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Structure and Properties of Hydrophobically End-Capped Poly(ethylene Oxide) Solutions in the Presence of Monovalent and Divalent Cations

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Hydrophobically modified poly(ethylene oxide), HMPEO, was studied in concentrated salt solutions. The influence of salts was compared to the effect of temperature on poly(ethylene oxide), PEO. As expected, the addition of monovalent cations (Na^+, K^+) has the same effect as an increase in temperature in agreement with the thermodynamic properties of PEO: a decrease in solubility, micelle size, and viscosity was observed. Moreover, the intensity of neutron scattering peaks (characteristic of the semi-dilute solutions of these associative polymers) increases due to the collapse of PEO coronae in micelles. Very peculiar behavior was observed in the presence of divalent cations (Ca^{2+}, Mg^{2+}): larger micelle aggregates and higher viscosities, relaxation times, and activation energies were observed by dynamic rheology. This behavior is attributed to interactions between divalent cations and oxygen in PEO backbones close to the micelle core, which may reinforce intermicellar bridges. © 2002 Elsevier Science (USA)

Key Words: **poly(ethylene oxide); associative; hydrophobically modified; salts.**

INTRODUCTION

Associative polymers, or APs, formed of hydrophilic poly(ethylene oxide), PEO, chains each modified with one or two aliphatic end-groups, α-HMPEO and α,ω-HMPEO respectively, are used in many industrial fields such as encapsulation, oil recovery, and colloidal suspension stabilization.

A wide range of studies on these polymers in pure water have enabled a good understanding of their behavior as a function of concentration at room temperature: in aqueous solutions, α-HMPEO and α,ω-HMPEO self-assemble to form respectively "micelles" and "flowers" above a well-defined critical association concentration, CAC (1–6). Such associations, limited by micelle size and repulsions between PEO in hydrophilic corona, follow a closed association model (7). At higher concentrations, near the overlap concentration, C_f^*, viscosity jumps abruptly with α,ω-HMPEO, while the increase in viscosity of α-HMPEO does not diverge much from that of unmodified PEO, even when $C > C_f^*$ (8). This result tends to emphasize the role of bridging on viscosity especially in the light of the theory of Semenov *et al.*, which predicts a jump in viscosity due to micelles interpenetration (9). Bridges are also responsible for micelle aggregation between CAC and C_f^*, in which case a more progressive open association model is relevant (7). When micelles are close to each other (concentration near C_f^*) they repel and organize either into a local cubic order, leading to a correlation peak in neutron scattering spectra, or into a long-range cubic order corresponding to up to 6 Bragg peaks in X-ray scattering spectra (4, 10). When the micelles as a whole are considered in X-ray or neutron scattering experiments, the correlation peak vanishes as micelle interpenetration increases: at very high concentration, micelles are fully interpenetrated and behave as semi-dilute solutions of PEO. Nevertheless, if the PEO chains are matched in the appropriate selective solvent (D_2O/H_2O mixtures), the hydrophobic cores are shown to remain organized. Recently, we demonstrated that the repulsive overlapped star-like micelle model gives a good account of neutron scattering spectra and their evolution with changes in concentration (8, 11).

It is well known that solvent quality decreases with increases in temperature for aqueous solutions of PEO. Above a certain temperature, which depends on the molar mass of PEO, such solutions separate into polymer-poor and polymer-rich phases (12). This phenomenon is characterized by a binodal demixing curve in which the minimum is called the lower critical solution temperature (LCST). In another work, we showed that HMPEO solutions also phase separate upon heating. Nevertheless, the phase diagrams of α-HMPEO and α,ω-HMPEO are quite different from those of pure PEO. In the first case, solubility is enhanced due to the formation of strongly repulsive micelles. In the case of α,ω-HMPEO, the solubility is strongly depressed, and this phenomenon is not only ruled out by the thermodynamic properties of PEO, but to a considerable degree by an attractive potential due to the presence of hydrophobic aliphatics at both chain ends which permit the formation of intermicelle bridges. However, PEO corona swelling decreases for both α-HMPEO and α,ω-HMPEO with increases in temperature. Thus if we consider HMPEO solutions at a given concentration in the semi-dilute regime, the neutron scattering peak intensity

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increases with an increase in temperature as the micelles become more compact and display reduced interpenetration.

It is well known that the addition of salt to aqueous solutions of PEO decreases the solvent quality, in a manner similar to that of a temperature increase (13, 14). The shifts in the demixing curve at lower temperatures strongly depend on the nature of the salt (13, 15). Despite this well-known behavior of PEO, it is surprising that very little research has dealt with salted aqueous solutions of HMPEO (16). The aim of this work was therefore to compare the effects of various mono- and divalent cation salts on aqueous solutions of HMPEO with predictions based upon the thermodynamic properties of PEO. The more prominent effects consistently appear at high salt concentrations, and as far as possible, we have worked with 3 M solutions.

EXPERIMENTAL

Materials

Poly(ethylene oxide) was functionalized with n-hexadeca ($-C_{16}H_{33}$) aliphatic groups to yield either mono-, α-C16PEO, or difunctional, α,ω-C16PEO, APs according to methods described elsewhere (5, 17). Molecular weight, polydispersity index or M_w/M_n, and functionalization, f, for α-C16PEO and α,ω-C16PEO were respectively 16,000 g mol^{-1}, 1.05, 100%, and 32000 g mol^{-1}, 1.02, 100%.

NaCl (Aldrich 99+% purity), KBr (Prolabo, 98.5% purity), $CaCl_2$ (Prolabo, 94% purity), and $MgCl_2$ (Aldrich, 98% purity) were dried for several hours at 90°C and used directly without further purification.

All solutions were prepared with water distilled three times from over quartz. Depending on their concentrations, the solutions were stirred between 24 h and several days before use.

Methods

(i) Phase Diagram

The phase diagrams of α,ω-C16PEO with or without salt were obtained by simple visual observation of clouding while temperature was increased for concentrations of polymers ranging from 0.1 to 10 wt%. The concentration of salt was 3 M. The solutions were heated in a thermostated oven.

(ii) Fluorescence

Fluorescence was used to determine CACs by measuring the emission spectra of pyrene as a probe solubilized at 5×10^{-7} mol L^{-1} in polymer solutions. The spectra were recorded on a Perkin–Elmer LS 50B. The ratio I_1/I_3 of the first-to-third peak intensities of pyrene correlates to the polarity of its immediate environment (18–20). It exhibits a strong drop from the value 1.8, generally measured in pure water or prior to polymer micellization and a much lower value (1.4–1.1, according to the system) after micellization.

(iii) Light Scattering

Static (SLS) and dynamic (DLS) light scattering measurements were performed using a photogoniometer (Sematech) with an He–Ne laser source (wave length $\lambda = 514$ nm). The scattering angle θ was varied between 30° and 150°. The autocorrelation function was analyzed using a Sematech RTG. Polymer solutions were prepared in water freshly distilled from quartz with 400 ppm sodium azide as bacteriostatic, stirred for at least 24 h at room temperature, and filtered through 0.1-μm Dynagard filters.

