysaccharide is a linearly linked β-1-3-D-glucan residues with one β-1-6-D-glucan side chain for every three main chain residues (Yanaki *et al.*, 1981; Rinaudo & Vincendon, 1982; Biver, 1986). Its viscosity, due to its triple helix conformation, remains very high even at high temperatures (Yanaki *et al.*, 1984) and ionic strengths. Nevertheless, under current pH conditions, close to neutrality, scleroglucan triple helices self associate and a plugging of porous material is observed. This aggregation constitutes a great disadvantage of scleroglucan and different methods have been proposed to reduce aggregate formation which is often attributed to the presence of proteinic impurities. Some of these methods are: purification by ultrafiltration, increasing the pH (Yanaki & Norisuye, 1983; Shuquin *et al.*, 1987), thermic treatment (Chauveteau *et al.*, 1987), removing impurities by adsorption on active carbon (Truong & Gadioux, 1987) and cyclotronic stirring (Biver, 1986). Aggregation and gelation are quite general phenomena in aqueous solutions of polymers which consequently have bad filterability properties. It is known that the addition of surfactants may lead to an improvement in the filterability (Truong & Gadioux, 1987). Such an effect is attributed to the formation of a polymer detergent complex.

In this paper, we study the influence of nonionic surfactants on the filterability properties of aqueous solutions of scleroglucan and try to optimize and understand their effects through a systematical study of the phase diagrams and interactions in such ternary systems.

## EXPERIMENTAL

### Materials

The scleroglucan sample (powder form) supplied by Sanofi Bio Ind. (Toulouse, France) is obtained by precipitation from the broth. Its characteristics obtained from light scattering (Wippler & Scheibling, 1954), viscosity and gel chromatography experiments under various pH conditions are given in Table 1.

The detergents are commercial samples of nonyl

*To whom correspondence should be addressed.

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**Table 1. Characteristics of the scleroglucan sample**

| Solvent | $<M_W> \times 10^{-6}$ | $[\eta]$ ($cm^3 g^{-1}$) | $K''$ | $<M_W/M_W>$ |
|---|---|---|---|---|
| Pure water | 7·2 | 6 355 | 0·9 | 4 |
| 0·01 N NaOH | 5·2[a]<br>4·5[b] | 8 300 | 0·64 | 1·4 |
| 0·05 N NaOH | 2·2 | 7 820 | 0·5 | — |
| 0·2 N NaOH | 0·6 | 214 | 0·4 | — |

$<M_W>$: Weight average molecular weight: [a]measured by light scattering at 25°C or [b]by coupling light scattering-gel chromatography.
$[\eta]$: Intrinsic viscosity and $K'$: Huggins constant measured at zero shear rate and at 25°C.

**Table 2. Characteristics of detergents**

| Soaps | $<M_N>$ | $\eta_{PEO}$ | HLB | CMC $\times 10^5$ ($g\,cm^{-3}$) | $T_c$ (°C) | $<M_W>/<M_N>$ |
|---|---|---|---|---|---|---|
| AP8 | 576 | 7·3 | 12·9 | 2·9 | 36 | 1·05 |
| AP9 | 607 | 8·1 | 13·3 | 3·5 | 52 | 1·04 |
| AP14 | 751 | 11·5 | 14·6 | 5·4 | 62 | 1·04 |
| AP20 | 986 | 17·7 | 15·9 | 7·5 | 94 | 1·04 |

$<M>$: Weight average molecular weight measured by tonometry, NMR, and elemental analysis.
$\eta_{PEO}$: Polymerization degree of the polyethylene oxide chain.
HLB: Hydrophilic lyophilic balance.
CMC: Micellar critical concentration measured by UV spectroscopy and superficial tension.
$T_c$: Cloud point.
$<M_W>/<M_N>$: Polydispersity index measured by gel chromatography.

phenol polyethylene oxide (from BASF) (Sepawet series or AP). From NMR measurements, the carbon number of the alkyl chain is to be found close to 9. In Table 2, the authors have gathered the main characteristics of the four samples used in this work. The hydrophilic-lyophilic balance (HLB) values for the detergents are determined using the Griffin relation between the hydrophobic group molecular weight $M_0$ and the overall detergent molecular weight $M$:

$$\text{HLB} = 20\left(1 - \frac{M_0}{M}\right)$$

The PEO samples are Hoechst products.

### Preparation of the solutions

The pure detergent was never directly added to the polymer solution. The authors preferred to prepare separately two well homogenized solutions; one of concentration $2 \times c_p$ of polymer and the second one of $2 \times c_s$ of surfactant. Two equal volumes of these were mixed to obtain the ternary solution of concentration $c_p + c_s$. Solutions of decreasing $c_p$ and $c_s$ were prepared by dilution of this initial ternary solution with a detergent solution of concentration $c_s$.

