Light-Scattering Studies of Hydroxyethylcellulose in Water/Nonionic Surfactant Binary Mixtures
Evidence for Preferential Solvation of Polymer Chains by Surfactant Micelles

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Summary

The following paper reports the occurrence of interactions in nonionic polymer (hydroxyethylcellulose : HEC)/nonionic surfactant (polyethylene oxide nonyl phenyl ether) systems through light-scattering studies (LS). In a given composition range of the binary mixture H_2O/surfactant, preferential solvation by surfactant micelles is observed. The variation of the preferential adsorption coefficient with surfactant concentration is governed by the size of the micelles.

Introduction

Until now, interactions of surfactants with polymers have been mainly investigated with anionic surfactant/nonionic polymer systems (1,2,3,4). Although evidence has been produced for interactions in the case of nonionic/nonionic species (5,6), they have been reported to be very weak, probably because the electrostatic repulsion acting between polar head groups is not so strong in nonionic surfactants as in anionic ones.

Experimental
Materials

HEC (WP 100 MH grade) was synthetized by BP Chemicals for the Institut Français du Pétrole. Its weight average molecular weight $\bar{M}_w$ was $1.28 \ 10^6$ as measured by LS and its limiting viscosity number, 14 dl/g at 30°C ($\bar{G} = 1,800 \ s^{-1}$). Polyethyleneoxide nonyl phenyl ethers were commercial products of Stepan, $(C_9H_{19}\!-\!\bigcirc\!-\!(OCH_2\!-\!CH_2)_x\!-\!OH = NP_x)$ called Polystep F_6 (NP_{14}) and F_8 (NP_{20}). The critical micelle concentrations (cmc) of NP_{14} and NP_{20} determined by ultraviolet spectroscopy (275nm), respectively 0.11 and 0.14g/l, are in good agreement with literature values (7,8).

All solutions were made in Milli-Q water from Millipore system (15,000 MΩ conductivity) to which a bactericide (Procida from Hoechst) was added (50µl/1).

Light scattering experiments

They were performed at 25°C over the angular range 30°–150° on a FICA 40 000 apparatus, home-modified with a red laser source (632nm). Refractive index increments were measured on a differential Brice-Phoenix refractometer provided with a similar laser.
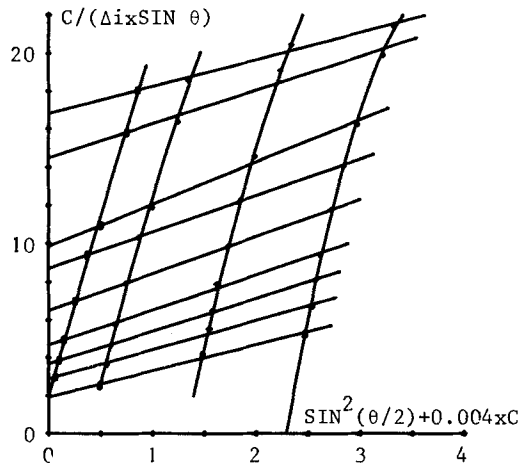
Fig. 1 : Zimm plot of HEC in binary mixture H_2O/NP_{14}

In all measurements, the solvent was a H_2O/NP_x binary mixture, prepared
by dissolving surfactant in water during 12 hours. A weight amount of HEC
(C = 0.4g/l) was dissolved in this binary mixture by slowly stirring for
60 hours to give clear solution. Dilutions were made with the binary sol-
vent.

Solution were freed from dust just before LS measurements by centrifugation
at high speed (18,000g), for 2 hours without reduction of concentration.

Reduced scattered intensities for zero concentration and angle were
obtained by the Zimm method, an example of which is given in fig. 1. From
such diagrams, an apparent polymer molecular weight $\bar{M}_w^*$ can be deduced for
the given binary solvent.

Results and discussion

Fig. 2 shows the evolution of $\bar{M}_w^*$, as determined from LS data, for several
compositions of the two kinds of H_2O/NP_x mixtures. For these media, we
consider that micellar surfactant solutions behave like classical binary
solvents. In the investigated surfactant concentration range (0.4 to 3g/l),
such an assumption seems to be supported by the absence of free species
(due to the low cmc values) and by the independence of aggregate molecular
weights on micellar concentration (7) ; furthermore, we verified that the
particle scattering fonction $P(\theta)$ was 1 for the NP_{14} and NP_{20} micelles.