Calculation of the refractive index increment (dn/dC) in the presence of salts implies the approximation

$$\left(\frac{dn}{dC}\right)_{\text{solution}} = \left(\frac{dn}{dC}\right)_{H_2O} - \left(n_{\text{solution}} - n_{H_2O}\right),$$

where $n_{H_2O} = 1.333$, $n_{CaCl_2}(3\ \text{mol L}^{-1}) = 1.405$, and $n_{KBr}(3\ \text{mol L}^{-1}) = 1.372$, then

$$\left(\frac{dn}{dC}\right)_{CaCl_{2(3\,\text{mol}\cdot\text{L}^{-1})}} = 0.063\ \text{ml}\cdot\text{g}^{-1}$$

$$\left(\frac{dn}{dC}\right)_{KBr_{(3\,\text{mol}\cdot\text{L}^{-1})}} = 0.096\ \text{ml}\cdot\text{g}^{-1}.$$

Remarks. In cases of ternary systems, it is often recommended to measure (dn/dC) under conditions of dialysis equilibrium between solution and mixed solvent in the case of preferential adsorption of one of the solvent constituents on the polymer. We have verified that no difference of molecular weight was found in pure water and in water containing 0.1 NaCl for a PEO polymer of molecular weight =10,000. It means that the selective sorption effects are negligible.

(iv) Small-Angle Neutron Scattering (SANS) Experiments

SANS experiments on the different solutions were performed on the PACE instrument at the Léon Brilloin Laboratory (LLB), Saclay, France. The range of the scattering vector covered was $0.006 < q < 0.2$ Å^{-1}. All experiments were performed at 20°C and D_2O was used instead of H_2O as solvent.

(v) Viscosity

A low-shear Couette flow-type rheometer, Contraves LS30, working in a shear rate range from 0.02 to 100 s^{-1} was used to measure the viscosity of the solutions at 25°C.

(vi) Rheological Measurements

The viscoelastic properties of solutions were investigated through dynamic spectroscopy experiments. On a Rheometrics dynamic stress rheometer operating with a Couette cell, a sinusoidal stress ($\tau = \tau_0 \cos(\omega t)$) was imposed on the solution, and the storage and loss modulii ($G'(\omega)$ and $G''(\omega)$) were recorded. For each pulsation, ω ranging from 10^{-3} to 100 rad s^{-1}, the maximum amplitude τ_0 was chosen to be small enough to show a linear variation between applied stress and measured strain. In order to limit the evaporation of water the rheological experiments were mostly performed at 5°C, except when activation energy was determined.

RESULTS

Monovalent Ions

PEO and α,ω-C16PEO were compared in pure water and in the presence of salts of monovalent cations: NaCl and KBr.

(i) Phase Diagrams

Phase diagrams are reported in Figs. 1a (NaCl) and 1b (KBr). As described in the literature, the LCST of pure PEO is lower in the presence of salts than in pure water (65 and 80°C for NaCl and KBr, respectively). The difference in solubility between the two salts agrees with the literature data which show that the effect of NaCl is greater than that of KCl (13, 14). α,ω-C16PEO also showed a strong drop in solubility in the presence of monovalent salts, with demixing at room temperature occurring at a low polymer concentration ($C < 1.5 \times 10^{-2}$ and 2×10^{-2} g ml^{-1} for NaCl and KCl, respectively).

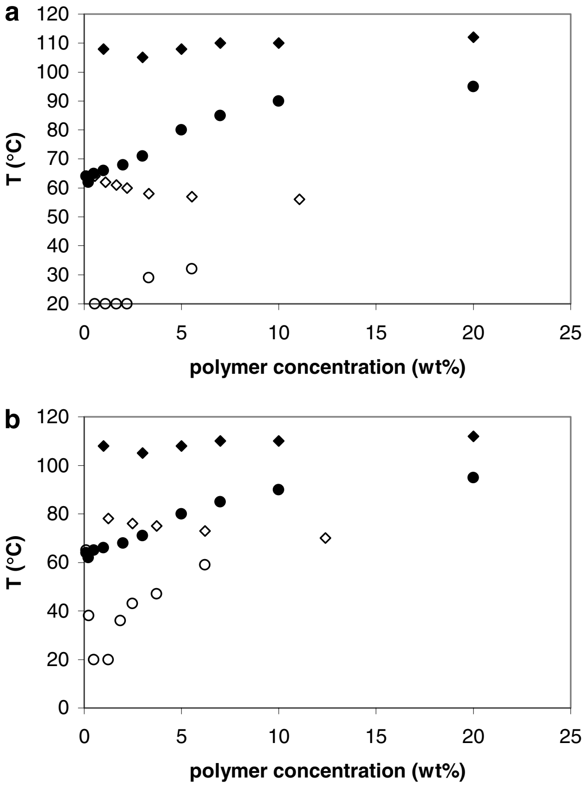

FIG. 1. Cloud points versus concentration: PEO 32000 in pure water (◆) and in 3 M salted solutions (◇); α,ω-C16PEO in pure water (●) and in 3 M salted solutions (○): NaCl (a) and KBr (b).

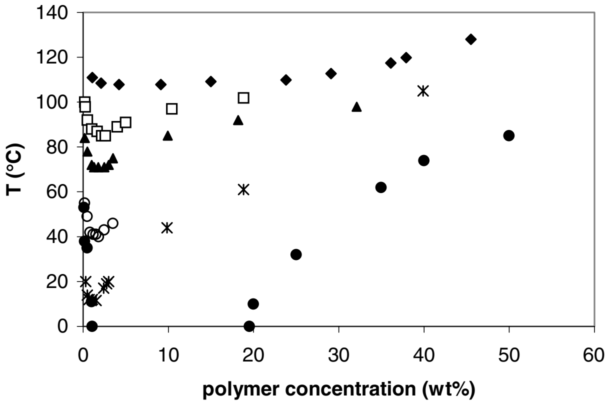

FIG. 2. Cloud points versus polymer concentration. PEO modified with $-C_{12}H_{25}$ aliphatic end groups: PEO 14000 (◆), 35000 C12 (□), 20000 C12 (▲), 10000 C12 (○), 6000 C12 (✱), and 2000 C12 (●).

It should be noted that the shape of the demixing lines is quite different for pure PEO and HMPEO. The behavior observed in the presence of salt has already been observed with the difunctional poly(ethylene oxide) didodecaamide ether with various molecular weights in pure water (Fig. 2). As explained in the Semenov *et al.* (9) approach and in another paper of this series (21), the main reason for demixing is no longer the loss of solvent quality but the attractive potential due to the presence of two hydrophobic end groups. This explanation is confirmed by the fact that the LCST of α-C16PEO—able to form only repulsive micelles—is no lower than that of the parent PEO but slightly higher. At a given temperature, formation of intermicellar bridges requires phase separation at a very low concentration, C_1, and the system returns to homogeneity at a higher concentration, C_2. It can be assumed that the lowest concentration when the system starts to phase separate, C_1, is close to the CAC. Besides, C_2 is expected to be very close to the overlap concentration of "flowers," C_f^*. In the case of samples with the same end groups but varied molecular weight $\overline{M_w}$ of PEO chains, one can predict that C_1 decreases when $\overline{M_w}$ decreases (due to the higher overall hydrophobicity of the polymers) while C_2 increases (overlap of small micelles higher than that of large ones). This tendency has been well verified by experiments (21). When temperature increases, due to a lower solvent quality, the repulsion between PEO chains—which hinders micellization—decreases and CAC value slightly decreases. Simultaneously, above the CAC, PEO chains inside micelle coronae start to collapse and it seems obvious that C_2 or C_f^* would increase. The effect of salts is qualitatively consistent with this description. At a given temperature the repulsion between PEO chains decreases upon the addition of salt; micellization is expected to be favored with the formation of smaller flower coronae, and the range in which the formation of bridges correlates with demixing broadens.