### Experimental methods

(i) Viscosity measurements were performed with a Low Shear 30 from Contraves AG (Zurich, Switzerland) equipped with the system 2T-2T in a shear rate range between 0·1 and 100 $s^{-1}$ at different temperatures controlled at ±0·01°C.
(ii) For filterability tests, the solution was injected through a Millipore filter (5 μm) at a constant flow rate of 20 $cm^3 h^{-1}$ and the variation of the pressure before filter was measured versus time with a pressure transducer (0–1000 mbar) for 25 h.
(iii) The solution turbidity was obtained by measuring the absorption at 700 nm with a spectrophotometer Shimadzu UV 240 and a thermostated cell of 1 cm of the optical path.
(iv) The gel modulus was measured with a home-built apparatus working in unidirectional compression. It includes a HBM amplifier coupled to a force transducer connected to a measurement

teflon cylinder. The force transducer can remove the cylinder to the gel surface by micrometric steps with the help of a micro-control translator. The gel is introduced in a cylindrical thermostated cell (diameter 36 mm and height 8 mm). This diameter is high enough compared with that of the teflon cylinder to allow us to neglect the wall effects.

(v) Differential spectroscopy: the critical micellar concentration of detergents in presence of polymer was determined according to the method described by Ray & Nemethy (1971) by using two twin compartment cells. One measures the difference of absorption at 275 nm between the reference cell which contains in each compartment the same detergent concentration $c_s$ and the sample cell which contains the pure polymer solution in the first compartment and a solution of concentration $2 \times c_s$ in the second compartment.

(vi) Measurements of adsorption by ultrafiltration at constant volume. The apparatus schematized in Fig. 1 consists of:

— an ultrafiltration cell of 20 $cm^3$ closed by a polycarbonate membrane of 2 cm diameter and 50 nm porosity in which is introduced a volume $V$ of polymer solution;

— a reservoir of 1000 $cm^3$ containing the detergent solution (concentration $c_{s0}$);

— a spectroscopic cell standing in the UV beam of the Shimadzu UV 240 spectrophotometer to measure the detergent concentration in the eluent;

— a pressure device which permits the flow of the surfactant solution in the ultrafiltration cell at constant volume.

After a time $t$, the detergent concentration in the eluent becomes constant; the relation between $c_{st}$ and the adsorbed quantity is then:

$$Q = (c_{s0} - c_{st})\,V \qquad (1)$$

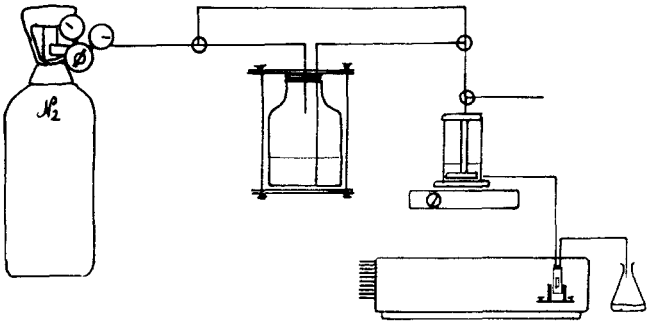


**Fig. 1.** Schema of the apparatus of ultrafiltration at constant volume.

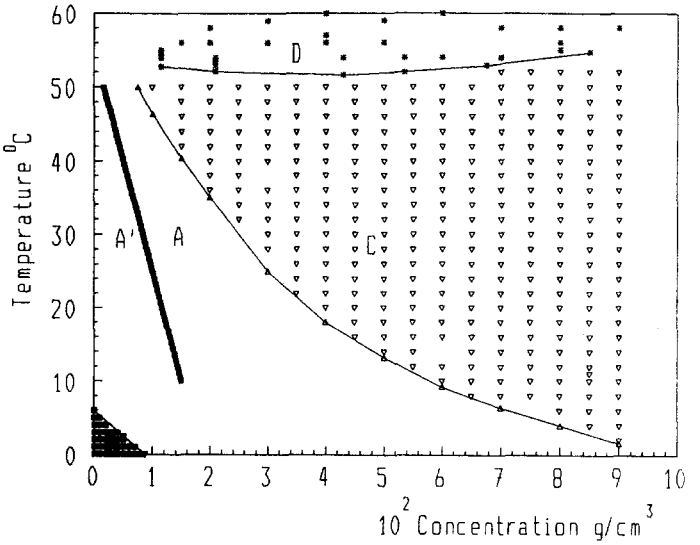


**Fig. 2.** Phase diagram (temperature-surfactant concentration) of the system AP9-scleroglucan ($c_p = 10^{-3}$ g $cm^{-3}$).

