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Interactions of ethylene oxide/methylene oxide copolymers with sodium dodecyl sulphate

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Abstract

The interactions of poly(1,3,6,9-tetraoxacycloundecane) (PTGF) and poly(1,3,6-trioxacyclooctane) (PDGF) with sodium dodecyl sulphate (SDS) were studied by conductimetry, viscosimetry and fluorescence. The results are compared to those obtained in the cases of poly-(ethyleneoxide) (PEO) and poly(1,3-dioxolane) (PDXL). The total amount of SDS bound along the polymer chain is found to decrease when the molar fraction of methylene oxide units (MO) increases, while the aggregation number of the bound micelles becomes much lower. Besides, when the polymer has a poor water solubility, addition of SDS improves this solubility, the lower critical solution temperature (LCST) being an increasing function of the SDS concentration. These results suggest that ethylene oxide (EO) units are mainly responsible for the SDS binding and that the absence of long EO sequences in PDXL hinders the micelle growth. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethers; Sodium dodecyl sulphate; Binding

1. Introduction

Poly(ethylene oxide) (PEO) was already the object of numerous investigations as well in its crystalline form in pure state or in solution [1]. It has the remarkable property to be soluble in solvents covering a broad domain of polarity. The "closed loop" phase diagrams of the aqueous solutions of PEO is one of the most known examples of phase separation upon heating (lower critical solution temperature (LCST)) observed in polymer solutions [2]. Qualitative explanations of such a behaviour can be found in several more or less recent theoretical approaches [3–7]. Among them, the most convincing [4,7] are based on a solvation equilibrium between "free" and "solvated sites" on the chain dependent on temperature. Starting from such an idea, we have tried to establish a correlation between the phase diagrams and the solvation effect and the chemical composition of the poly(ether) series. For this purpose, we have compared the behaviours in aqueous solutions of the poly(1,3-dioxolane) (PDXL) [8,9] made of alternating ethylene oxide and methylene oxide units:

$[–(CH_2CH_2O)–CH_2O–]_n$

and poly(1,3,6,9-tetraoxacycloundecane) (PTGF) [10] whose chemical formula is:

$[–CH_2CH_2O)_3–CH_2O–]_n$

We have shown that the main sites of hydration are the EO units and this observation allowed us to understand the differences between their aqueous solution properties and those of PEO.

On the other hand, the interactions between PEO and anionic surfactant, such as sodium dodecyl sulphate in aqueous solution have been investigated for many years. Well-documented reviews describe and discuss the experimental and theoretical results [11,12]. Numerous investigations using, conductimetry [13–16], viscosimetry [13,16], surface tension [13,14], dialysis [17], NMR [18], neutron scattering [19] and fluorescence [16,20] lead to a model where SDS is bound to the macromolecular chain, not as isolated molecules but under the form of micelles. If the hydrophobic interactions are the driving forces of the adsorption of SDS on PEO, it is not clear how the hydrophobic parts of both surfactant and polymers are associated in the complex. In order to understand the respective role played by the hydrophobic (CH_2–CH_2) and the hydrophilic part (–O–) of the chain, we have carried out a study of the PDXL–SDS interactions [21]. It turns out that the total

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amount of bound SDS is lower for PDXL than for PEO, as compared for the same composition of the mixtures [21]. We concluded that our observations stem from the relative hydrophobicity of the two polymers. The values of the solubility parameters as calculated from Van Krevelen [22] (δ PEO $= 22.8$ and δ PDXL $= 25.4$ ($J^{1/2}$ $ml^{-1/2}$)) supports such an idea, even if one must be sceptical how far these parameters can be used to correlate behaviours in aqueous solution. This paper presents and discusses the results of an investigation of the behaviour of the PTGF and the poly(1,3,6-trioxacyclooctane) (PDGF) of chemical formula:

$[–CH_2CH_2O)_2–CH_2O–]_n$

in the presence of SDS. By comparing these new results with the previous ones obtained with PEO and PDXL, it will be possible to establish a correlation between the SDS–polymer interactions and their composition. The comparison was made with samples of different polymers of similar molecular weight ($15\,000 < M_w < 50\,000$) and for this reason, the experimental part contain details about the synthesis of PDGF whose high molecular weight samples are very difficult to obtain.

2. Experimental

2.1. Materials

The *PDXL* sample was cationically prepared [8,9,23]. It is terminated by two methyl groups.

The *PTGF* sample was prepared by cationic polymerization of the corresponding cyclic acetal, 1,3,6,9-tetraoxacycloundecane, abbreviated as TGF (triethyleneglycol formal). This method allows the control of the molar mass and of the nature of chain end groups [24]. The details of the polymerization and purification are given elsewhere [10]. The sample has the following end groups:

$CH_3O[–CH_2CH_2O)_3–CH_2O–]_n–$

and

$CH_3O[–CH_2O–(CH_2CH_2O)_3–]_n–$

Cyclic species containing 9–620 monomer units are still present but account for less than 6% of the purified sample.