(ii) Fluorescence

In Fig. 3, we report the variation of the ratio I_1/I_3 characteristic of the pyrene fluorescence emission for α,ω-C16PEO in

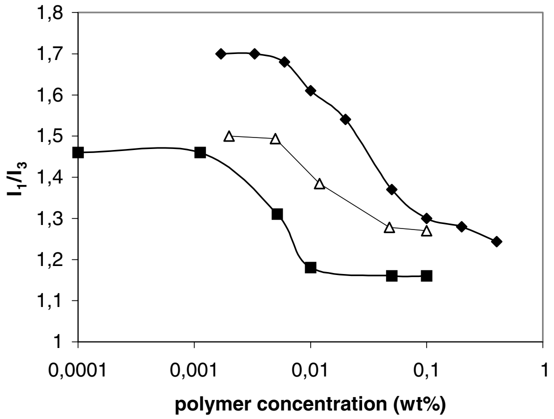

FIG. 3. Ratio of first-to-third pyrene emission peaks in fluorescence experiments in function of polymer concentration: in pure water (◆), in 3 M KBr (△), and in 3 M $CaCl_2$ (■).

pure water and in the presence of 3 M KBr. The value of I_1/I_3 in the absence of polymer is slightly lower in the salt solution than in pure water, which probably reflects changes in the polarity medium. Nevertheless, in both cases, when polymer concentration increases, a drop in I_1/I_3 is observed. The shift between the curves indicates that the CAC is approximately ten times lower in the presence of 3 M KBr than in pure water. This can again be related to the lower solubility of PEO in the presence of salt: the lower the repulsion between PEO chains, the lower the CAC.

(iii) Light Scattering

Static light scattering experiments have already been performed on these associative polymers in pure water (7). It is known that the variation in scattered intensity versus concentration reflects the increase in average molecular weight, $\overline{M_{\text{w}}}$, due to association and the terms of interaction between micelles (viriel coefficients A_2, A_3, etc.) are expressed according to the classical law

$$\frac{KC}{\Delta I} = \frac{1}{\overline{M_{\text{w}}}} + 2A_2C + 3A_3C^2 + \cdots, \quad [1]$$

where K is the product of the square dn/dc by an optical constant. The variation of the "apparent molecular weight" $\overline{M_{\text{wapp}}}$ ($\overline{M_{\text{wapp}}} = \Delta I/KC$) versus concentration for α,ω-C16PEO obtained in pure water is reported in Fig. 4. This behavior is quite general and as described previously, several ranges can be distinguished:

(i) up to $C = 10^{-4}$ g ml^{-1}, the value of the CAC measured by fluorescence, $\overline{M_{\text{wapp}}}$, remains close to the molecular weight of the unmodified polymer;

(ii) for $10^{-4} < C < 10^{-3}$ g ml^{-1} the increase of $\overline{M_{\text{wapp}}}$ reflects at first the formation of flower-like micelles. By comparing the concentration dependence of the scattered intensity of monofunctionalized samples and difunctionalized ones, we were able to demonstrate that micellization can be described through a model of "closed association" (7). Independent experimental studies have led another group to the same conclusions (22).

(iii) for $10^{-3} < C < 6.10^{-3}$ g ml^{-1}, the more abrupt increase of $\overline{M_{\text{wapp}}}$ corresponds to interflower bridging and the formation of large aggregates. This second association step can be described as an "open association" (7, 22).

(iv) for $C > 6.10^{-3}$ g ml^{-1}, $\overline{M_{\text{wapp}}}$ decreases.

In the first three concentration ranges, the increase of molecular weight due the two successive steps of association induces an increase of scattered intensity because the viriel terms are initially negligible (see Eq. [1]). Nevertheless, at higher concentrations, as the flowers or micelles are strongly repulsive, the viriel terms of Eq. [1] become important and $\Delta I/KC$ decreases (7).

When static light scattering experiments were performed in the presence of 3 M KBr (Fig. 4), we saw no difference in the concentration dependence of $\overline{M_{\text{wapp}}}$ with respect to pure water. We cannot conclude that the flowers have the same molecular weight because: (i) micelle interactions are expected to change in the presence of salts, and (ii) as the CAC is much lower in the presence of salt, the experimental points do not correspond to the same regime as in pure water. As the viriel terms are expected to be lower in the presence of salts (salting-out effect), the repulsions between flowers must be lower and the aggregation number of the flowers is expected to be higher. Nevertheless, in these experiments, we do not consider a regime of free flowers but more likely the range where micelle aggregates are already formed, due to the much lower value of CAC. Alternatively, the decrease of the viriel terms should depress the difference between the true and the apparent molecular weights. The only conclusion we can draw from these static light scattering measurements is that flower bridging is disfavored by the presence of salt. In addition, we could not observe the decrease in scattered intensity at higher concentrations, due to the phase separation phenomenon (see Fig. 1b), which made measurements very difficult.

The dynamic light scattering measurements shown in Fig. 5 are more significant. We observed that the diffusion coefficient D

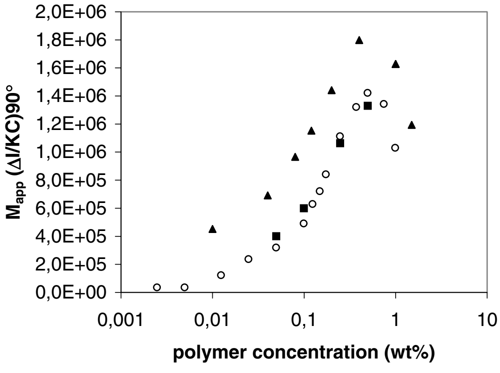

FIG. 4. Apparent mass ($\Delta I/KC$) versus concentration from static light scattering for α,ω-C16PEO in pure water (○), in 3 M KBr (■), and in 3 M $CaCl_2$ (▲).

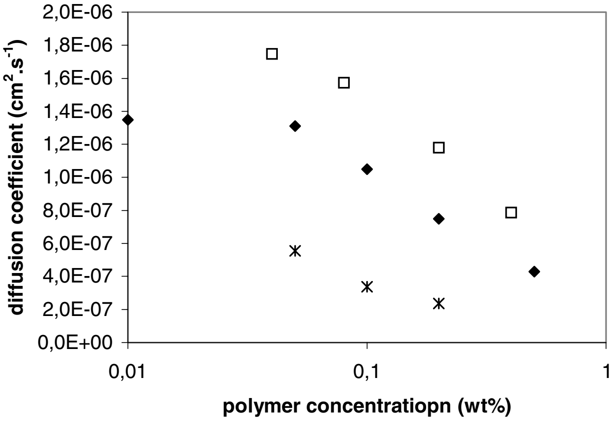

FIG. 5. Hydrodynamic diameter versus polymer concentration from dynamic light scattering for α,ω-C16PEO in pure water (◆), in 3 M KBr (□), and in 3 M $CaCl_2$ (✱).

is higher in the presence of 3 M KBr than in pure water equally for isolated and aggregated micelles. For isolated micelles, one can use in a first approximation the Stokes–Einstein equation to calculate the hydrodynamic radius: $R_H = 135$ Å, in 3 M KBr instead of 175 Å in pure water. This collapse of the coronae is consistent with the poorer quality of the salt solutions. However, at this stage one cannot say anything about the aggregation number since this decrease in flower size is mainly due to the collapse of PEO coronae. Furthermore, for concentrations where bridges are expected to create micelle aggregates, the diffusion coefficient decrases more slowly than that of those in pure water. As a consequence, bridges seem to be disadvantaged, in agreement with the static light scattering results.