## RESULTS

### Phase diagrams

*Scleroglucan + AP9*

One example of a phase diagram (temperature, surfactant concentration) obtained by turbidimetry with AP9 for polymer concentration $c_p = 10^{-3}$ g $cm^{-3}$ is given in Fig. 2; four regions are observed:

— A: transparent and homogeneous solution
— B: transparent gel
— C: demixing in two phases
— D: demixing in three phases

(i) The sol-gel transition temperature is 6°C in the pure polymer solution, in agreement with literature data (Biver, 1986), and decreases by adding surfactant: AP9 is able to hinder gelation of scleroglucan solutions.

(ii) In the range of temperature $6 < T < 52$°C, the surfactant addition induces a demixing for a concentration which is a decreasing function of temperature. This result means that a turbid solution becomes transparent on cooling and such behaviour is reminiscent of aqueous solutions of polyethylene oxide (Saeti, 1976) or nonionic detergent (of the Sepawet type) which present a lower critical solution temperature (LCST). One can conclude that ternary solutions of scleroglucan - AP9 have the same thermodynamic properties as the binary surfactant solutions.

The two phases do not separate spontaneously but the separation can be obtained by centrifugation. Their analysis by viscosimetry and UV spectroscopy revealed a supernatant phase which contains mainly AP9 and a dense phase which essentially consists of the scleroglucan with the residue of AP9 adsorbed on it.

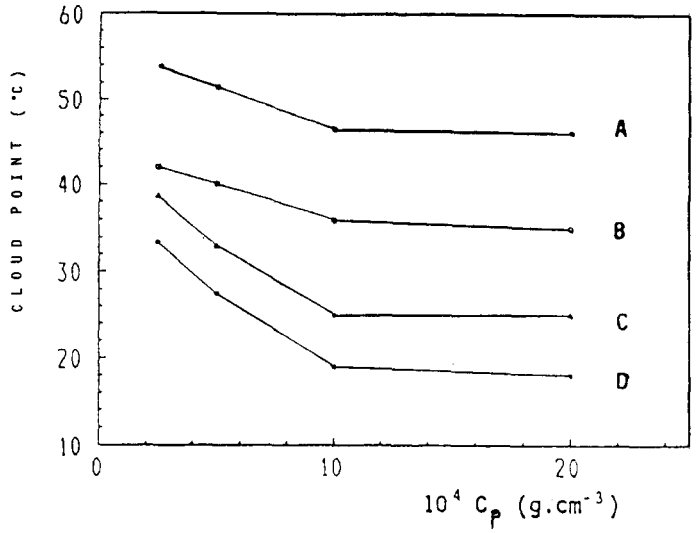


**Fig. 3.** Variation of the cloud point versus the concentration of surfactant of various HLB for a scleroglucan solution equal to $10^{-3}$ g cm$^{-3}$.

(iii) The line between regions C and D is very close to the demixing curve of pure AP9. For $T > 51$°C, the system consists of three phases: the polymer precipitate, a rich surfactant phase and a poor surfactant phase.
Figure 3 shows that the cloud point $T_c$ is a decreasing function of $c_p$ at constant $c_s$; the solution stability decreases when $c_p$ increases, behaviour which looks like the variation of the cloud point for aqueous solutions of PEO or nonionic surfactant (Saeki *et al.*, 1976; Saito, 1987).

This first series of results demonstrates the incompatibility of scleroglucan and AP9 in some ranges of concentrations and temperature, and illustrates the peculiar properties of the demixing limit: this diagram will be referred to as 'Type I'.

*Scleroglucan + PEO*

In order to establish the respective roles played by the hydrophobic and hydrophilic parts of the detergent on this incompatibility, it is useful to know the compatibility degree of scleroglucan with pure PEO. At 25°C, the addition of PEO of molecular weight 600 and 1000 induces the precipitation of scleroglucan in the form of dense fibres for concentrations equal to 0·11 and 0·07 g cm$^{-3}$, respectively. In contrast with AP9, this precipitate does not dissolve on cooling and it does not contain adsorbed PEO molecules. The solutions become clear by heating and the concentration of POE at the solubility limit is an increasing function of temperature (Type II diagrams).

There exists, as with AP9, a compatibility limit with PEO but the origin of the demixing is probably different. In this case, it seems that it is due to enthalpic effects and could be described by the Flory-Huggins theory (Flory, 1978) which well predicts the variation of this limit with the molecular weight of PEO. The same behaviour has been obtained for the system polyvinylalcohol-PEO-water by Inamura (1986) and these authors have explained their results in the framework of this theory.

From such observations, one can deduce that the surfactant HLB must play an important role.

*Variations of the phase diagram with the HLB of the detergent*

Figure 4 shows the phase diagram obtained with the most hydrophilic surfactant, AP20. The symbols of the different regions are the same as in Fig. 2. In Fig. 5, we can compare the limits between regions A and C for the five surfactant samples.

It can be concluded that:

(i) AP8 and AP10 have the same behaviour as AP9 (a Type I diagram) while in the case of the more hydrophilic detergents AP14 and AP20, the diagrams are of Type II.