More details will be given about *PDGF* sample preparation. Indeed, the cationic polymerization of 1,3,6-trioxacyclooctane, abbreviated as DGF, gives limited molar masses [25,26] and important chain scission is observed [27]. Thus it was decided to prepare PDGF by a two step method to overcome some of these drawbacks. DGF was first polymerised cationically by the so-called “activated monomer mechanism”, which has already been described in the case of PTGF [28]. DGF (21 ml) was reacted with under dry nitrogen, in methylene chloride solvent (50 ml) using diethylene glycol (0.75 ml) as an initiator and trifluoromethanesulfonic acid (4.4×10^{-3} ml) as a catalyst. The polymer obtained at equilibrium was neutralised with triethylamine and the insoluble salt formed eliminated by centrifugation. Its polymeric nature was checked by size exclusion chromatography (SEC) in water, which reveals the presence of oligomers. On the basis of PEO calibration, the following molar masses were determined: $M_w = 5300$, $M_n = 2100$. The polymer was then reacted with hexafluoroacetone and the resulting compound analysed by ^{19}F NMR: the chemical shift of the hemiketal formed shows definitely that all the alcohol groups present are located at the end of the PDGF chains. However, it has been shown that in all these cyclic acetal polymerisations, whatever the cationic mechanism, cyclic species are formed besides the linear ones. This is confirmed experimentally and it is well documented in the case of PDGF for which the absolute values of the concentration of the various rings formed have been determined [29]. As the SEC of our sample shows degrees of polymerization ranging from 1 (monomer) to about 300, we can thus calculate that the rings present at equilibrium represent 0.403 mol of monomer base units per litre. Since the initial monomer concentration is 2.77 mol per litre, the rings represent 14.6% of the crude sample. As a consequence one can calculate M_n of the dihydroxylated linear chains knowing the concentration of those hydroxyl groups: a value of 2400 is found. In order to increase the molecular weight of the crude polymeric sample, the linear α,ω-dihydroxylated chains were coupled by a method based on the preparation of ethers by the Williamson reaction [30]. Thus 9.03 g of PDGF were dissolved in 5 ml of methylene chloride, added to 8.5 g of potassium hydroxyde and further diluted with 8 ml of toluene. After reaction the solution was filtered and washed several times with water and the polymer recovered by evaporation. The SEC shows a large distribution of the molecular weights but still a definite increase in the average molar mass. Thus the polymer was submitted to a fractionated precipitation using the toluene/cyclohexane mixture. Three fractions were obtained showing indeed a fractionation according to the molecular weight. The second one presents the smallest polydispersity and is free from oligomers smaller than octamers, as shown by SEC. This fraction was used in the present study. Its molar mass was determined by SEC in salt containing water, using both PEO calibration and direct measurements by light scattering. Results in good agreement were obtained $M_w = 17\,300$, $M_n = 11\,300$. Assuming that no large cycles could be obtained by intramolecular reaction during the polycondensation, one should consider that the only cycles present are those already formed during the cationic polymerisation except the smaller ones (monomer to heptamer) which were eliminated during the fractionation. It is then easy to estimate the amount of rings still present which are all non-strained, since its absolute value in terms of moles of monomer units per litre is given by the equation:

$$\sum_{8}^{300} [cM_x]x = A\sum_{8}^{300} x^{-1.5} \approx 0.18 \times 0.807 = 0.14 \qquad (1)$$

Table 1
Characteristics of the polymers

Type of copolymer	Repeat unit	x(EO)	x(MO)	δ J$^{1/2}$ ml$^{-1/2}$	Samples used	M_W	Polydispersity
PEO	EO	1.00	0.00	22.8			
PTGF	EO_3MO	0.75	0.25	24.1	PTGF	38 000[a]	
						32 000[b]	1.6
						37 000[c]	1.7
PDGF	EO_2MO	0.57	0.43	24.5	PDGF	17 000[c]	1.5
PDXL	EO + MO	0.5	0.50	25.4	PDXL-1	50 000[a]	
						53 000[b]	
PMO	MO	0.00	1.00				

[a] The weight average molecular weight M_W was obtained by light scattering in water.
[b] The weight average molecular weight M_W was obtained by size exclusion chromatography (SEC) in THF using a PEO calibration.
[c] The weight average molecular weight M_W was obtained by SEC coupled with multiangle light scattering in water 0.1 N NaCl.

where $[cM_x]$ is the concentration in moles per litre of a ring possessing x monomer units and A is a constant already determined to be equal to 0.18. Thus one finds 0.145 mol of monomer units per litre present in cycles. When compared to the initial 2.77 mol per litre of monomer of the cationic polymerisation this represents about 5% of monomer units incorporated in rings, 95% being linear species. In fact this value of 5% is overestimated since the two other fractions also contain some cyclic species, the different factions overlapping in a large molecular weight domain.

Table 1 gives the molecular characteristics of the different polymer samples as determined by light scattering and size exclusion chromatography. The SDS sample from Serva was used without purification.

2.2. Techniques

2.2.1. Turbidimetry

The cloud points T_c of the polymer solutions in the presence and the absence of SDS were measured with a Mettler FP81 apparatus. The solutions contained in cylindrical cells (1 mm i.d. and 79 mm length) were heated at a rate of 2°C/min.

2.2.2. Conductimetry

The conductivity experiments were carried out on a Wayne Kerr B 905 A autobalance bridge, with a relative accuracy of 2×10^{-4} on the conductivity values. The solutions were contained in a double-wall glass vessel thermostated at 25 ± 0.1°C. A Tacussel conductivity cell (whose constant is equal to $0.7\ \text{cm}^{-1}$) was used in all the measurements. A typical experiment was conducted as follows: a given volume of surfactant-free polymer solution was introduced in the conductivity cell and aliquot samples of a polymer solution containing SDS at a concentration much higher than CMC (critical micellar concentration) were added and the conductivity was measured after each addition. The variation of the specific conductivity κ as a function of the SDS concentration (C_{SDS}) was generally obtained by keeping the polymer concentration C_p constant. In another series of measurements, the conductivity was measured at constant C_{SDS} and increasing C_p. All the experiments were performed without added salt.

2.2.3. Viscosimetry

An automatic capillary viscometer of the Gramain–Libeyre type [31] was used. The apparatus was thermostated at 25 ± 0.1°C and the reproducibility of the flow time was 0.02%.

2.2.4. Static fluorescence

The solutions were prepared as above for conductimetry except that pyrene-saturated deionised water was used as a solvent. Fluorescence spectra were recorded on a Hitachi F-4010 between 350 and 500 nm. The excitation wavelength was set at 335 nm. The vibronic fluorescence spectra of pyrene exhibit five peaks noted 1–5 and it is well known that the ratio I_1/I_3 of the intensities of the first to the third peak correlates with the polarity of its immediate environment where the probe (pyrene) is located [32,33]. I_1/I_3 is equal to about 1.9 when pyrene is in an aqueous medium and drops to 1.2 when pyrene is solubilised in a medium of lower polarity, for example in SDS micelles and to an even lower value when it is located in a non-polar organic solvent.

In the first set of experiments, I_1/I_3 was measured as a function of SDS concentration in order to follow the micellization process and to determine an order of magnitude of the CMC.