(iv) Neutron Scattering

Neutron scattering curves obtained in pure heavy water and in the presence 3 M KBr are compared in Fig. 6 for two polymer concentrations, i.e., 3×10^{-2} and 1×10^{-1} g g^{-1}. They exhibit a maximum at a given value, $q_{\max}$, of the scattering vector q, which roughly corresponds to the average distance d between the centers of the micelles ($d = 2\pi/q_{\max}$). We have already shown that, in pure heavy water, the maximum peak intensity, $I_{\max}$, passes through a maximum at a concentration value close to C_f^*, and this behavior has been modelized (11). Indeed, scattering curves can be well fitted using a model of polymer stars in the semi-dilute regime: the part of the PEO coronae that does not overlap is responsible for the peaks—due to their repulsions—while the overlapped part behaves as a classical semi-dilute polymer solution that does not exhibit a scattering peak. Upon increasing concentration, the second part dominates and this explains the disappearance of the peak. This picture is confirmed by the evolution of the peaks when temperature increases (8, 11). At a given concentration, heating induces an increase in $I_{\max}$. This can be simply explained by a lower overlap degree of the micelles due to the collapse of coronae.

In the presence of KBr, smaller micelles and smaller aggregates of micelles should result in a reduced degree of micelle overlap and thus a higher C_f^* value. As a structural consequence, the neutron scattered intensity at the correlation peak should increase in the same manner as when temperature increases. Experimental curves (Fig. 6) with 3 M KBr are in perfect agreement with this assessment: $I_{\max}$ is higher in the presence of salt than in pure heavy water. The higher the polymer concentration, the less pronounced the effect.

One can observe that the peaks are slightly shifted toward higher q values in the presence of KBr. Nevertheless, in the case of homogeneous solutions (no micelle aggregates) the aggregation number can be simply estimated through the equation

$$N_{ag} = \left(\frac{2\pi}{q_{\max}}\right)^3 \frac{CN_a}{\overline{M_u}} \times 10^{-24}, \quad [2]$$

where C is no longer expressed in grams per gram but in grams per milliliter, N_a is the Avogadro number, and $\overline{M_u}$ is the molecular weight of the polymer. In fact the variations of d with C is

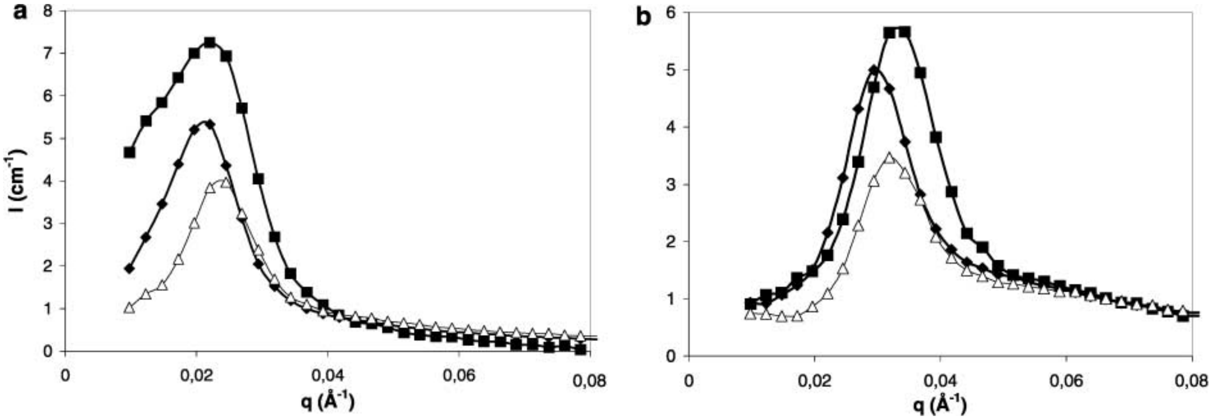

FIG. 6. SANS scattering curves for 3% (a) and 10% (b) α,ω-C16PEO in pure water (◆), in 3 M KBr (■), and in 3 M $CaCl_2$ (△).

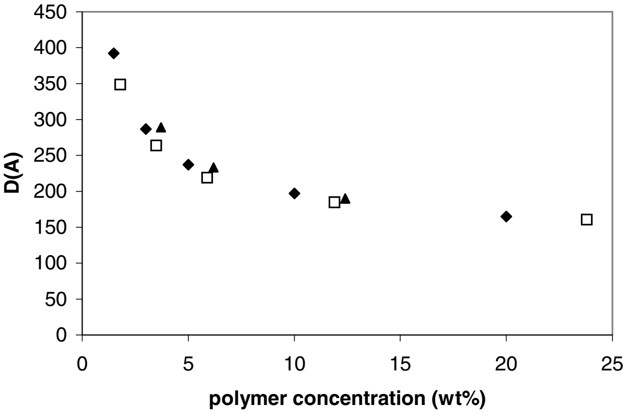

FIG. 7. Distance between scattering centers versus concentration for α,ω-C16PEO in pure water (◆), in 3 M KBr (□), and in 3 M $CaCl_2$ (▲).

similar in the absence and presence of salts, as shown in Fig. 7, and consequently the aggregation number is not significantly modified by the presence of monovalent cations.

(v) Viscoelasticity

Viscoelastic properties are mostly dependent on bridging between micelles and on the degree of interpenetration. As both are disadvantaged in the presence of monovalent ions, as we demonstrated above, we can guess that viscoelastic properties will be reduced. Low-shear relative viscosity η_{rel} is represented versus concentration in Fig. 8 for different systems. In pure water one can see that η_{rel} of α,ω-C16PEO strongly diverges from that of the parent PEO above 6×10^{-3} g ml^{-1}. Qualitatively the same behavior is observed in the presence of KCl and NaCl but the jump of viscosity occurs at higher concentrations, and in the intermediate range ($6 \times 10^{-3} < C < 4 \times 10^{-2}$ g ml^{-1}) η_{red} remains lower in the presence of salt than in pure water. Once again, this result is consistent with the presence of smaller flowers.