(ii) In the case of diagrams of Type I and at a given temperature, the compatibility limit is shifted towards the low $c_s$ values when HLB decreases:

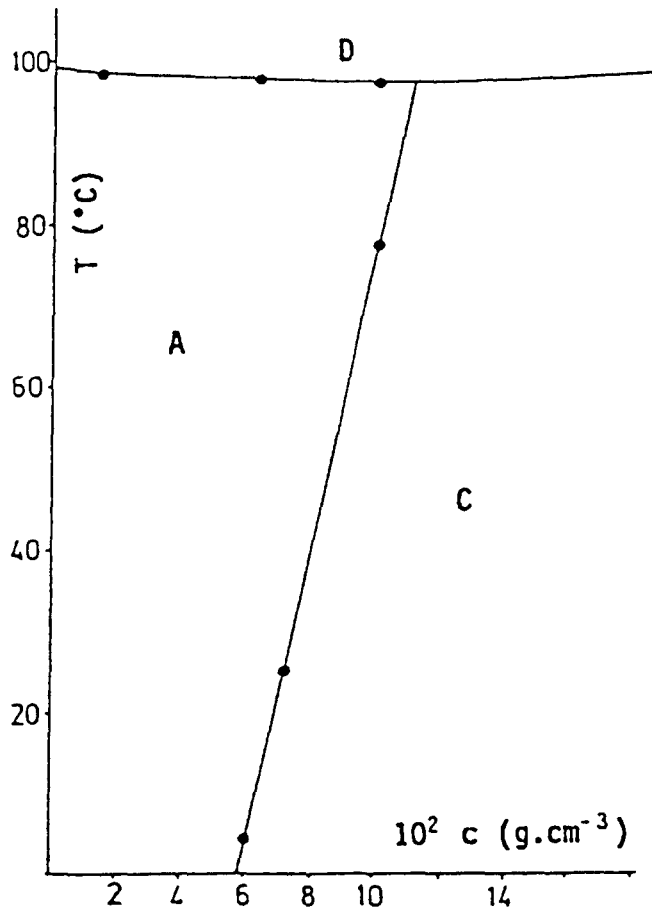


**Fig. 4.** Phase diagram (temperature-surfactant concentration) for the system AP20 - scleroglucan ($c_p = 10^{-3}$ g cm$^{-3}$).

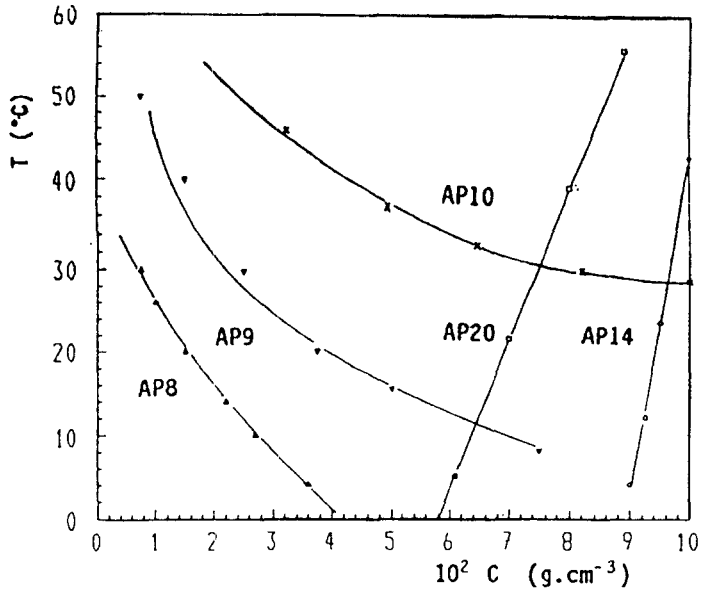


**Fig. 5.** Variation of the cloud point versus the concentration of surfactant of various HLB for a scleroglucan solution ($c = 10^{-3}$ g cm$^{-3}$).

this shows that the paraffinic chain plays the preponderant role.

(iii) In the case of diagrams of Type II, the higher the HLB, the lower the compatibility limit is; the hydrophilic part of the detergent molecule is predominant.

(iv) The maximum of compatibility is obtained around HLB = 14 and one can predict a slight increase of this value when the temperature rises.

One can deduce that diagrams of Type I are due to the interactions between scleroglucan and the aliphatic chain of the detergent. In order to explain the demixing by heating which has generally an entropic origin, the authors propose the following model: the interactions between scleroglucan and detergent molecules lead to the formation of a complex polymer-detergent. The molecular weight of this hypothetical complex is equal to that of scleroglucan plus that of all the adsorbed detergent molecules, and is consequently much higher than that of detergent micelles ($1{\cdot}5 \times 10^5$ in the case of AP9). It is well known that the LCST of polymers is a decreasing function of their molecular weight and it seems reasonable to think that, if the complex keeps the thermodynamical properties of the detergent, its LCST value must be much lower than that of pure micelles. When the HLB of the detergent increases, the strength of the hydrophobic interaction with the polymer decreases as well as the number of adsorbed molecules and the free micelles become more hydrophilic and tend more and more to play the same role as PEO. AP20 behaves almost as a polymer incompatible with scleroglucan above a given concentration.

