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Interactions of polyethers with a cationic surfactant

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Abstract

The paper deals with the interactions between a cationic surfactant dodecyl tetrabromide (DTB) and polyethers containing variable mole fraction (τ) of methyleneoxide units MO: (poly(ethylene oxide), PEO without MO, poly(1,3,6,9-tetraoxacycloundecane), PTGF with a MO fraction of 0.25 and poly(1,3-dioxolane) PDXL with a fraction of MO of 0.5. Conductivity measurements show weak interactions at a temperature $T = 50$°C, while they are absent for the three polymers at room temperature. The solubility of PDXL which has a relatively lower critical solution temperature in water is improved by the presence of the surfactant. Besides, at $T = 50$°C the viscosity increases upon addition of DTB. The association diagrams do not significantly differ for the three polymers which is very different from what was observed with an anionic surfactant. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethers; Dodecyl trimethylammonium bromide; Binding

1. Introduction

The interactions between ionic surfactants and various non-ionic polymers in aqueous solutions have been extensively studied for many years and well-documented papers describe and discuss the experimental results and the theoretical approaches [1,2]. While various polymers can interact with surfactants, the system that was certainly the most known is the system poly(ethylene oxide) (PEO)–sodium dodecyl sulphate (SDS). Many experimental tools were used and all the investigations have led to a qualitative model where SDS molecules bind onto the PEO chain under the form of micelles [3–10]. From a theoretical point of view, the adsorption isotherms may be predicted from equilibrium laws whereby the phenomenon observed would be the result of a competition between micellization in the bulk of the solution and on the polymer [11–13]. Nevertheless, the driving forces for these polymer–surfactant interactions is not clearly understood. Hydrophobic interactions are generally invoked, however, this is not completely satisfactory as this does not explain the absence of interactions between cationic surfactants and PEO at room temperature. It must be pointed out that recent studies have revealed the appearance of interactions between such surfactants and PEO upon heating [14]. As it is known that hydrophobic interactions are enhanced by increasing temperature, this result confirms the preponderant role played by these type of interactions. We have recently compared the behaviours towards SDS of several polyethers containing variable mole fractions of methyleneoxide units MO (τ) poly(ethylene oxide, (PEO without MO), poly(1,3,6,9-tetraoxacycloundecane) (PTGF, $\tau = 0.25$), poly(1,3,6-trioxacyclooctane) (PDGF, $\tau = 0.33$) and poly(1,3-dioxolane) (PDXL $\tau = 0.5$). We have found that the strength of the interactions measured through the total quantity of SDS bound on the chains and by the aggregation number of the bound micelles decreases significantly when this ratio τ increases. This suggests that the ethylene oxide units (EO) are the most interactive and that the presence of MO units hinders the growth of the micelles. This is a further argument in favour of the preponderance of the hydrophobic interactions, since the EO units are expected to be more hydrophobic than the MO ones. Nevertheless, the differences observed between the cationic and anionic surfactants must be related to another type of interaction and it seems reasonable to also take into account the negative charge of the oxygen of polyethers which can provoke a binding of the cations. One may think that the sodium ion of SDS would be directly bound on PEO thus inducing micellization.

This paper provides some further information particularly on the influence of the polyether composition on their interaction with a cationic surfactant, the dodecyl trimethylammonium bromide (DTD).

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Table 1
Characteristics of the polymer samples

Type of copolymer	Repeat unit	× (EO)	× (MO)	Samples used	M_w	Polydispersity
PEO	EO	1.00	0.00	PEO	35 000[a]	1.05
PTGF	EO_3MO	0.75	0.25	PTGF	38 000[a]	
					32 000[b]	1.6
					37 000[c]	1.7
PDXL	EO MO	0.5	0.50	PDXL	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.

2. Experimental

We present here only the experimental information necessary for the understanding of the work, but many other experimental details can be found elsewhere [13,15–18].

2.1. Samples

PTGF and PDXL were prepared by cationic polymerization of the corresponding cyclic acetals. The amount of cyclic species in the polymer samples were shown to be negligible. The PEO sample was a commercial product from Hoecht.

Table 1 gathers the values of the molecular characteristics of the polymers. DTB was provided from Merck and used without further purification.

2.2. Techniques

2.1.1. Turbidimetry

The cloud points T_c of the polymer solutions in the presence and absence of DTB were measured with a Mettler FP81 turbidimeter. This apparatus is based on the abrupt change of the intensity of a light scattered at 90°, when an increase of temperature is applied to the sample (1°/min). This corresponds to the appearance of turbidity in the sample and then gives the lower critical solution temperature (LCST).

2.1.2. Conductimetry

The conductivity measurements were carried out with a Wayne Kerr B 905 A autobalance bridge in a double-wall glass vessel thermostated at 25 or 50 ± 0.1°C and a Tacussel conductivity cell. The experimental procedure is described already [13,15].