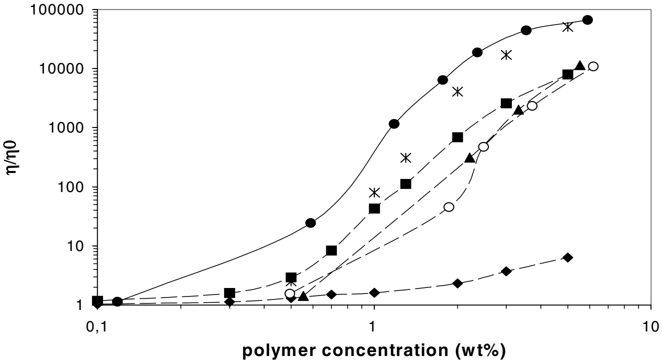

FIG. 8. Relative viscosity versus polymer concentration for PEO 32000 in pure water (◆) and for α,ω-C16PEO in pure water (■), in 3 M NaCl (▲), in 3 M KBr (○), in $CaCl_2$ (✱), and in $MgCl_2$ (●).

TABLE 1

Plateau Modulus (G'_0), Relaxation Time, and Activation Energy for α,ω-C16PEO in Pure Water and in 3 mol · L^{-1} Salted Solutions (KBr, $CaCl_2$, and $MgCl_2$)

Solution	G'_0 (Pa)	Relaxation time (5°C) (s)	Activation energy (25°C)
Pure water	2.5×10^3	0.01	16.3 kT
3 mol L^{-1} KBr	2.1×10^3	0.01	15.2 kT
3 mol L^{-1} $CaCl_2$	3.0×10^3	0.2	27.8 kT
3 mol L^{-1} $MgCl_2$	3.2×10^3	0.4	—

Dynamic measurements were performed at different temperatures in order to measure relaxation time and activation energy. We report loss and conservation modulii versus frequency in Fig. 9 in pure water (9a) and in 3 M KBr (9b) for 0.05 g ml^{-1} polymer concentration at 5°C. Despite the appearance of a G' plateau at low frequency, of which the origin is up to now not well understood, relaxation times were calculated using a Maxwell model with a single relaxation time, at all temperatures ($5 < T < 25$°C). Due to water evaporation, measurements were not made at higher temperatures. This time is attributed to the hydrophobe disengagement from the micelle cores. Activation energy is calculated using an Arrhenius law

$$\tau = \tau_0 e^{\left(\frac{Em}{kT}\right)}, \qquad [3]$$

where k is the Boltzman constant: $k = 1.38 \times 10^{-23}$ J K^{-1}.

The results are reported in Table 1. Relaxation time is exactly the same in pure water and in the presence of KBr. Activation energy in pure water is very close to the value of 1 kT by aliphatic carbon obtained by Annable *et al.* (23) and Maître (5) over a broader temperature range. This energy is just 1 kT lower with 3 M KBr but the difference is not significant.

This adjustment allows also the determination of the value of G' at the rubber plateau, i.e., G'_0. The values are reported in Table 1. The addition of KBr induces a slight decrease in G'_0, which is consistent with fewer bridges than that in pure water.

Divalent Ions

(i) Phase Diagrams

Phase diagrams with divalent ions are reported in Figs. 10a ($CaCl_2$) and 10b ($MgCl_2$). LCST is shifted toward lower temperatures for unmodified PEO in the same manner as with monovalent ions and in agreement with literature data (14, 15). This confirms that the addition of $CaCl_2$ and $MgCl_2$ decreases the LCST of PEO in water. Surprisingly, interesting results were observed with modified PEO: solubility was increased in the presence of divalent ions, resulting in a LCST higher than that in pure water, at least up to a polymer concentration of 0.05 g ml^{-1}. In such a case, we can no longer refer to the simple description of the contraction of micelle coronae, as might be reasonable when considering the effects of monovalent ions.

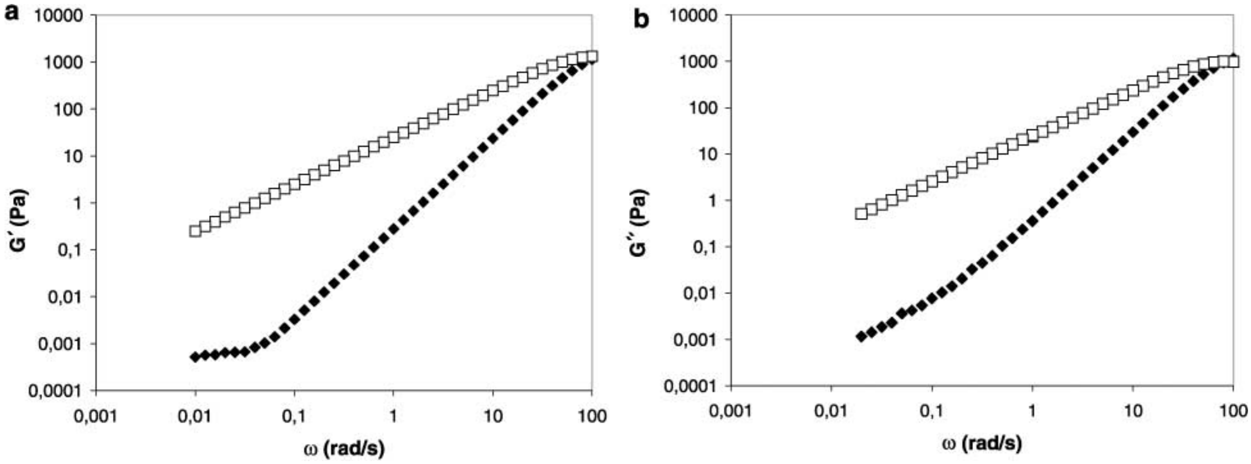

FIG. 9. Conservation (◆, G') and loss (□, G'') modulii versus frequency in dynamic spectroscopy for 5% α,ω-C16PEO in pure water (a) and in 3 M KBr (b).

(ii) Fluorescence

Fluorescence results in the presence of 3 M $CaCl_2$ are represented in Fig. 3. As with monovalent ions, the CAC is shifted toward lower values with divalent ions. In both cases, the CAC is about 10 times lower with salts than with pure water. This result is in agreement with the fact that poor solvent quality favors micellization. In addition to that, CAC is slightly lower with $CaCl_2$ than with KBr, which is in agreement with the more pronounced salting-out effect on pure PEO (compare Figs. 1 and 10). As opposed to the phase diagrams, CAC is in agreement with salting-out effect predictions.

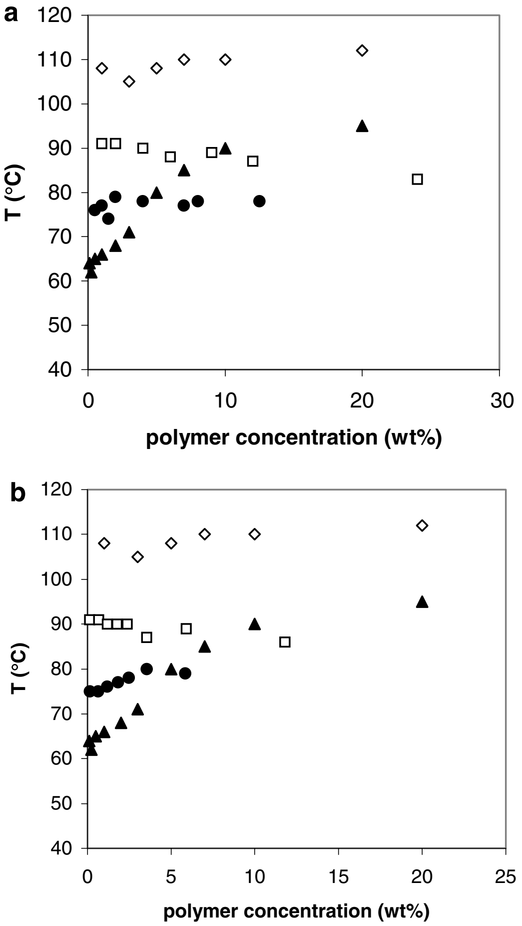

FIG. 10. Cloud point temperatures versus concentration of PEO 32000 in pure water (◇) and in 3 M salted solutions (□) and α,ω-C16PEO in pure water (▲) and in 3 M salted solutions (●): $CaCl_2$ (a) and $MgCl_2$ (b).