In a second set of measurements, we determined the aggregation number of the micelles from the fluorescence decrease of the probe as a function of the concentration $[Q]$ of a fluorescence inhibitor [34,35] that also lies in the micelles. The fluorescence intensity I_I in the presence of the inhibitor is given by:

$$I_I = I_0 \exp(-[Q]/[M]) \qquad (2)$$

I_0 is the fluorescence intensity in the absence of inhibitor and $[M]$ is the concentration of micelles. $[M]$ is directly obtained from the slope of a $\log((I_I/I_0) = f(([Q]))$ plot and the

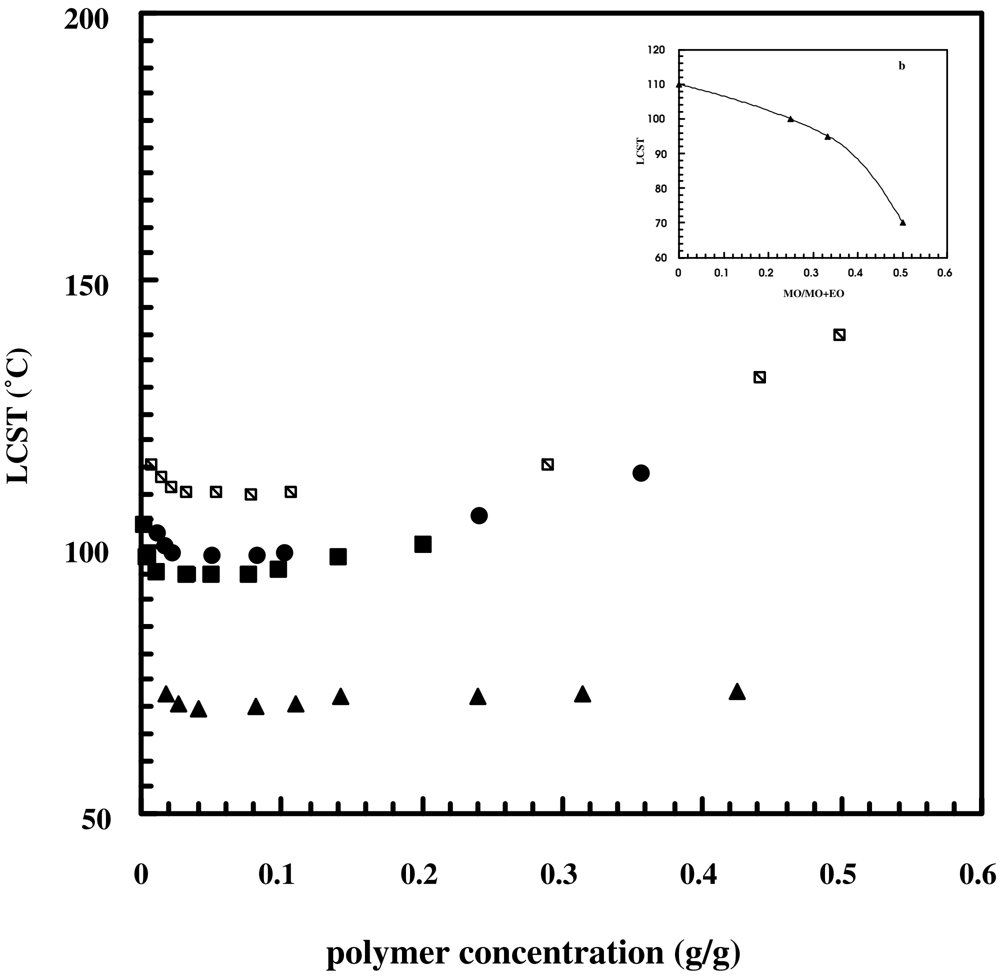

Fig. 1. (a) Variation of the cloud point with polymer concentration for PEO ($M_W = 35\,000$) (□), PTGF ($M_W = 35\,000$) (●), PDGF (17 000) (■) and PDXL (($M_W = 50\,000$) (▲). (b) Variation of the LCST versus the ratio x(MO).

aggregation number N_A is calculated from:

$$N_A = (C_{SDS} - \mathrm{CMC})/[M] \qquad (3)$$

Dodecylpyridinium chloride was used as an inhibitor at a concentration low enough to not perturb the self-assembly of the SDS molecules. The experiments were carried out by keeping the pyrene concentration constant (saturated solutions) and increasing [Q]. It is not necessary to remove oxygen from the solutions.

3. Results and discussions

3.1. Turbidimetry

3.1.1. Polymers in pure water

The PEO in water exhibits a particular solubility diagram so-called “closed loop diagram” which reveals the existence of a LCST (around 100°C for an infinite molecular weight) and an upper critical solution temperature above 210°C (UCST = 230° for $M_W = 2300$) [2]. The more accessible demixing line is that which corresponds to the LCST. In Fig. 1(a) we report such demixing lines for PEO ($M_w = 35\,000$) [8,9], PTGF ($M_w = 35\,000$) [10], and PDXL ($M_w = 50\,000$)$^{(8,9)}$ as obtained in previous works and that of PDGF ($M_w = 17\,000$). Fig. 1(b) gives the variation of the LCST versus the ratio $x(\mathrm{MO}) = \mathrm{MO}/[\mathrm{EO} + \mathrm{MO}]$ where MO and EO are the number of methylene oxide and ethylene oxide repeating units in the polymer. One must take into account the differences in the molecular weight of the samples in this comparison, but the results of Saeki et al. [2] obtained for PEO show that in this range of molecular weight the discrepancy in the LCST values cannot exceed 4°C. Such a behaviour can be qualitatively related to the hydration number which decreases when r increases. Indeed, differential scanning calorimetry measurements carried out on PEO, PDXL and PTGF solutions suggest that the EO units are the only sites of water binding in these polymers. On the other hand, the thermodynamic and conformational properties of PEO, PDXL and PTGF vary with temperature as expected from the polymer theories [9,10].