This hypothesis implies that diagrams of Type I are associated with a great adsorption of detergent on scleroglucan.

### Adsorption isotherms of the surfactant

The association between polymers and surfactants is generally characterized by two critical $c_s$ concentrations: $c_{s1}$ and $c_{s2}$ (Cabanes, 1977; Boscher, 1983; François *et al.*, 1985)

(i) $c_{s1}$ corresponds to the onset of the fixation when the polymer properties begin to be modified. This concentration is usually lower than the CMC (critical micellar concentration) and is independent of the polymer concentration.

(ii) $c_{s2}$ corresponds to the polymer saturation. The amount of associated molecules depends on the polymer concentration and can be determined by dialysis equilibrium or diafiltration until the adsorption plateau is reached.

Other works from Boscher (1983) have shown that the interaction between uncharged detergents and HEC (hydroxyethylcellulose) obeys the same scheme.

For the scleroglucan-AP9 system the authors have attempted to determine $c_{s1}$ values by using the differential UV spectrophotometry (see the Experimental section) and the polymer was found to not affect the CMC of the surfactant in the polymer concentration range from $10^{-4}$ to $10^{-3}$ g cm$^{-3}$.

Two examples of ultrafiltration results for pure water and polymer solution are reported in Fig. 6, in the case of AP9. The high discrepancy between the two plateaus observed at high elution volumes demonstrates the fixation of detergent molecules on scleroglucan. The results obtained in a large range of polymer and detergent concentrations reveal some differences with respect to the usual behaviour of the isotherms already described in other works (Boscher, 1983; François *et al.*, 1985).

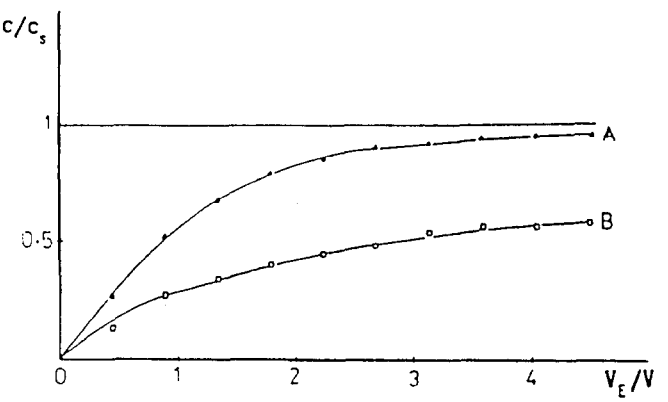


**Fig. 6.** Ultrafiltration experiments: characteristic elution curves for concentration of AP9 = $10^{-3}$ g cm$^{-3}$: curve A, pure water; curve B, scleroglucan solution.

The amount of surfactant adsorbed by the polymer, $Q'$ (expressed in mmole of surfactant per g of polymer) can be obtained from the value of $Q$ (1) at the plateau and is usually found to be independent of the polymer concentration. In the present case, we find that $Q'$ is a decreasing function of $c_p$: for $c_p$ equal to $10^{-4}$ and $5 \times 10^{-4}$ g cm$^{-3}$, $Q'$ is 92 and 26 mmole g$^{-1}$, respectively. On the other hand, $Q'$ is expected to linearly vary with the concentration of free surfactant $c_{sl}$, before the isotherm plateau while the results of the present study can be described by the following scaling law:

$$Q' \alpha c_{sl}^{1.6} \quad (2)$$

Then, the thermodynamic properties of the scleroglucan - AP9 interactions seem to be more complex than for other polymer surfactant systems. In fact these results may confirm the previous hypothesis of surfactant adsorption inducing a process of chain disaggregation. The fraction of macromolecular sites available for surfactant binding probably decreases when $c_p$ increases due to the presence of entanglements, which may explain the decrease of $Q'$. However, the binding of the surfactant by disaggregating the chains releases new sites and this is consistent with the high value of the exponent of relation (2). Moreover, it must be pointed out that the values of $Q'$ at the isotherm plateau are surprisingly high, although they are of the same order of magnitude as those obtained by Boscher (1983) for the hydroxyethylcellulose-AP10 system. Such $Q'$ values are much higher than those usually found for nonionic polymers-ionic surfactant systems (e.g. POE - sodium dodecyl sulfate (SDS) where $Q' = 6$–$8$; François *et al.*, 1985). These discrepancies may be due to the big difference in the aggregation number of AP9 and SDS (250 and 40, respectively) if the polymer-surfactant interactions lead to the micelle adsorption.