(iii) Light Scattering

Static (Fig. 4) and dynamic (Fig. 5) light scattering measurements were performed with 3 M $CaCl_2$. Both tend to demonstrate that micelle aggregates appear at lower concentration and the behaviors observed are completely different from that obtained in pure water and in the presence of KBr. Over the whole range of concentration, the values of $\overline{M}_{\mathrm{wapp}}$ are highest and those of D are lowest in the presence of $CaCl_2$. The value estimated for the hydrodynamic radius in $CaCl_2$ at low concentration is 350 Å, which cannot be attributed to isolated micelles. This result shows that, at a given concentration, aggregates of micelles are larger in the presence of calcium ions, which suggests an easier bridge formation. Once again, the effect is not obvious regarding salting-out effects and tends to demonstrate a particular effect in the presence of divalent ions.

(iv) Neutron Scattering

The high-concentration domain was studied by SANS, in the presence of $CaCl_2$ and $MgCl_2$. Scattering spectra obtained with 3 M $MgCl_2$ are shown in Figs 6a and 6b, polymer concentrations of 0.03 and 0.1 g g^{-1}, respectively. As opposed to what happens with monovalent cations, scattered intensity is lower than that in pure water. The same results were obtained with $CaCl_2$. The effect of divalent cations is equivalent to a decrease in temperature and must correspond to a higher degree of interpenetration of the flowers. The explanation that micelle coronae are collapsed and less entangled in salt solutions, which appears quite correct

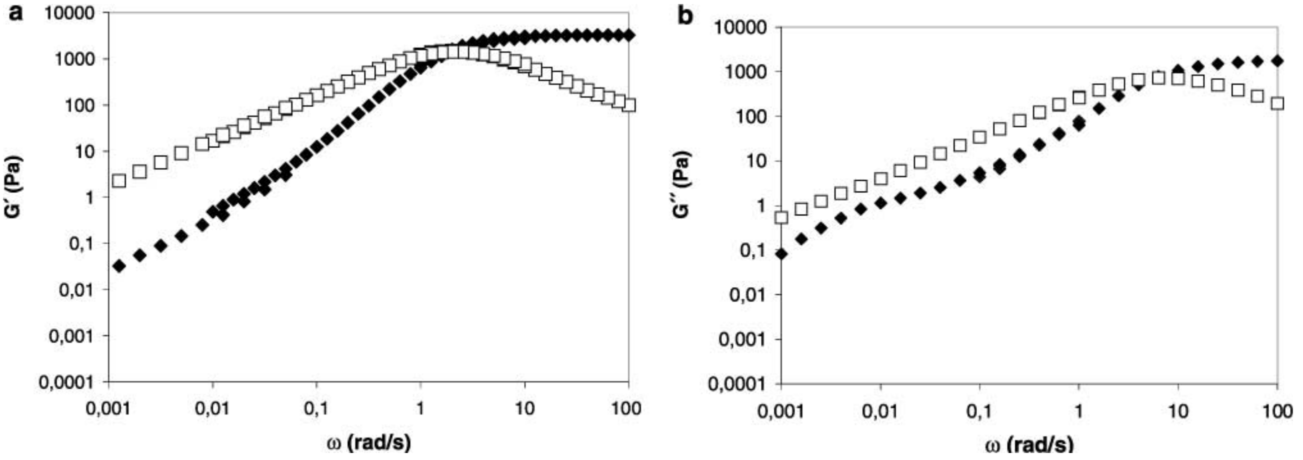

FIG. 11. Conservation (◆, G') and loss (□, G'') modulii versus frequency in dynamic spectroscopy for 5% α,ω-C16PEO in 3 M $MgCl_2$ (a) and in 3 M $CaCl_2$ (b).

in the case of monovalent cations, is no longer viable in the case of divalent ions. This can be due both to larger micelles and to larger aggregates of micelles. This second hypothesis is in agreement with the higher apparent mass in static light scattering and the larger radius in dynamic light scattering, which cannot be attributed to isolated micelles. As a result, bridges, which are responsible for micelles aggregation, seem to be reinforced by divalent ions.

(v) Viscoelasticity

The comparison of viscosities in pure water and in the presence of mono- and divalent ions is shown in Fig. 8. We can clearly see that while the addition of KBr and NaCl leads to a decrease in relative viscosity, the presence of divalent cations strongly enhances viscosity. The higher the polymer concentration, the more important the viscosity jump is in the presence of divalent ions. This phenomenon is consistent with the hypothesis of the presence of larger aggregates, as deduced from the previous experiments.

Oscillatory dynamic measurements were performed in 3 M $MgCl_2$ (Fig. 11a) and $CaCl_2$ (Fig. 11b) salt solutions with 0.05 g ml^{-1} polymer concentration and at various temperatures. While the crossover of G' and G'' curves only appears at the highest frequency value available with our apparatus in pure water and in the presence of KBr, this characteristic frequency is strongly shifted toward lower values with $CaCl_2$ and $MgCl_2$. This indicates that the residence time of the hydrophobes inside the micelles is increased by a factor of almost 100 when divalent ions are present in the solution. This means that not only the bridges are favored by these salts but that also the dynamics of the system is strongly modified. Table 1 summarizes results obtained from rheology measurements. One can clearly see a strong increase of both relaxation time and activation energy.

Moreover, the curve of Fig. 11b clearly exhibits two relaxation times. The slowest mode, which may be considered as a measurement artifact (very low values of G' and G'') in pure water or 3 M KBr, can be well identified by a plateau for $10^{-2} < w < 10^{-1}$ rad s^{-1}, in the presence of $CaCl_2$.

The value of G'_0 can be directly obtained from the curves of Fig. 11. One observes a slight increase of G'_0 with respect to that in pure water, in agreement with the formation of more bridges, in the presence of divalent cations.

DISCUSSION

Monovalent ions give rise to the results expected according to a decrease of the solvent thermodynamic properties with regards to PEO chains in micelle coronae. This effect can be compared with an increase in temperature, as suggested by neutron scattering experiments.

Divalent ions surprisingly give rise to very different results, for both solution structure (larger aggregates of micelles, higher degree of micelle interpenetration) and visco-elastic properties (increases in viscosity, relaxation time, and activation energy). In addition the polymer solubility was improved with respect to that in pure water. The only expected result was the decrease in the CAC value. One must note that our experiments were performed in very concentrated salt solutions and that we have considered the molarity and not the normality. The observed phenomena could be related to the fact that the solvent is quite different to water especially with divalent salts. Nevertheless, other measurements have been made for lower concentrations (between 0.1 and 1 M) of various salt of divalent cations ($CaCl_2$, $MgCl_2$, $BaCl_2$), and an increase of viscosity was always obtained with the following order of effectiveness, Ca < Mg < Ba, while at same molarity, KBr or NaCl provoke a loss in viscosity. We can conclude that the enhancement in viscosity is not simply due to high divalent ion concentration.