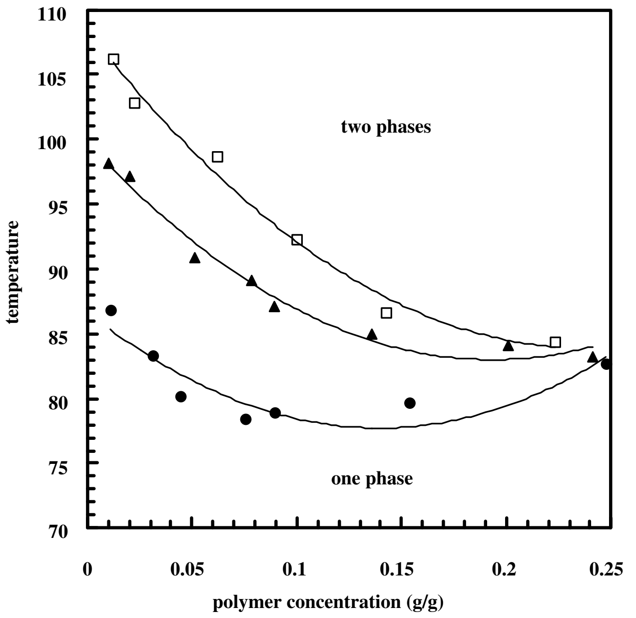

Fig. 2. Variation of the cloud point of PDXL aqueous solutions versus polymer concentration: in pure water (●), in the presence of 0.01 M SDS (▲) and 0.02 m SDS (□).

3.1.2. *Polymers in the presence of SDS*

If the SDS molecules bind onto the polymer chains, the polymer/SDS complex formed through such an association is expected to exhibit thermodynamic properties quite different to those of the pure polymer. In particular, a question arises from its solubility limit or cloud point compared to that of the pure polymer. Such an effect was difficult to observe with PEO since its LCST considered in aqueous solution without additives are always higher than 100°C and its measurement requires special devices working under pressure. The other polymers used in this work and particularly PDXL of lower LCST in pure aqueous solutions is much better adapted to such a study. In Fig. 2, the cloud points of the PDXL–SDS solutions are plotted as a function of polymer concentration for different values of C_{SDS}. It turns out that at the lower C_{p} the SDS binding results in a significant increase of the cloud point, this effect decreasing when the ratio $C_{\mathrm{SDS}}/C_{\mathrm{p}}$ decreases. This binding induces a polyelectrolyte character to the polymer and the electrostatic repulsion between the charges of the SDS molecules improves the stability of these polymers in water, hindering the phase separation due to the loss of hydration upon heating. The complex may be considered as a copolymer where a fraction of monomers are associated with SDS and a fraction associated with water molecules. The first type of monomers are much more soluble at high temperature than the second type.

3.2. *Conductimetry*

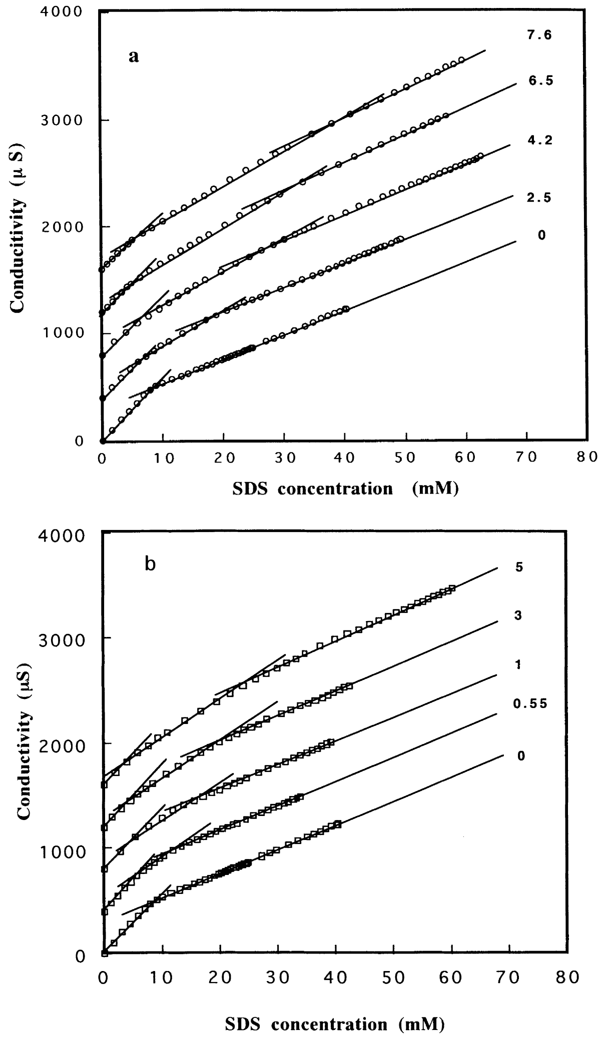

Fig. 3. Variation of the specific conductivity as a function of SDS concentration for different concentrations c_{p} (expressed in g/l) of (a) PDXL and (b) PDGF aqueous solutions. All the curves start at the origin. They have been shifted for better readability.

Conductivity or superficial tension measurements can be used to characterise the interactions between non-ionic polymers and ionic surfactants. Conductivity studies are relatively easy to carry out due to their low sensitivity to the impurities and they allow us to determine the association diagram of the components. It is well known that in aqueous solutions of surfactant, the micellization is revealed by a break in the plot of the specific conductivity κ as a function of concentration, as shown in Fig. 3(a), curve 0. We find the standard value of $\mathrm{CMC} = 8$ mM for SDS. Conductivity measurements, in the presence of SDS, are generally conducted by keeping constant the polymer concentration C_{p} and varying the SDS concentration C_{SDS}. The same plot of $\kappa = f(c_{\mathrm{p}})$ as for pure SDS is observed if there is no interaction with the surfactant (example of PEO-cationic surfactant systems [11] at room temperature). A polymer–surfactant association can be detected through the existence of two breaks in the curves. The first one, at $C_{\mathrm{SDS}} = C_1 < \mathrm{CMC}$ is generally considered as the onset of the binding of SDS onto the polymer; the second one at $C_{\mathrm{SDS}} = C_2 > \mathrm{CMC}$ is assumed to correspond to the polymer saturation in SDS [3–6] (e.g. PEO–SDS). By plotting C_1 and C_2 versus polymer concentration, almost two straight lines are obtained which give the limits of three regions: region A for ($C_{SDS} < C_1$) where there is no interaction between the surfactant and the polymer, region B ($C_1 < C_{SDS} < C_2$) where association takes place and region C ($C_{SDS} > C_2$) where an excess of SDS is present in equilibrium with a polymer–surfactant complex. It is generally accepted for the system PEO–SDS [18,19] that, in region B, (with $C'_2 < C_2$) all the added SDS molecules bind on the polymer under the form of micelles. Then, the concentration in the bulk increases up to a value close to the CMC in pure SDS solution, (at C_2) at which free micelles begin only to be formed. This implies a very high value of the association constant of SDS with the polymer and the true amount of SDS bound onto the polymer is in this case $C_2 - C_1$. For other systems corresponding to weaker polymer–SDS interactions, the formation of free micelles begins before complete saturation of the polymer is attained. This is the case of PVA (poly-(vynilic alcohol)–SDS [33,34] and PDXL–SDS [21] systems, as demonstrated through the equilibrium model proposed by Gylanyi et al. [33,34]. The amount of SDS bound onto the polymer is then expected to be higher than $C_2 - C_1$.