More precisely, the present authors use simple geometrical considerations, starting from structural dimensions of each component, to characterize the complex. The authors have measured by light scattering the molecular weight of the AP9 micelles, $M = 1{\cdot}35 \times 10^5$ and the dimensions of the ellipsoidal micelles have been deduced from viscosity measurements: length = 325 Å and diameter = 40 Å (El Ouriaghli, 1989). So with a 18 Å scleroglucan rod diameter and 10 000 Å for the contour length, the maximum capacity of adsorption per rod is either about 120 or 6000 micelles if one assumes that the principal axis of the micelles is parallel or perpendicular to the macromolecular rod, respectively. The $Q'$ ratio obtained for a polymer concentration $c_p = 10^{-4}$ g cm$^{-3}$ and a AP9 concentration $c_s = 10^{-2}$ g cm$^{-3}$ leads to a value of 900 micelles adsorbed on a free rod which seems rather reasonable and corresponds to a quasi total covering of the scleroglucan triple helices by the surfactant.

**Filterability experiments**

*The scleroglucan-AP9 binary mixture*

(i) It is shown here that the addition of surfactant greatly improves the filterability of concentrated scleroglucan solutions. Some experimental results for the semi-dilute commercial batch with $c_p = 1{\cdot}5 \times 10^{-3}$ g cm$^{-3}$ containing various amounts of surfactant are reported in Fig. 7 for different stirring times. This improvement is obviously time dependent and is related with the homogenization kinetics of the mixture. This leads to very good filterability for $c_s = 1{\cdot}4 \times 10^{-2}$ g cm$^{-3}$ and a stirring time of 60 h before measurement (see curve *V* on Fig. 7).

(ii) For polymer solutions prepared with dry powder the best results were obtained for AP9 concentration $c_s = 10^{-3}$ g cm$^{-3}$ and a dilute polymer concentration $c_p = 10^{-4}$ g cm$^{-3}$.

*The HLB influence*

Figure 8 compares the efficiency of the different surfactants under the same conditions and it is shown that AP9 leads to the best results. This was already underlined by the phase diagram features without quantitative relations.

The improvement of the filterability test of HEC solutions by detergents has already been pointed out by Bosher (1983). He established the occurrence of aggregation of pure HEC provoked by the flow through filter pores. The filterability improvement by nonionic surfactant was then interpreted by the strong detergent-polymer interaction which hinders this aggregation process. In the present case the authors know the associative ability of scleroglucan in pure water as

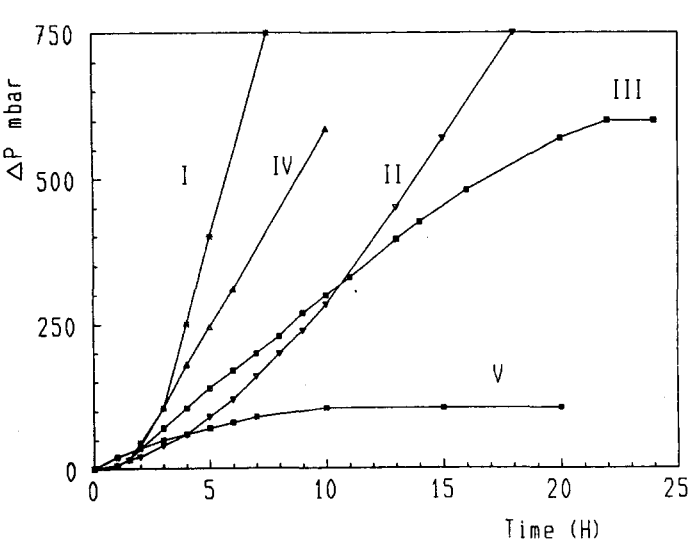


**Fig. 7.** Filterability tests: for a scleroglucan solution ($c_p = 1{\cdot}5$ g cm$^{-3}$) with different amounts of AP9: I, $c_s = 0$; II, $c_s = 5 \times 10^{-3}$; III, $c_s = 10^{-2}$; IV, $c_s = 2 \times 10^{-2}$, for a stirring time of 2 h; V, $c_s = 1{\cdot}4 \times 10^{-2}$ for a stirring time of 60 h.