2.1.3. Viscosimetry

An automatic capillary viscometer of the Gramain–Libeyre type [19] was used. The apparatus was thermostated at 50 ± 0.1°C and the reproducibility of the flow time was 0.02%.

2.1.4. Static fluorescence

Fluorescence spectra were recorded on a Hitachi F-4010 between 350 and 500 nm. The excitation wavelength was set at 335 nm.

In a first series of experiments, the ratio I_1/I_3 of the intensities of the first to the third peak of pyrene used as probe was measured. The surfactant concentration at which this ratio abruptly decreases is generally considered as its micellar critical concentration, CMC [20,21].

In a second set of measurements, the aggregation number of the micelles was deduced from the fluorescence decrease of the probe as a function of the concentration $[Q]$ of a fluorescence inhibitor [22,23] which also lies in the micelles. The fluorescence intensity I_I in the presence of the inhibitor is given by

$$I_I = I_0 \exp(-[Q]/[M]). \quad (1)$$

I_0 is the fluorescence intensity in the absence of inhibitor and $[M]$ the concentration of micelles. The aggregation number N_A is calculated from

$$N_A = (C_{SDS} - \mathrm{CMC})/[M]. \quad (2)$$

Dodecylpyridinium chloride was used as an inhibitor at a concentration low enough not to perturb the self assembly of the DTB molecules.

The fluorescence measurements were performed at 25 or 50 ± 0.1°C.

3. Results

3.1. Conductimetry

We used in the first step the classical conductimetric method in order to detect interactions between DTB and polymers. In the absence of polymer, the variation of the specific conductivity versus DTB concentration (C_{DTB}) exhibits two linear parts, the slope breakdown occurring for the critical micellar concentration (CMC) as shown in Fig. 1. In the presence of a polymer able to bind surfactant molecules, two breakdowns can be observed

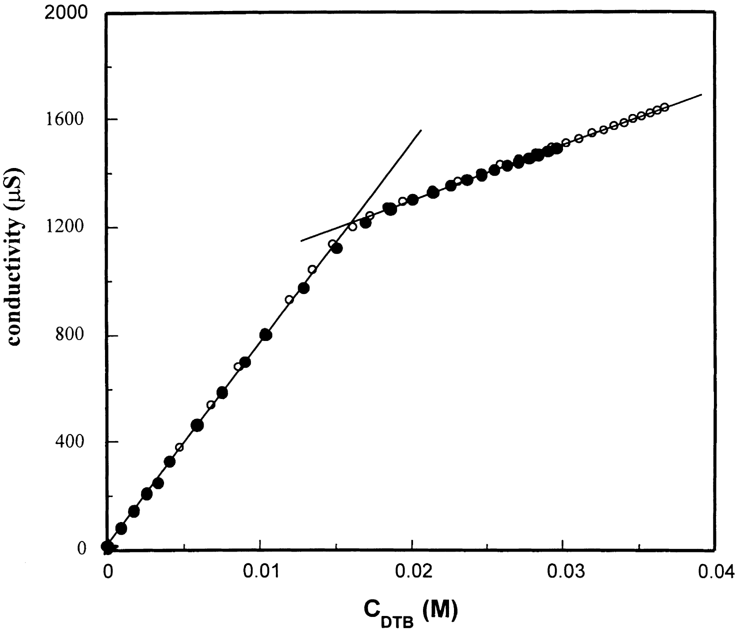

Fig. 1. Variation of the specific conductivity as a function of DTB concentration for pure DTB (○) and PEO (C_p = 0.2 g/l) with DTB (●); T = 25°C.

at concentrations $C_1 <$ CMC and $C_2 >$ CMC. C_1 indicates the onset of surfactant binding while C_2 corresponds to the polymer saturation. Fig. 1 shows that DTB and PEO do not interact at room temperature which is a well-known result. The features of the conductivity curves obtained at T = 50°C for different PEO concentrations (Fig. 2) are completely different from that of pure DTB, meaning that the polymer–surfactant interactions are enhanced upon heating, in agreement with the recent literature data [14]. Such behaviour is consistent with an increase in the hydrophobic interactions. It appears that for the same aliphatic chain of the surfactant, the charge of the surfactant plays an