Fig. 3(a) and (b) shows typical plots of $\kappa = f(C_{SDS})$ obtained for various PTGF and PDGF concentrations and that of pure SDS solutions for comparison. They exhibit the features described above for a PEO–SDS system [13–16] and provide the values of C_1 and C_2.

Table 2
Amount of SDS bound onto the different polymers and solubility parameters

Polymer	Y_W mol g^{-1}	Y_M	Y_O
PEO	0.0074	0.33	0.33
PTGF	0.0044	0.71	0.24
PDGF	0.0036	0.42	0.21
PDXL	0.0025	0.18	0.18

In Fig. 4, the variations of C_1 and C_2 versus C_p for the PTGF and PDXL can be compared with the results already deduced from conductivity measurements for the PEO–SDS and PDXL–SDS systems [21]. While the onset of binding is slightly dependent on the polymer composition, the value of C_2 strongly increases when the content of ethylene oxide increases. If we assume in a first approximation that ($C_2 - C_1$) is close to the amount of SDS bound onto the polymer, we can define two parameters Y_W and Y_M which represent the number of SDS molecules bound per gram of polymer or per mole of monomer unit, respectively. In Table 2, we give the values of Y_W and Y_M obtained for the four polymers. Y_W decreases when the ratio x(MO) increases while Y_M passes through a maximum which is due to the x(MO) dependence of the molecular weight of the monomer unit. What is more interesting is to express the amount of bound SDS with respect to the number of ethylene oxide units in the chain, Y_O (Table 2). This parameter strongly decreases with the percentage of methylene oxide units, as shown in Fig. 5, and tends to zero for a pure "hypothetical" poly(methylene oxide) in solution. This indicates that the binding of SDS is hindered by the presence of methylene

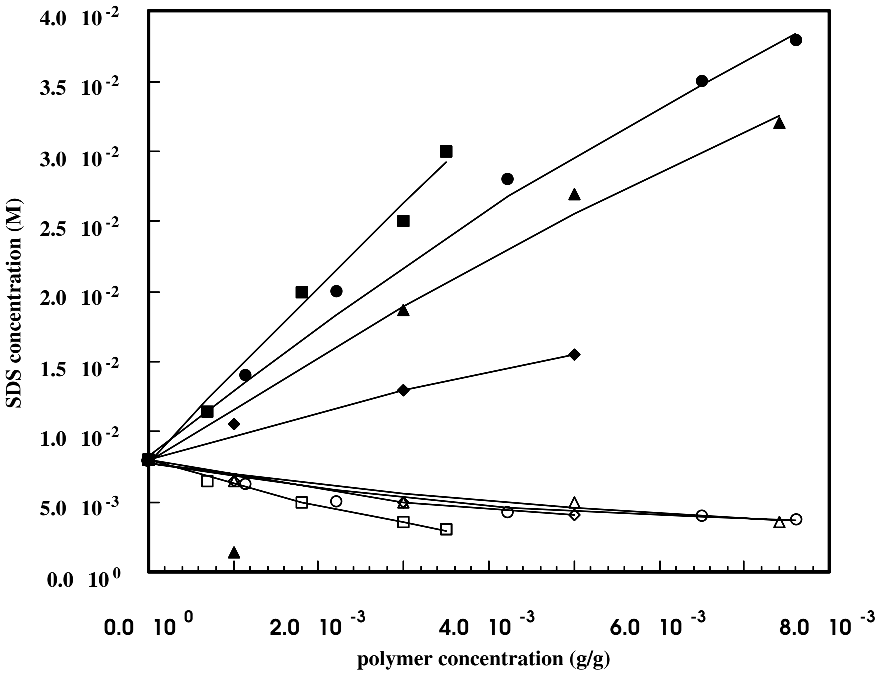

Fig. 4. Phase diagrams of PEO–SDS (□,■), PTGF–SDS (○,●), PDGF–SDS (△,▲) and PDXL–SDS (◇,◆) systems, as deduced from conductivity measurements: C_1 (open symbols); C_2 (full symbols).

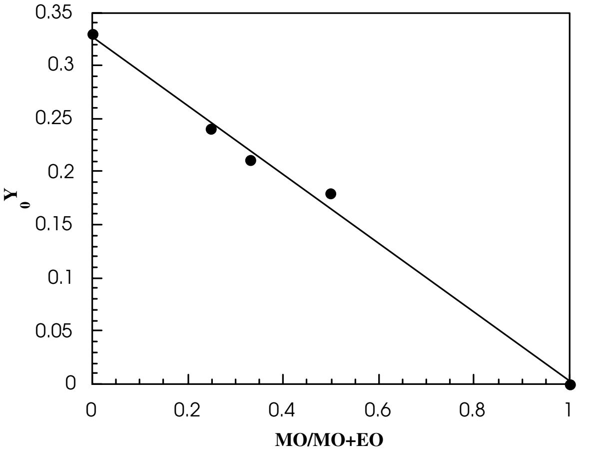

Fig. 5. Variation of the parameter Y_o (see text) as a function of the ratio *r*.

oxide units. This result fits quite well with the hypothesis according to which the hydrophobicity is the relevant parameter to describe the association between a polymer and sodium dodecyl sulphate (see values of the solubility parameters deduced from Van Krevelen [22] given in Table 2).

We have studied under the same conditions the SDS–PTGF system at two other temperatures 35 and 45°C. We wanted to verify if the SDS binding is amplified by enhancing the hydrophobic character of the polymer upon heating. In fact, we have not observed significant variations of $C_2 - C_1$ with temperature. This suggests that, even if $C_2 - C_1$ does not increase with T as expected, the polymer probably remains decorated with SDS micelles up to the phase separation temperature. This information will be useful to understand the results by turbidimetry.