We have then determined the preferential adsorption coefficient α (see
fig. 3) from the $\bar{M}_w^*$ variations, using the Benoit and Strazielle relation-
ship (9)

$$\bar{M}_w^* = \bar{M}_w \left(1 + \alpha \frac{(dn_{12}/d\phi_1)}{(dn/dC)_{\phi_1}}\right)^2$$

Where $(dn/dC)_{\phi_1}$ is the refractive index increment at constant binary sol-
vent composition and $(dn_{12}/d\phi_1)$, the binary solvent refractive index
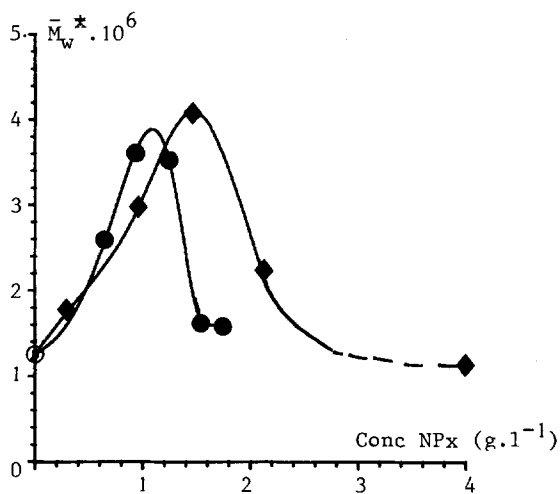increment.

Fig. 2 : Dependence of $\bar{M}_w^*$ on concentration of NP_x
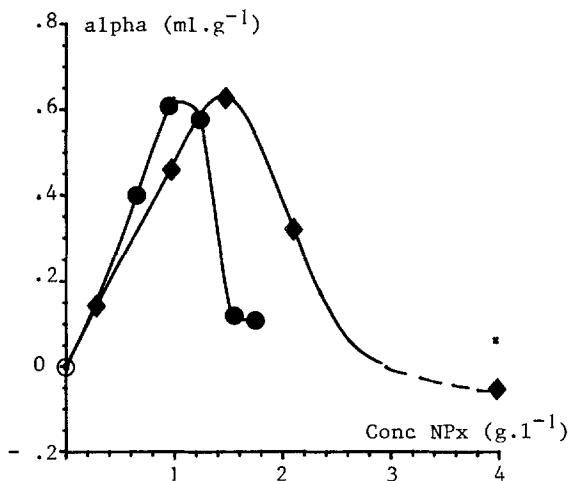
◆ = NP_{14} ; ● = NP_{20}

Fig. 3 : The preferential adsorption parameter α, as a funtion of solvent composition for $HEC/NP_x/H_2O$ system. ◆ = NP_{14} ; ● = NP_{20}

In fig. 3, we can see that α values are positive, what indicates a prefe-
rential adsorption of micelles around polymer chains, for surfactant con-
centrations lower that about 2g/l for NP_{20} and 3g/l for NP_{14}. At higher
NP_x concentrations, preferential solvation no longer occurs since we found
$\bar{M}_w^* \simeq \bar{M}_w$ (α = o) and the binary solvent composition becomes the same in the
neighbourhood of HEC chains as in the bulk.

We also tried to explain the differences observed between NP_{14} and NP_{20} for
the coordinates of the two adsorption maxima (fig. 2 and 3). We think
that they may proceed from the differences in size (r) of the two types
of micelles, since

$$r\ NP_{20}\ >\ r\ NP_{14} \tag{7}$$

Owing to a greater steric hindrance for NP_{20} micelles, the preferential
adsorption maximum is reached at lower concentration (1.1g/l) than for NP_{14}
ones (1.5g/l). These preliminary results demonstrate that interactions
occur in HEC/NP_x non ionic systems. Further investigations are on course
with other surfactants and other techniques in order to get better under-
standing of the phenomenon.

Acknowledgement

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