Such differences between mono- and divalent ions should be explained by specific interactions between PEO chains and cations, as often described in the literature. It has been reported

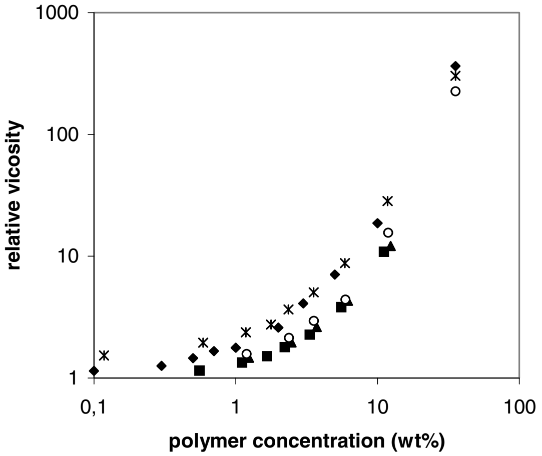

FIG. 12. Relative viscosity of unmodified PEO 32000 solutions versus concentration in pure water (◆), in 3 M NaCl (■), in 3 M KBr (▲), in 3 M $CaCl_2$ (○) and in 3 M $MgCl_2$ (✱).

that the intrinsic viscosity [η] of PEO in the presence of various salts decreases with the salt concentration, and Bailey and Callard (13) have shown that the salts have the same order of effectiveness in reducing [η] at a given temperature as in lowering LCST. This means that [η] decreases with KBr or NaCl as with $CaCl_2$ or $MgCl_2$. Nevertheless, there is not a great deal of information about the viscosimetric behavior of PEO in salt solutions at higher polymer concentrations. As it is known that cations are able to bind specifically with the oxygen of the ethylene oxide units (24, 25), one may expect the formation of intermolecular bridges in semi-dilute solutions, but only with divalent cations. In the case of associative PEO, these possible bridges could be created between the chains of different micelles, enhancing viscosity. In order to verify such an hypothesis, we have measured the viscosity of the unmodified PEO 32000 in the presence of mono- and divalent ions (Fig. 12). Even for highly concentrated solutions, viscosity does not increase at all with mono- or divalent ions, in agreement with the observations made in the dilute regime. As a consequence, it is not possible to cite interactions between ions and PEO chains in the coronae, where the PEO concentration corresponds to a semi-dilute unmodified PEO solution.

Besides, low-shear viscosity experiments performed with α-C16PEO in the presence of divalent ions did not indicate any viscosity change with respect to α-C16PEO in pure water (Fig. 13). This verified that no specific interactions occur inside the coronae and means that the increase in viscosity and relaxation time is specific to the case where PEO chains form bridges between micelles. Then we must consider the effect of divalent cations on the intermicellar bridges. Indeed, we have seen that $CaCl_2$ has the expected effect on the micellization concentration (CAC). At such a concentration, the driving force is only the repulsion between the PEO chains, which compensates the hydrophobic interactions. These repulsions decrease upon that addition of salts, whatever their nature.

Finally, we propose a model that may explain at least a part of the experimental results. It is based on knowledge about PEO/cations interactions. It is well known that the free electrons doublets on PEO oxygen atoms display an attractive force with respect to cationic species, and specially to divalent cations (26). One can suppose that there are interactions between PEO and cations at the inner part of the coronae close to the hydrophobic/hydrophilic interface. At this interface, PEO chains are very close to each other, reaching local concentrations far more important than those explored in Fig. 12 (PEO semi-dilute solution). The cation binding in this region would have no consequence with monovalent ions, whereas they could create local bridges with divalent ions due to the two positive charges able to interact with two oxygen atoms belonging to different chains. Such local interactions would stabilize the micelles and increase the residence time of hydrophobic groups inside micelles. As a consequence, one expects the formation of loose aggregates, which are more soluble in water. This effect should mainly play a role in the rheological behavior, in agreement with the experimental observations. Indeed, one expects from this picture an increase in the characteristic times and activation energies.

Finally, the rheological measurements made of these systems in the presence of divalent cations confirm the existence of a high second relaxation time. Indeed, it appears in the same frequency range as in pure water or in the presence of monovalent cations, but for much higher values of G': then, it is easier to measure and cannot be considered an artifact. Nevertheless, the origin of this behavior is not easy to identify. It appears in many other associative systems such as PPO/PEO block copolymers (Pluronic or Tektronic) (27, 28). If the attribution of the fast relaxation time is correct (corresponding to the disengagement of the hydrophobic groups from the micelles), intermicellar bridges have no influence on the low-frequency rheological behavior. We could invoke cooperative motions of the micelles due to their self-hindrance in organized systems. As in this frequency range, bridges, which seem to depend on the nature of salt, no longer have an influence; it is reasonable to obtain the same order of magnitude of relaxation times for all solutions.

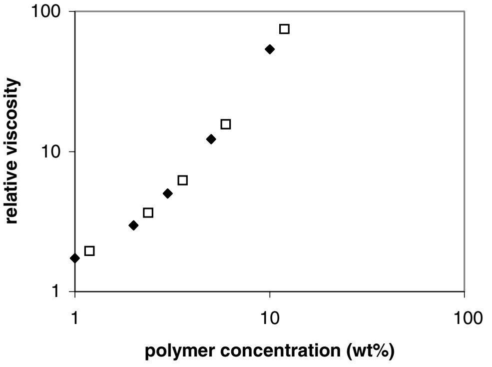

FIG. 13. Relative viscosity of unmodified PEO 32000 solutions versus concentration in pure water (◆) and in 3 M $CaCl_2$ (□).