It is also interesting in these measurements, to keep C_{SDS} constant and increase C_p. Fig. 6 shows the results obtained with PEO, PTGF and PDXL. Two situations must be considered $C_{SDS} < \text{CMC}$ and $C_{SDS} > \text{CMC}$. In the first one, the addition of polymer induces a loss of conductivity which means that the transfer of isolated molecules from the bulk to the polymer chains corresponds to a decrease of the average ionisation degree and/or to a decrease of the electrophoretic mobility of the charges due to the fact that they are bound onto the polymer of a larger hydrodynamic radius. On the contrary, when $C_{SDS} > \text{CMC}$, i.e. when micelles are already formed in the bulk before polymer addition, κ increases for lower C_p values, then passes through a maximum. This effect is much more pronounced for PDXL than for PEO, and PTGF behaves almost as PEO. The average contribution of a SDS molecule to the conductivity increases when it passes from a micelle in the bulk to a micelle located on the macromolecule chain and this necessarily must be attributed to a higher ionisation degree of the SDS molecules bound to the polymer. At higher polymer concentration, when all the SDS already present in the free micelles of the bulk is adsorbed on the polymer, only isolated SDS molecules remain in solution; they are in equilibrium with the polymer–SDS complex and further addition of polymer provokes a loss of conductivity comparable to the situation when the initial C_{SDS} was lower than the CMC. The contribution of the micelles, either isolated or

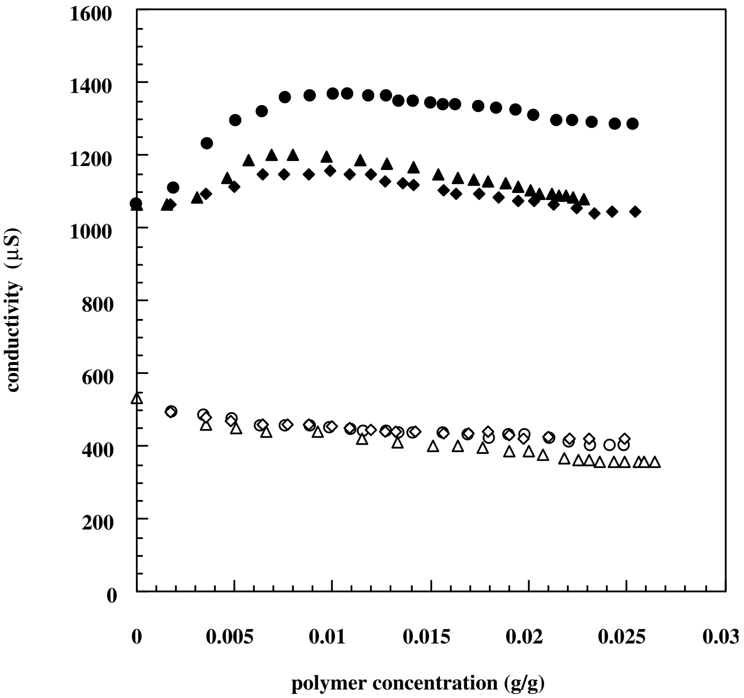

Fig. 6. Variation of the specific conductivity as a function of the polymer concentration for two constant values of the SDS concentration: 0.01 M (open symbols) and 0.034 M (full symbols): PEO (□,■), PTGF (△,▲) and PDXL (○,●).

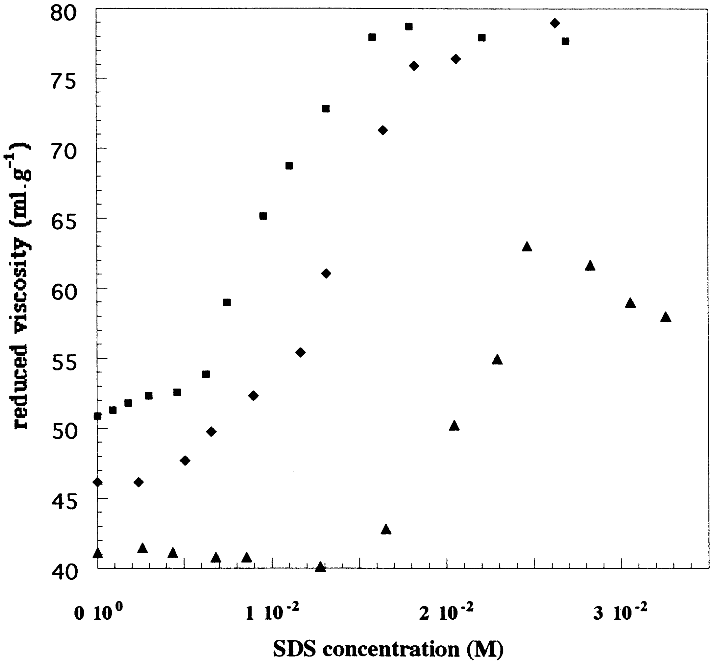

Fig. 7. Variation of the reduced viscosity versus SDS concentration for PTGF–SDS (▲), PEO–SDS (◆) and PDXL–SDS (□).

polymer-bound, are essentially related to their ionisation degree. This result shows that the degree of ionisation of the micelles bound on the polymer varies as a function of the polymer with the following order:

PEO < PTGF < PDXL

We find again through this experiment, the systematical evolution of the properties of the bound micelles with the polymer hydrophobicity.

3.3. Viscosimetry

An other consequence of the binding of ionic surfactant on non-ionic polymers is a change of the polymer conformation when C_{SDS} increases at constant C_{p}. We have already shown that the variation of the viscosity of a solution of polymer and SDS, η_{red} versus C_{SDS} exhibits three parts: the first one at $C_{\mathrm{SDS}} < C_1$, where η_{red} varies with C_{SDS} with almost the same slope as for pure SDS solution, the second one where η_{red} abruptly increases for $C_1 < C_{\mathrm{SDS}} < C_2$ and the third one where η_{red} reaches a region where it decreases slowly. Fig. 7 shows that the same behaviours are observed for PTGF as well. It is now well established that such a behaviour is due to the electrostatic repulsion between the charged SDS micelles bound along its chain. The behaviour of PTGF in this figure is surprising, because the changes in the viscosity curves are shifted with respect to the values of C_1 and C_2 determined by conductivity. Moreover, while for the other measurements PTGF exhibits a behaviour close to that of a PEO of the same molecular weight, the amplitude of the η_{red} increase is lower for PTGF.