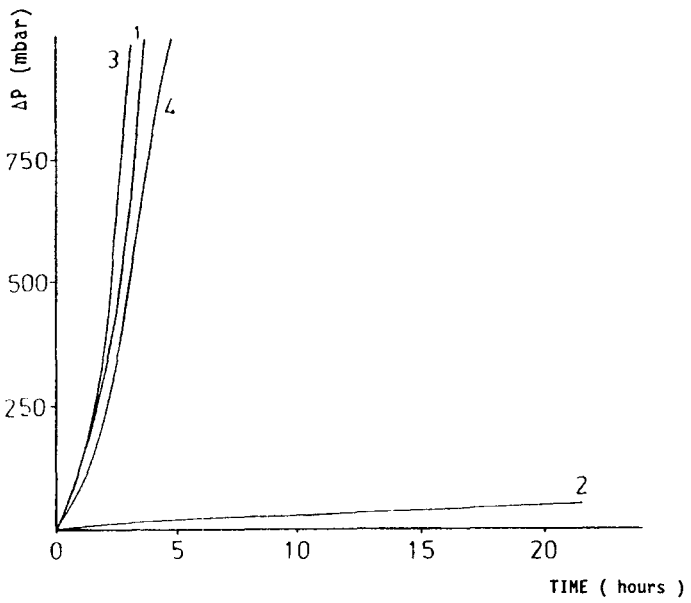


**Fig. 8.** Filterability tests for a scleroglucan solution $10^{-4}$ g $cm^{-3}$ with $10^{-3}$ g $cm^{-3}$ of (1) AP8, (2) AP9, (3) AP14 and (4) AP20.

shown in Table 1 independently of filtration. Therefore the present authors explain the filterability test by the breaking of aggregates by surfactant before injection. These results are supported by the viscosity measurements as followed.

**Viscosity results**

*Detergent AP9*

The viscosity measurements must be considered in the light of the phase diagram features. The general viscosity behaviour is quite complex as we shall see here, and different ranges of polymer concentration have to be distinguished. It is indeed well known that the intrinsic viscosities of polymer $[\eta]$ must be determined from the measurements of reduced viscosities $\eta_{red}$ by extrapolation at $c_p = 0$, for a range of $c_p < c_p^*$ if $c_p^*$ is the critical concentration of chain overlapping. In this range, one expects for the Huggins constant $K'$ values to be lower than 0·5 and higher values usually indicate aggregation.

$c_p^*$ may be obtained by two different ways:

(i) by assuming, as for flexible polymers, that $c_p^* = 1/[\eta]$ (De Gennes, 1979);

(ii) by using the value given for rods: $c_p^* = M_w/N \times L^3$ where $N$ is the Avogadro number and $L$ is the rod length. One obtains $c_p^* = 1{\cdot}6 \times 10^{-4}$ and $3 \times 10^{-7}$ g $cm^{-3}$, respectively.

In fact, viscosity studies on the scleroglucan solutions have shown that the first value is the more realistic.

(i) *Polymer concentrations below* $c_p^*$ ($c_p < c_p^*$). Table 3 summarizes the results obtained in this polymer concentration range. The addition of surfactant in scleroglucan solutions leads to an increase of $[\eta]$ and a lowering of $K'$. The same behaviour was obtained by increasing the pH (El Ouriaghli, 1989). So surfactant or NaOH addition has the same effect on the dispersion of scleroglucan molecules in water.

*Remarks:* it is obvious that the increase in $[\eta]$, and the decrease in $K'$ also, may simply be related to a disaggregation process for scleroglucan in NaOH but should be more intricate for the soap solutions where we are also dealing with an adsorption mechanism.

The following observations must be considered:

— The solvent viscosity is no more that of the pure soap solution but that of a solution with less free soap molecules. This difference occurs when the soap molecules are adsorbed by the polymer and can be neglected for a low polymer concentration.

— The true concentration of the complex is higher than the pure polymer one. So, for the complex we should have lower reduced viscosity values and also a lower value for the Huggins constant $K'$.

— It is obvious that the interpretation of the viscosity behaviour of these solutions requires further data about the complex stoichiometry. Qualitatively, the results lead to a disaggregation process of the three-fold scleroglucan helix in that concentration range.

Table 3 shows that viscosity behaviour proceeds to a maximum value while the $K'$ coefficient proceeds to a minimum for the AP9 concentration of $10^{-3}$ g $cm^{-3}$. This concentration leads also to the optimum filtration test of the dilute scleroglucan solution. Such a maximum may be explained following the phase diagram features as follows: for the low concentration the onset of soap adsorbtion leads to the unwinding of the three-fold helix

**Table 3. Intrinsic viscosity $[\eta]$ and Huggins coefficient $K'$ of the dilute commercial scleroglucan batch versus detergent concentration**

| AP9 concentration (g $cm^{-3}$) | $[\eta]$ ($cm^3$ $g^{-1}$) | $K'$ |
|---|---|---|
| 0 | 9 500 | 1 |
| 0·001 | 14 800 | 0·36 |
| 0·005 | 13 200 | 0·43 |
| 0·03 | 12 400 | 0·45 |
| 0·05 | 7 600 | 0·52 |