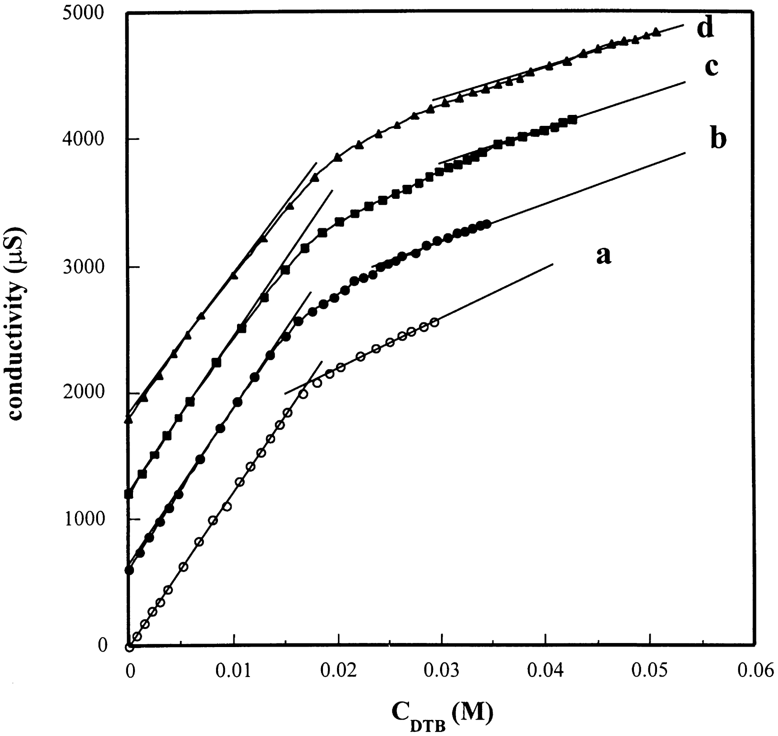

Fig. 2. Variation of the specific conductivity as a function of the DTB concentration for several concentrations of PEO: (a) C_{PEO} = 0 g/l; (b) C_{PEO} = 5 g/l; (c) C_{PEO} = 10 g/l; (d) C_{PEO} = 20 g/l (the curves are vertically shifted to improve readability); T = 50°C.

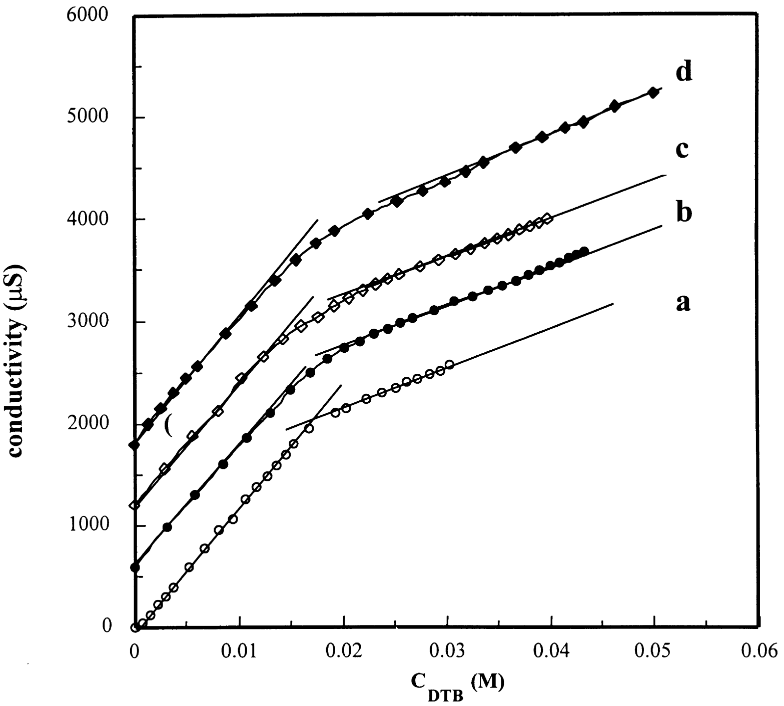

Fig. 3. Variation of the specific conductivity as a function of the DTB concentration for several concentrations of PTGF: (a) $C_{PTGF} = 0$ g/l; (b) $C_{PTGF} = 3$ g/l; (c) $C_{PTGF} = 12$ g/l; (d) $C_{PTGF} = 20$ g/l (the curves are vertically shifted to improve readability); $T = 50$°C.

important role, as SDS interacts strongly with PEO even at room temperature.

Since interactions were observed between DTB and PEO at 50°C, the behaviour of the other polymers was studied at the same temperature. Curves of Figs. 3 and 4 for PTGF and PDXL, respectively, exhibit the same features as for PEO.