This study may give an order of magnitude of the PEO chain expansion, upon SDS binding. In a first approximation, we will assume that the polymer concentration is low enough to assimilate η_{red} to the intrinsic viscosity $[\eta]$, by using the classical Flory–Fox expression:

$$[\eta] \propto \frac{\left\langle R_{\mathrm{g}}^2 \right\rangle^{3/2}}{M} \tag{4}$$

where R_{g} and M are, respectively, the radius of gyration and the molecular weight of the macromolecule assumed to be a coil. The chain expansion α is obtained from:

$$\alpha = \left(\frac{[\eta]_2}{[\eta]_1} \right) \tag{5}$$

Values of α equal to 1.19, 1.15 and 1.15 were found for PEO, PTGF and PDXL, respectively. Finally the chain expansion does not vary much with the polymer composition. This is not surprising since we have already seen that if the amount of bound SDS decreases when the ratio x(MO) increases, the ionisation increases. As the enhancing of viscosity is clearly related to a polyelectrolyte like behaviour of the complex, it is quite normal that viscosity will depend on both the total number of SDS and on its ionisation degree. In our case, when the three polymers are compared, there is a compensation of the two effects.

3.4. Fluorescence

The drop of the ratio of the first to the third peak intensities of the fluorescence spectrum of pyrene when $C_{\mathrm{SDS}} = \mathrm{CMC}$ is well correlated to the micellisation, for pure SDS. Similarly, a decrease of this ratio was observed at SDS concentrations slightly lower than C_1 in the presence

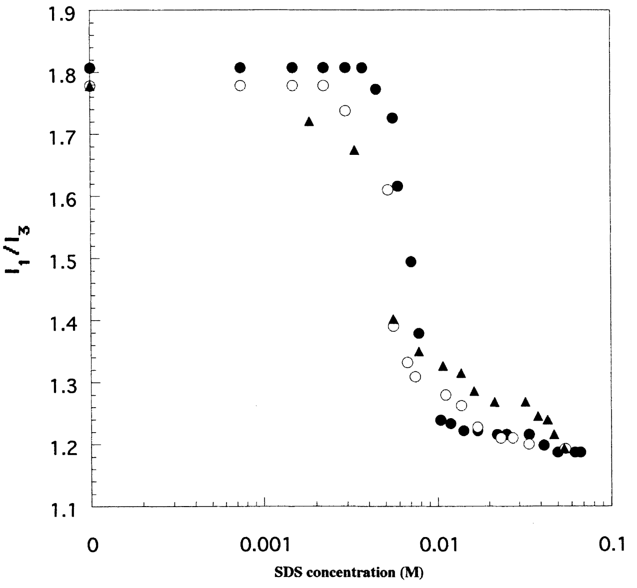

Fig. 8. Variation of I_1/I_3 versus SDS concentration for pure SDS (●), and PTGF–SDS with $c_p = 5$ g/l (○) and $c_p = 10$ g/l.

of POE and PDXL. We have verified that the same behaviour appears in the presence of PTGF (Fig. 8).

The aggregation numbers N_A as measured by static fluorescence of pyrene in the presence of an inhibitor are plotted versus C_{SDS} for different systems. We have already discussed the experimental limits of such an experiment [21]. A good accuracy on the N_A values requires SDS concentration larger enough than CMC and in the presence of a polymer, some conditions must be respected: since the C_1 value was used instead of CMC in relation (2), $C - C_1$ must be large enough and $C < C_2$, so that the free micelles do not interfere with bound micelles. These conditions are obtained only for large polymer concentrations and the results obtained here correspond to $c_p = 20$ g/l. Our previous results have shown that the aggregation number remains in the range 35–37 and 12–15 for POE and PDXL, respectively, when $C_1 < C_{SDS} < C_2$; for $C_{SDS} \gg C_2$, the same value of about 60 is again obtained, but here, one essentially measures the aggregation number of the bulk micelles. As expected PTGF and PDGF exhibit an intermediate behaviour, the aggregation number of the bound micelles are slightly lower than for PEO: $N_A = 31$ and 20 for PTGF and PDGF, respectively, (see Fig. 9). Fig. 9 shows the continuous decrease of N_A when the ratio x(MO) increases.

These results confirm our previous observations that demonstrated that the aggregation number of the micelles bound on polymers is smaller than that of the free micelles. Besides, lower the fraction of EO units, lower the N_A value. Our different results are self-consistent since the decrease of the aggregation number of a micelle is generally accompanied by an increase of their ionisation degree, as observed by conductimetry.

4. Discussion

The experimental results are in general agreement with the previous literature data dealing with the interactions between non-ionic polymers and anionic surfactants. They indeed confirm that binding proceeds by a co-operative way meaning that SDS binds under the form of micelles and not

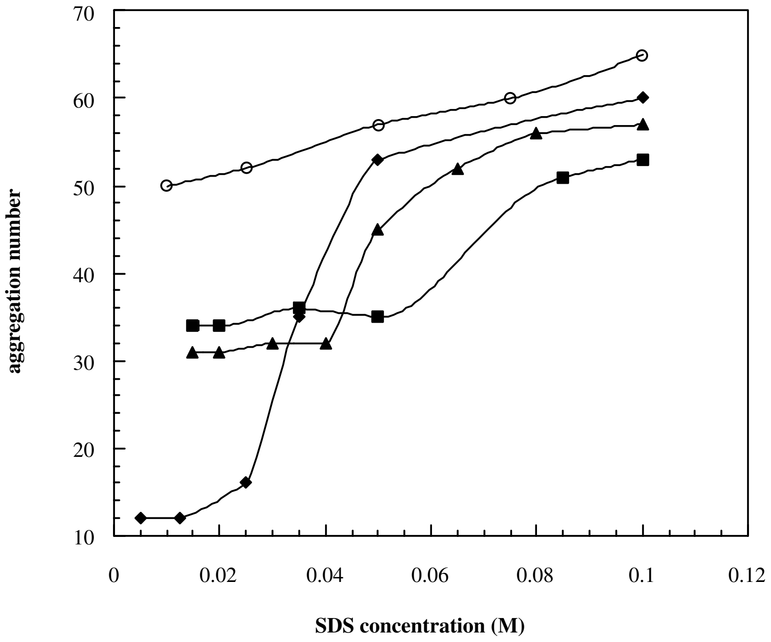

Fig. 9. Variation of the aggregation number N_A versus SDS concentration in SDS (○) and polymer–SDS solutions ($c_p = 20$ g/l) PEO (■), PTGF (▲) and PDXL (◆).