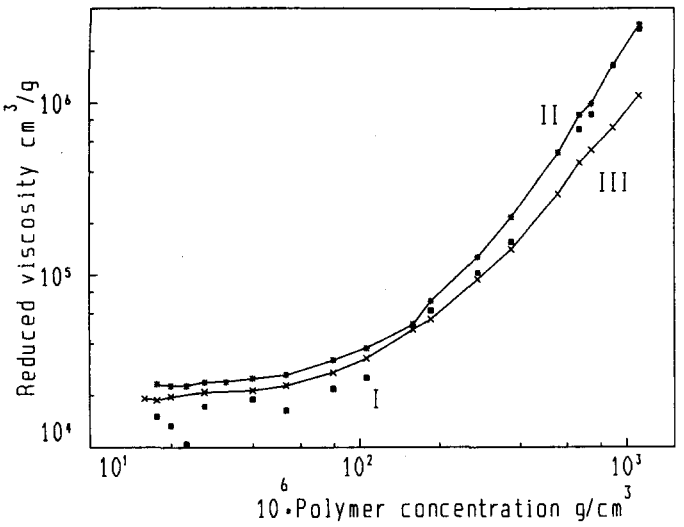


**Fig. 9.** Reduced viscosity of scleroglucan as a function of concentration for different concentrations of AP9: I, $c_s = 0$; II, $c_s = 10^{-3}$ g cm$^{-3}$; III, $c_s = 3 \times 10^{-2}$ g cm$^{-3}$.

aggregates and for higher soap concentrations the thermodynamical properties of the complex change and tend towards the collapse of the chains with a decrease in the viscosity.

This phenomenon is depicted in the phase diagram (Fig. 2) by the line between the *A* and *A'* region which allows the AP9 concentration to optimize for special aim.

(ii) *Above the overlapping concentration* $c_p^*$. In this range, two types of viscosity behaviour are pointed out on Fig. 9. First, no change occurs in the reduced viscosity by adding soap till $3 \times 10^{-2}$ g cm$^{-3}$. Second, at higher concentrations a fall in the viscosity value takes place which corresponds to the demixion, i.e. for $c_{soap} = 8 \times 10^{-2}$ g cm$^{-3}$ and $c_p = 10^{-3}$ g cm$^{-3}$ the value $\eta = 400$ cm$^3$ g$^{-1}$ is 20 times lower than that in pure water for scleroglucan. scleroglucan.

## CONCLUSION

From a practical point of view, the results presented here clearly show the improvement of filterability properties of scleroglucan solutions by surfactant addition. Such an effect can be explained by the strong interactions between polymer and surfactants according to their HLB. Phase diagrams, viscosimetry and adsorption measurements permit us to show the formation of a complex scleroglucan-surfactant which is also at the origin of a three-fold helix disaggregation.

## REFERENCES

Biver, C. (1986). Thesis, Formation d'amas dans les solutions de polymères hydrosolubles. Influence sue le comportement en solution d'un polysaccharide végétal: Le scléroglucane. Université Pierre et Marie Curie, Paris VI.

Boscher, Y. (1983). Thesis, Caractérisation physico-chimique de l'hydroxyéthylcellulose en solution aqueuse et des interactions avec des tensioactifs non ioniques. Université Pierre et Marie Curie, Paris VI.

Cabanes, B. (1977). *J. Phys. Chem.*, **81**, 1639.

Chauveteau, G., Lecourtier, J. & Noik, C. (1987). *Amer. Chem. Soc., Div. Polymeric Mat., Proc.*, **57**, 380.

De Gennes, P. G. (1979). *Scaling Concepts in Polymer Physics.* Cornell University Press, Ithaca.

El Ouriaghli, T. (1989). Etudes des interactions scleroglucane tensioactifs non ioniques. Thesis at the Université Louis Pasteur, Strasbourg.

Flory, P. J. (1978). *Principles of Polymer Chemistry.* Cornell University Press, Ithaca.

François, J., Dayantis, J. & Sabbadin, J. (1985). *Eur. Polym. J.*, **21**, 165.

Inamura, I. (1986). *Polymer J.*, **18**, 269.

Ray, A. & Nemethy, G., *J. Phys. Chem.*, **75**, 804.

Rinaudo, M. & Vincendon, M. (1982). *Carbohydr. Polym.*, **2**, 135.

Saeki, S., Kuwahara, N., Nakata, M. & Kaneto, M. (1976). *Polymer*, **17**, 685.

Saïto, S. (1987). *Nonionic Surfactants*, ed. M. J. Schick. Marcel Dekker, New York, **15**, 881.

Shuquin, B., Milas, M. & Rinaudo, M. (1987). *Int. J. Biol. Macromol.*, **9**, 153.

Truong, D. N. & Gadioux, J. (1987). French Patent 87 15663, issued to SNEAP Ind.

US Patent 4299 825 (1981)

US Patent 3355 447 (1968)

Wippler, C. & Scheibling, J. (1954). *Chem. Phys (F)*, **51**, 201.

Yanaki, T. & Norisuye, T. (1983). *Polymer J.*, **5**(15), 389.

Yanaki, T., Kojima, T. & Norisuye T. (1981). *Polymer J.* **13**, 1135.

Yanaki, T., Tabata, K. & Kojima, T. (1985). *Carbohydr. Polym.*, **5**, 275.