From the conductivity curves of Figs. 2–4 values of C_1 and C_2 can be determined and they are plotted versus

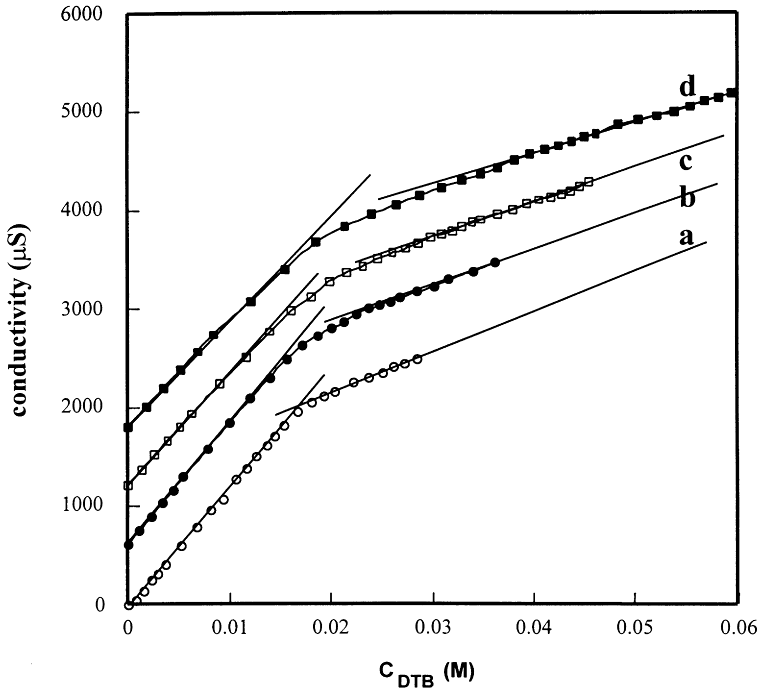

Fig. 4. Variation of the specific conductivity as a function of the DTB concentration for several concentrations of PDXL: (a) $C_{PDXL} = 0$ g/l; (b) $C_{PDXL} = 2$ g/l; (c) $C_{PDXL} = 7$ g/l; (d) $C_{PDXL} = 10$ g/l (the curves are vertically shifted to improve readability); $T = 50$°C.

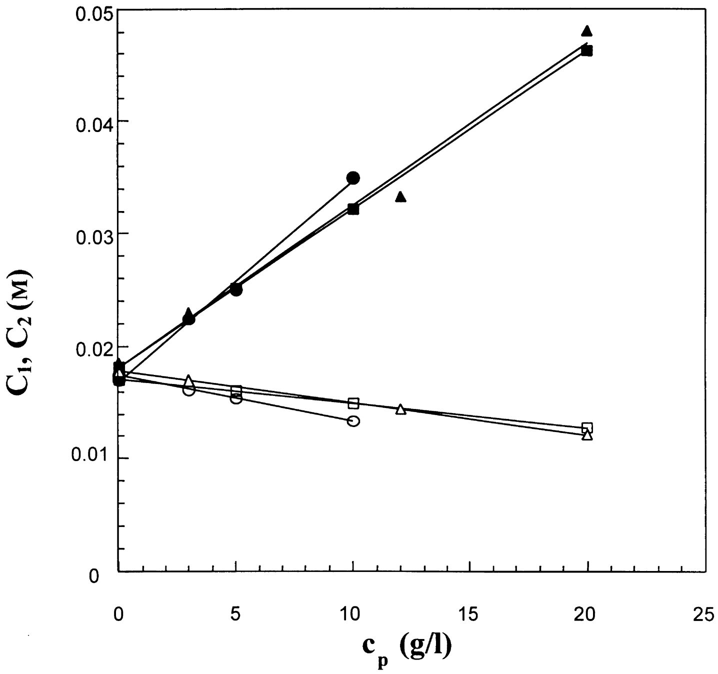

Fig. 5. Phase diagrams of PEO-DTB (△,▲), PTGF-DTB (□,■), and PDXL-DTB (○,●) systems, as deduced from conductivity measurements: C_1 (open symbols); C_2 (full symbols) $T = 50$°C.

polymer concentration in Fig. 5, which corresponds to the so-called phase diagram for each polymer. No big differences between the three polymers are observed, if one considers the bad accuracy on the determination of C_1 and C_2. In Table 2 are reported the values of Y_W and Y_M which represent the number of DTB molecules bound per gram of polymer or per monomer unit, respectively. It seems that PDXL interacts slightly more with DTB than PEO, if these values are considered. It is interesting to observe that these differences subsist if one measures the binding by the number of DTB bound per EO units, Y_{EO}, while it disappears if one uses another parameter, Y_O, which is the number of DTB molecules per ether oxide. In Table 2 are also given the values of Y_W, Y_M and Y_{EO} obtained with SDS at 25°C. The comparison demonstrates that in the case of an anionic surfactant, the EO units play the main role while the MO and EO seem to have the same interactions with a cationic surfactant. For PDXL, the behaviours obtained with DTB at 50°C are approximately the same as that observed with SDS at 25°C. PEO binds much more SDS at room temperature than DTB at 50°C.