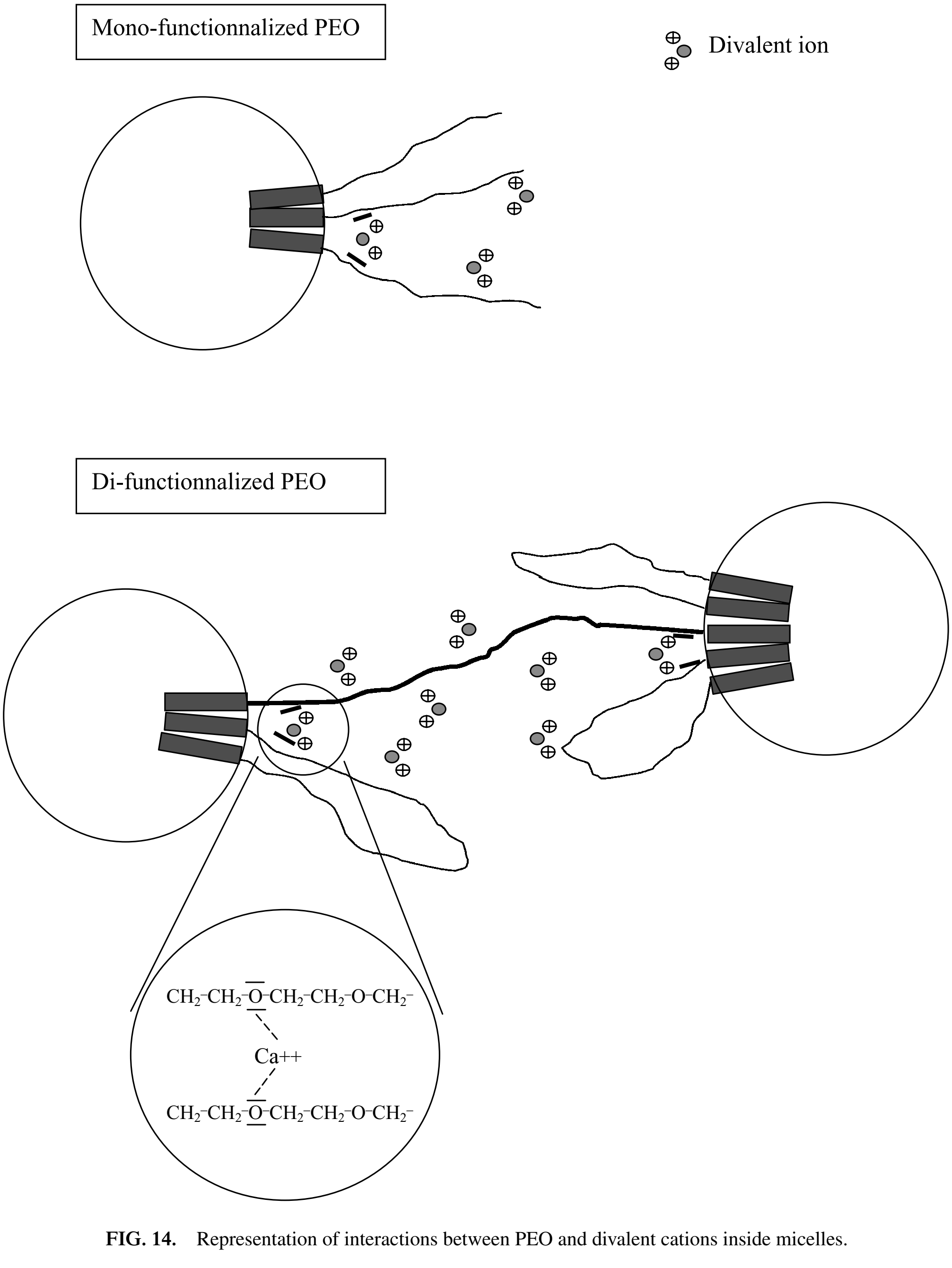

FIG. 14. Representation of interactions between PEO and divalent cations inside micelles.

Nevertheless, there are other points that may be interesting to verify experimentally and discuss more deeply before concluding definitively on the validity of the model proposed in Fig. 14. For example, we have neglected in the discussion the effects of anions, which are only chloride in this work. However, it is well known that anions affect considerably the solubility of PEO in water.

CONCLUSION

We studied the influence of salts of different mono- and divalent cations on hydrophobically modified PEO. Experiments in the presence of monovalent cations are in agreement with the description of a salting-out effect on PEO chains. The PEO coronae collapse, resulting in decreased solubility, smaller micelles, and diminished micelle overlapping. In contrast to these results, divalent cations induce surprising effects. The most interesting results indicate increased solubility, greater micelle overlapping, and an increase in the residence time of the hydrophobic groups in the micelle. In our opinion, this remarkable behavior could find its origin in ion–dipole interactions used to describe PEO in the presence of divalent cations. We have proposed a qualitative model able to take into account most of the experimental results.

REFERENCES

1. Maechling-Strasser, C., François, J., Clouet, F., and Tripette, C., *Polymer* **33,** 627 (1992).
2. Yekta, A., Xu, B., Duhamel, J., Adiwidjaja, H., and Winnik, M. A., *Macromolecules* **28,** 956 (1995).
3. Alami, E., Almgren, M., Brown, W., and François, J., *Macromolecules* **29,** 2229 (1996).
4. Alami, E., Rawiso, M., Isel, F., Beinert, G., Binana-limbele, W., and François, J., *in* "Hydrophilic Polymers, Performance with Environmental Acceptability" (J. E. Glass, Ed.), Advances in Chemistry Series 248, p. 343. Amer. Chem. Soc., Washington, DC, 1996.
5. Maitre, S., Ph.D. thesis. Université Louis Pasteur Strasbourg, France, 1997.
6. Chassenieux, C., Nicolai, T., Durand, D., and François, J., *Macromolecules* **31,** 4035 (1998).
7. Gourier, C., Beaudoin, E., Duval, M., Sarazin, D., Maître, S., and François, J., *J. Colloid . Interface Sci.* **41,** 230 (2000).
8. Beaudoin, E., Ph.D. thesis. Université de Pau et des Pays de l'Adour, Pau, France, 2001.
9. Semenov, A. N., Joanny, J. F., and Khokhlov, A. R., *Macromolecules* **288,** 1066 (1995).
10. Rawiso, M., Maitre, S., Sarazin, D., and François, J., *Colloids Surf.* **112,** 251 (1996).
11. Beaudoin, E., Borisov, O., Lapp, A., Billon, L., Hiorns, R. C., and François, J., *Macromolecules*, accepted (2002).
12. Saeki, S., Kuhawara, N., Nakata, N., and Kanako, N., *Polymer* **17,** 685 (1976).
13. Bailey, F. E., and Callard, R. W., *J. Appl. Polym. Sci.* **1,** 56 (1959).
14. Boucher, E. A., and Hines, P. M., *J. Polym. Sci.* **16,** 501 (1978).
15. Ataman, M., *Colloid Polym. Sci.* **265,** 19 (1987).
16. Beaudoin, E., Gourier, C., Lapp, A., and François, J., *Macromol. Symp.* **146,** 171 (1999).
17. Beaudoin, E., Lapp, A., Hiorns, R. C., Grassl, B., and François, J., *Polymer* **43,** 2677 (2002).
18. Kalyianafundaran, K., and Thomas, J. K., *J. Am. Chem. Soc.* **99,** 2039 (1977).
19. Turro, N. J., and Yekta, A. J., *J. Am. Chem. Soc.* **100,** 5951 (1978).
20. MacNeil, R., and Thomas, J. K., *J. Colloid Interface Sci.* **83,** 57 (1981).
21. Borisov, O., Beaudoin, E., and François, J., *Langmuir*, submitted (2001).
22. Chassenieux, C., Nicolai, T., and Durand, D., *Macromolecules* **30,** 4952 (1997).
23. Annable, T., Buscall, R., Ettelaie, R., and Wittelsetone, T. J., *J. Rheol.* **37,** 695 (1993).
24. Da Silva, L. H. M., and Loh, W., *J. Phys. Chem. B* **104,** 10,069 (2000).
25. Balasubramanian, D., and Chandani, B., *J. Chem. Educ.* **60,** 77 (1983).
26. Erlander, S. R., *J. Colloid Interface Sci.* **34,** 53 (1970).
27. Perreur, C., Habas, J. P., Peyrelasse, J., François, J., and Lapp, A., *Phys. Rev.* **63,** 31,505 (2001).
28. Perreur, C., Ph.D. thesis. Université de Pau et des Pays de l'Adour, 2001.