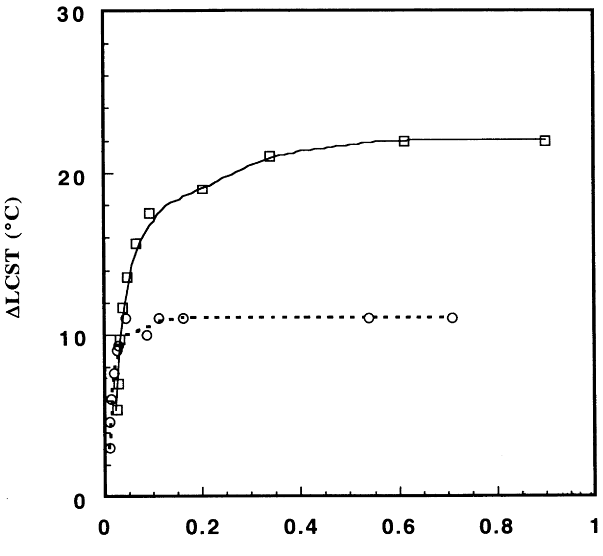

Fig. 10. Variation of ΔLCST versus the average fraction of PTGF units bound to SDS (τ) for two constant SDS concentrations: 0.01 M (○) and 0.02 M (□).

as isolated molecules. The SDS binding confers to the non-ionic polymer a polyelectrolyte character which is reflected by a chain expansion and by an increase of the reduced viscosity.

Our study provides several new informations:

1. In the case where the solubility of the polymer in water is poor (relatively low value of LCST) the SDS binding enhances the solubility (increase of LCST upon addition of surfactant)
2. In the series of polyethers studied here, empirical variations of several parameters characterising the SDS–polymer interactions versus the polymer composition were established:

- the total amount of bound SDS as measured by conductimetry decreases when the fraction of ethylene oxide units decreases and tends to 0 for an hypothetical water soluble poly(methylene oxide)
- the ionisation of the complex is an increasing function of x(MO).

Point 1 (enhancing of solubility) must be discussed in relation with the other data. In Fig. 10, we have plotted ΔLCST (i.e. the difference between the LCST values in the presence and in the absence of SDS) versus τ, the average fraction of EO units bound to SDS calculated by assuming that this fraction increases linearly with C_{SDS} in the region $C_1 < C_{\mathrm{SDS}} < C_2$. Such a behaviour is that obtained through a model of association where two different equilibria are considered: the micellisation equilibrium of SDS in the bulk and the complexation equilibrium of SDS and polymer [21,36,37]. Above, we suggest that the SDS–polymer complex behaves simply as a copolymer constituted of pure EO monomer units of poor solubility and PEO monomer units bound to SDS and then charged and of higher solubility. One could expect almost the same value of LCST for the two SDS concentrations considered in our experiments, as far as the corresponding values of τ are equal. In fact, one observes that ΔLCST is much higher for $C_{\mathrm{SDS}} = 0.02$ M than for $C_{\mathrm{SDS}} = 0.01$ M, as compared at the same $\tau > 1$. Moreover, in each case, ΔLCST reaches a plateau for very low values of τ, $\tau > 0.1$ and $\tau > 0.3$, for 0.01 and 0.02 M, respectively. Our qualitative explanation remains correct, but the phenomenon is probably much more complicated and other aspects must be taken into account such as the influence of the free SDS molecules on the thermodynamical properties of complex PDXL/SDS.

Points 2 shows a correlation between size and ionisation of the micelles. As a general conclusion, it clearly appears that EO units are responsible for the SDS binding in this polyether series. In the case of PEO, starting from a basis of Na = 35 and $Y_{\mathrm{M}} = 0.32$, one finds that PEO is decorated by one micelle per approximately 100 monomers. This ratio is, respectively, 45, 59 and 66 for PTGF, PDGF and PDXL. However the number of EO units per micelle is 135, 120 and 66. Then, a high fraction of MO in the polymer chain hinders not only the SDS binding but also constitutes a limiting factor for the co-operative process and for the micelle growth. This suggests that the formation of relatively high aggregation number micelles require sequences of EO units. A reasonable hypothesis may be that either MO units and SDS have a repulsive interaction or that the formation of SDS–polymer complex implies a minimum number of consecutive EO units. Cabanes et al. [19] have found that the radius of the bound SDS micelles is close to 21 Å. On the other hand, RMN experiments [18] have revealed that only the segments close to the ionic group of SDS are perturbed by the binding along PEO chains. It is reasonable to assume that the methine groups (CH_2–CH_2) of PEO interact with these first segments of the aliphatic chain. The comparison between the monomer unit length (approximately 5 Å) and the size of the micelle may indicate that much more than one monomer unit is included in the micelle and this effect stabilises micelles of relatively large size. When the sequence of EO units is interrupted by MO units which do not enter in the micelles, the equilibrium aggregation number becomes lower. At this stage of the discussion, one must also consider the role played by the polar part of these polymers constituted by the oxygen which is always assumed to be able to bind cations [38]. By this way, PEO bearing cations becomes a positively charged polymer which has a attractive electrostatic interaction with the SD anions. Such an effect may contribute to the complex stabilisation. Through the role played by –O– it may be possible to understand why the interaction of PEO with cationic surfactants are much lower than those observed with SDS. The accessibility of –O– may be sterically hindered in the MO units and may also explain the evolution of the SDS–polymer interactions when the fraction of MO units increases.

5. Conclusion

This work provides a rather complete description of the interactions of SDS with polyethers according to the polymer composition. Ethylene oxide units are the most interactive and the presence of MO hinders the growth of the micelles. This suggests that a minimum length of EO units is necessary for the complex formation. Nevertheless, such an idea has to be confirmed by spectroscopic measurements in order to get information on the structure of the complex.

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