3.2. Fluorescence

It is well known that the fluorescence emission spectrum of pyrene exhibits five peaks (noted 1–5) and that the ratio I_1/I_3 of the intensities of the first to the third peak correlates with the polarity of the medium where pyrene is solubilized. This behaviour is currently used to detect a micellization or association phenomenon when nano-domains are formed at the CMC. Fig. 6 shows that I_1/I_3 of pyrene in DTB solutions drops from 1.86 to 1.4 when C_{DTB} increases. At 25°C (Fig. 6), no difference in such curves obtained in the presence and in the absence of PEO can be detected. PTGF and PDXL probably weakly interact with DTB since the drop of I_1/I_3 starts at lower DTB concentrations. Nevertheless, the phenomenon is more pronounced at 50°C as shown in Fig. 7. Micelles appear at much lower concentration in the presence of PDXL. This result confirms that interactions are enhanced upon heating.

The aggregation number of DTB was also measured at 50°C in the absence and in the presence of 1% of the three polymers. The results which are reported in Fig. 8 show that

Table 2
Amount of DTB and SDS bound onto the different polymers

	DTB (50°C)				SDS (25°C)		
Polymer	Y_w (mol/mol)	Y_M (mol/g)	Y_{EO} (mol/mol)	Y_M (mol/mol)	Y_w	Y_M	YEO
PEO	0.0017	0.076	0.076	0.076	0.0074	0.32	0.33
PTGF	0.0018	0.298	0.09	0.074	0.0044	0.71	0.24
PDXL	0.0022	0.16	0.16	0.08	0.0025	0.18	0.18

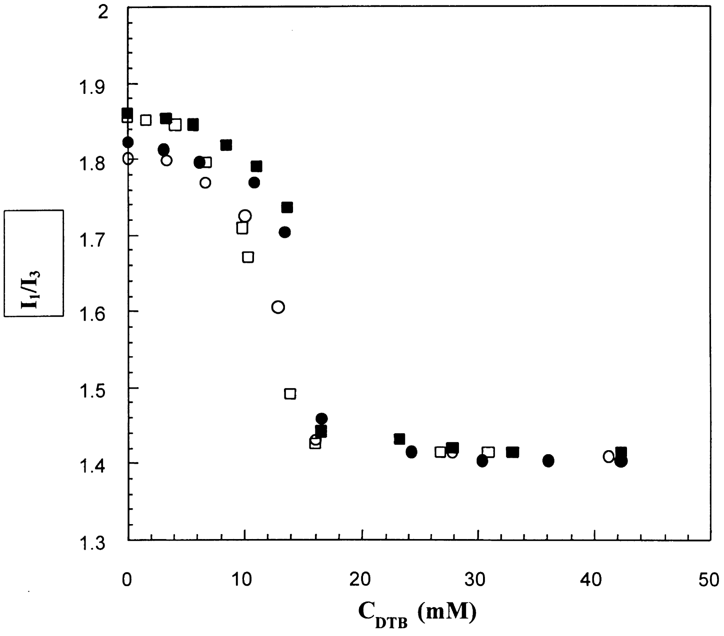

Fig. 6. Variation of I_1/I_3 versus DTB concentration for pure DTB (□), PEO–DTB (■); PTGF–DTB (○) and PDXL–DTB (●); $C_p = 10$ *g/l*; $T = 25$°C.

for the same DTB concentration, the aggregation number is lower in the presence of polymer. The same observation was made in the case of SDS. There are no significant differences between the curves obtained with the three polymers, while the aggregation number of the bound micelles of SDS was found to decrease when the fraction of MO unit increases. While in the case of SDS, a plateau in the values of N_A was found up to a concentration of SDS close to C_2, a continuous increase of N_A with C_{DTB} is found for the three polymers. This behaviour probably reflects the differences in the interactions strength. Indeed, a plateau can only be observed in a given concentration range when mainly bound micelles are formed. Such a situation corresponds to strong interactions with a high association constant of the surfactant on the polymer. If this constant is low, both free micelles and bound micelles may be formed as far as the concentration of unassociated surfactant molecules is higher than CMC. We can conclude that cationic surfactant interacts weakly with polymers even at 50°C.

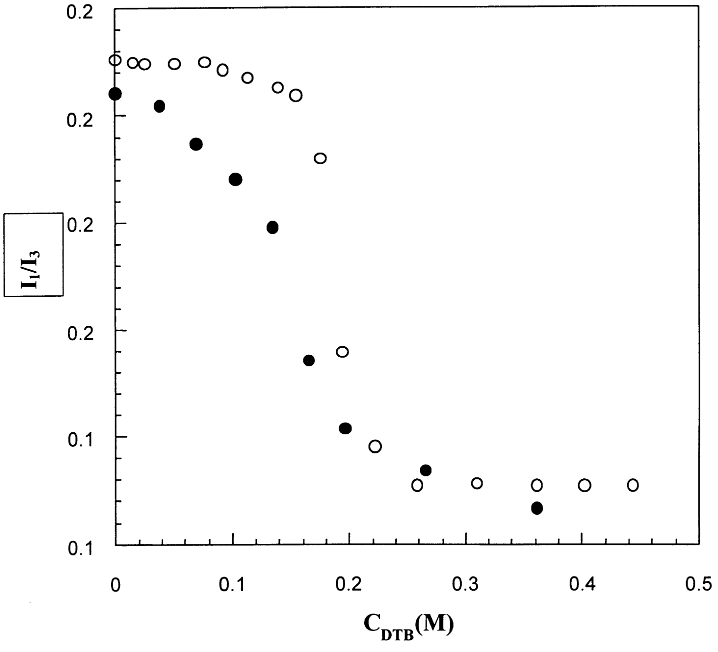

Fig. 7. Variation of I_1/I_3 versus DTB concentration for pure DTB (○), and PDXL–DTB (●); $C_p = 10$ g/l; $T = 50$°C.

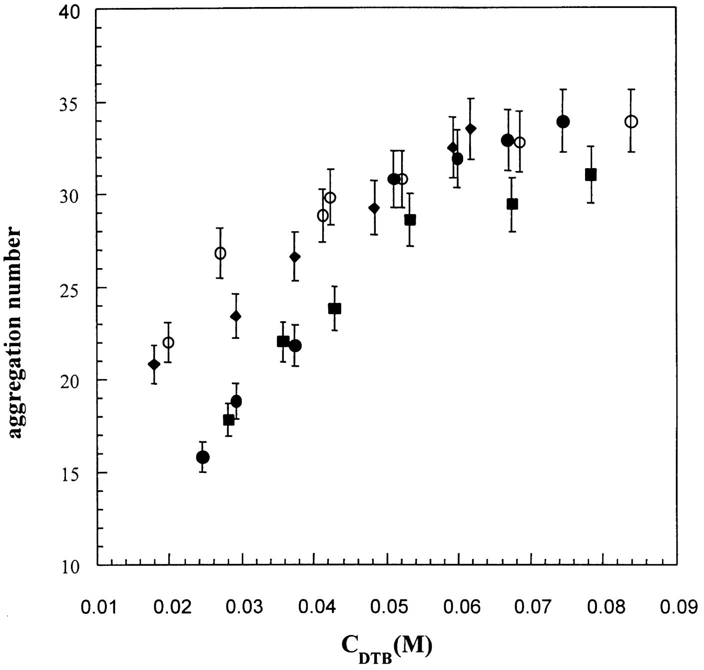

Fig. 8. Variation of the aggregation number N_A versus DTB concentration for pure DTB (○), PEO–DTB (●); PTGF–DTB (■) and PDXL–DTB (◆); $C_p = 20$ g/l; $T = 50$°C.

3.3. Viscosity

The binding of an ionic surfactant on a non-ionic polymer in aqueous solution generally results in an increase of the viscosity. In the first step, the flowing time in a capillary viscosimeter was measured for pure DTB solution as a function of concentration, as reported in Fig. 9(a), and the reduced viscosity of the polymer in the presence of increasing concentration of DTB is obtained from the classical relation:

$$\eta_{\mathrm{red}} = \frac{t - t_0}{t_0 C_p} \tag{3}$$

where t_0 and t are, respectively, the flowing time of the polymer–DTB solution and of the DTB solution of the same C_{DTB}. Fig. 9(b) obtained with PDXL ($T = 50$°C) exhibits the classical features of reduced viscosity curves observed with many other polymer/surfactant systems. In the first region, no variation of η_{red} is obtained and a jump of η_{red} occurs in the second region $C'_1 < C_{\mathrm{DTB}} < C'_2$ and finally η_{red} slightly decreases for $\mathrm{C}_{\mathrm{DTB}} > \mathrm{C}'2$. Generally C'_1 and C'_2 coincides approximately with the values of C_1 and C_2 determined by conductimetry (Fig. 5). In the present case, $C_1 = 10^{-2}$ M/l while $10^{-2} < C'_1 < 1.2 \times 10^{-2}$ and $C_2 = 5 \times 10^{-2}$ M/l to be compared with $C'_2 = 2.6 \times 10^{-2}$ M/l. This may be explained by considering the variation of the average aggregation number in the region $C_1 < C_{\mathrm{DTB}} < C_2$. As discussed above, in the case of SDS, N_A was found not to vary in this region and the ionization degree can be considered as a constant. Thus a viscosity increase is expected up to the polymer saturation as it is simply related to the ionization of the polymer–surfactant complex because the ionic strength of the bulk is low. After the polymer saturation, free micelles are formed which increase the ionic strength and this provokes a decrease of viscosity. In the case of our PDXL/DTB system characterized by weak interactions, there is a fixation of a part of DTB molecules while another non-negligible part contributes to increase the ionic strength of the bulk which results in limited viscosity increase.

3.4. Turbidimetry

We have already shown that in the case of ionic surfactant–polymer interactions, the water solubility of the polymer is enhanced upon addition of surfactant. In Fig. 10, are reported the cloud points of PDXL solution versus polymer concentration for several $\mathrm{C}_{\mathrm{DTB}}$. PDXL aqueous solutions exhibit at least at low polymer concentration a classical demixing curve with a lower critical solution temperature (LCST) equal to 79°C and a critical concentration $C_p^* = 0.06$ g/ml [16]. Upon addition of DTB, the cloud point increases almost in the whole range of concentration, but the effect becomes lower when the ratio DTB:polymer decreases. The same behaviour was observed with SDS [15] and this result constitutes a clear confirmation of DTB–PDXL association. The polymer with charged micelles must be considered as a polyelectrolyte and it is well known that the presence of charges along a polymer strongly increases its water solubility. In Fig. 11, the effects of SDS and DTB are compared for $C_p = 0.06$ g/g. SDS has

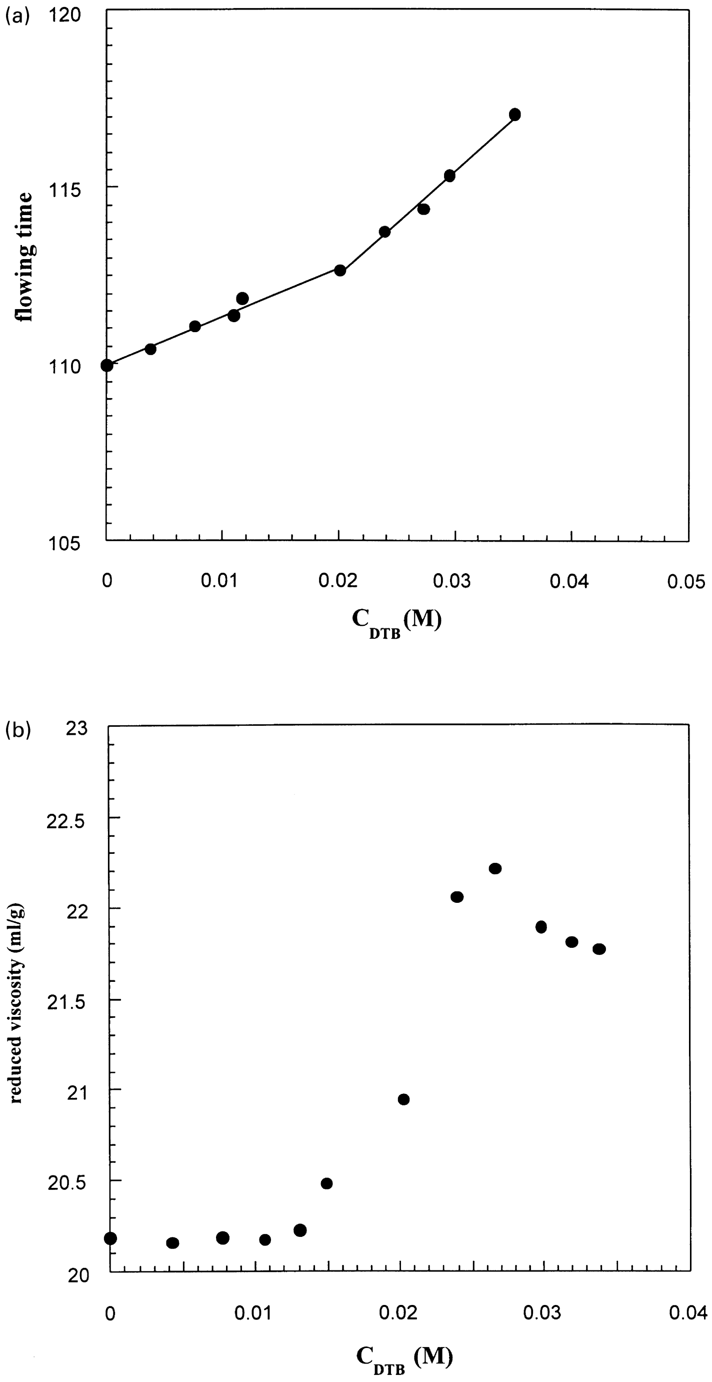

Fig. 9. Viscosity experiments (a) variation of the flowing time versus DTB concentration for pure DTB solutions; (b) variation of the reduced viscosity versus SDS concentration for PDXL–DTB $C_p = 20$ g/l and $T = 50$°C.

a greater influence, which may be correlated with a higher binding.

4. Discussion and conclusion

This work shows that polyethers do not interact with a cationic surfactant such as DTB at room temperature while the interactions are enhanced upon heating as measured by conductimetry, fluorescence and viscosimetry at 50°C. The total amount of cationic surfactant was determined for three polymers PEO, PTGF and PDXL. It was found that the number of DTB molecules adsorbed on the polymer per ether oxide does not depend on the respective fractions of methylene oxide and ethylene oxide units. This result is completely different from what was observed for the interactions of SDS with same polyethers at room temperature. It was indeed found that the number of SDS

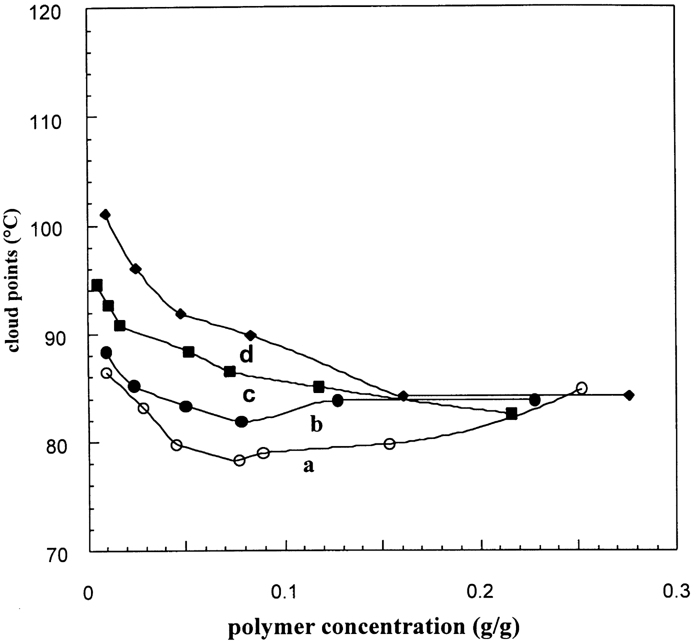

Fig. 10. Variation of the cloud point with polymer concentration for PDXL at various DTB concentrations: $C_{DTB} = 0$ (○); $C_{DTB} = 10$ mM (●); $C_{DTB} = 20$ mM (■); $C_{DTB} = 30$ mM (◆).

molecules bound per ether oxide decreases when the fraction of MO units increases and tends to 0 for an hypothetic water soluble poly(methylene oxide). This reveals that the association mechanisms is different according to the charge of the surfactant and the chemical composition of the polymer.

This whole set of results may be summarized by invoking as main effect the well known properties of complexation of the cations by PEO and as secondary effect the hydrophobic interactions between the methine groups of all the polyethers and the aliphatic chain of the surfactant. In the case of SDS/PEO system, the complexation of the sodium ions by PEO is accompanied by an attraction of the DS^- anions: this results in a cooperative micellization of SDS on the polymer, the micelles being stabilized by hydrophobic interactions. This stabilization requires sequences of EO units. When the fraction of methylene oxide units of much lower solvation power, increases, the attractive effect of the DS^- anions disappears. For PDXL which is a perfectly alternated EO–MO copolymer, only small micelles can be stabilized. It should be interesting to vary the nature of the surfactant counterion and change by this way the complexation which is much dependent on the ionic radius.

In the case of a cationic surfactant, the solvation effect does not exist, then the only driving forces for the polymer/surfactant association are due to hydrophobic interactions

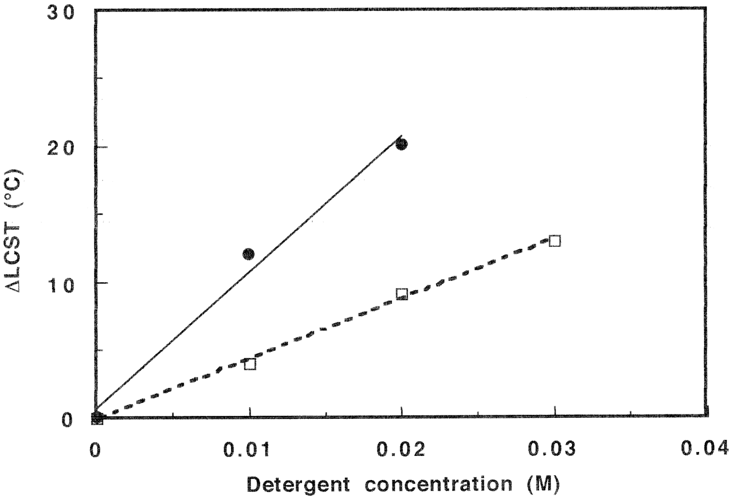

Fig. 11. Variation of (ΔLCST) (see text) versus SDS (●) and DTB (□) concentration of PDXL ($c_p = 0.06$ g/g).

which are low at room temperature and increase upon heating. Formation of complexes is observed only at high temperature and there is no significant difference between the binding on OE or MO units, as the solvation effect, specific of the EO units in the case of SDS, does not exist.

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