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Calorimetric investigation of the aggregation of lithium perfluorooctanoate on poly(ethyleneglycol) oligomers in water

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Abstract

The aim of this work is to investigate the effect of the nature of the counterion on the thermodynamics of aggregation of an ionic perfluorosurfactant on poly(ethyleneglycol) (PEG) of varying molecular weight in aqueous solution. The physicochemical properties of micellization and aggregation on PEG of lithium perfluorooctanoate (LiPFO) were investigated at 298.15 K by microcalorimetry, electrical conductivity, and viscosity. They were then compared with the same properties measured for the CsPFO/PEG system. As in the latter system, when wrapping around LiPFO micellar clusters the PEG polymers undergo a conformational change and form a compact complex. This complex reaches a constant thermodynamic behaviour for molecular weights larger than ∼2400 Da, which nicely matches the value ∼2600 Da found for CsPFO-PEG aggregates. The electrostatic screen provided by the polymer chain practically cancels the differences in the thermodynamic properties of the free micelles. This leads to thermodynamic parameters of aggregation of the two salts on the polymers, which are practically independent of the nature of the counterion.

Keywords: Surfactants; Polymers; Micelles; Counterion effect; Isothermal titration calorimetry

1. Introduction

Polymer–surfactant (P–S) systems have received much attention because of their practical applications in many industrial fields [1]. These applications originate from aggregation phenomena, mainly driven by hydrophobic effects, which characterize these systems and impart unique physicochemical properties to their aqueous solutions. In particular, the use of perfluorosurfactants proves to be very interesting owing to their greater hydropobicity as compared with their hydrocarbon homologues and their consequent ability to promote aggregation phenomena at much lower concentrations.

In previous papers we investigated the micellization reaction of two perfluoroalkanoates in water and their aggregation on poly(ethyleneglycol) (PEG) chains of different molecular weights: cesium perfluorooctanoate (CsPFO) [2] and lithium perfluorononanoate (LiPFN) [3]. The very similar thermodynamic behaviour of these two surfactants both in the micellization and the aggregation on PEG is obviously related to the perfluorocarbon chain that they have in common. However, an exact comparison to highlight the sole effect of hydrophobicity on the aggregation properties of these surfactants would have required the use of the same cation.

The effect of the nature of the counterion on the thermodynamic properties of self-aggregation and/or aggregation of anionic surfactants on non-ionic polymers has been discussed by many authors. Generally speaking, a clearly different behaviour for counterions of different charges [4] or particularly hydrophobic as tetralkylammonium ions [5,6] has been observed. In the case of alkali-metal ions, no univocal indication has been found so far. As far as the micellization process is concerned, the nature of the alkaline counterion has been shown to affect the binding constants with the micelle [7,8] or the counterion ionization degree [9] and the aggregation number in the presence [10] or absence [11,12] of electrolytes. It has also been shown that the Kraft point or solubilization power is affected, but not as much the cmc [13,14]. A strong counterion effect seems to be observed on the properties of the monolayer at the air–water interface [15].On the other hand, other authors have pointed out the scarce effect of the alkaline ion on several thermodynamic and transport properties of perfluoroalkanoate micelles [16], particularly on volumetric [6,17] and enthalpic properties [4].

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As far as the formation of P–S complexes is concerned, the cluster formed by different dodecyl sulphates with PEG may differ in terms of their size [18], or their enthalpy [19] or the critical concentration [20] of aggregation. Conversely, other studies have found that the counterion has little effect on the calorimetric properties [4] and on the thermodynamic stability, stoichiometry and ionic dissociation degree of the aggregates formed [21].

In this paper we study the thermodynamics of the aggregation of lithium perfluorooctanoate (LiPFO) on PEG polymers to understand how the counterion affects the polymer–surfactant systems previously studied in our laboratory [2,3]. We investigated the LiPFO/PEG system at 25 °C by examining polymer molecular weights ranging from 300 to 20,000 Da and used the same experimental techniques already used for the CsPFO/PEG system [2]. We thus performed calorimetric, conductivity and viscosity experiments in which the aqueous surfactant was added to 0.1% PEG aqueous solutions. Isothermal calorimetry (ITC) titrations were performed systematically with a series of PEG samples of increasing molecular weight (indicated as PEG M_W). On the other hand, conductivity and viscosity titrations were performed only with PEG 8000, the same polymer used in previous studies. The results were compared with those obtained for previous systems and they revealed a negligible cation effect.

2. Experimental

2.1. Materials

Poly(ethylene glycol) (PEG) samples with nominal molecular weights of 300, 600, 1500, 2000, 3400, 4600, 8000 and 20,000 Da were obtained from Aldrich. Standard samples of PEG of certified molecular weights, characterized by a low polydispersity index ($D = M_w/M_n$) were provided by Fluka. For these samples the effective molecular weight was chosen as the average between M_w and M_n: PEG 6000 ($D = 1.03$) and PEG 11200 ($D = 1.07$).

Pentadecafluorooctanoic acid 99% (Fluorochem) was neutralized with lithium hydroxide monohydrate 99.95% (Aldrich) in an aqueous solution. After water had been removed, the salt was crystallized from a *n*-butanol/*n*-hexane mixture and dried at 80 °C under vacuum for 2 days.

Doubly deionized water was used as the solvent. All solutions were prepared by weight. The concentration of LiPFO was expressed as moles per kg of water (m). PEG solutions were allowed to stand overnight before use, and their concentration was expressed as % weight.

2.2. Isothermal titration calorimetry

The isothermal titration calorimeter used was a Thermal Activity Monitor 2277 (TAM) from Thermometric, equipped with a 612 Lund syringe pump. Titrations were performed at 298.15 ± 0.02 K by adding aliquots of a few microliters (10–50) of 0.999 m aqueous LiPFO into a 20 ml cell containing 15–16 g of a 0.1% (w/w) PEG aqueous solution, covering a surfactant concentration range $0 < m_S < 0.06\ \mathrm{mol\,kg^{-1}}$. The heat effects observed were measured mostly on the 300 μW full-scale detection range, allowing an average uncertainty of ±1%. The concentration of PEG (m_{EO}), expressed as the molality of the repeat unit (–CH_2–CH_2–O–), was 0.0227 mol kg^{-1}, and was constant for all 0.1% PEG solutions. Blank titrations showed negligible heat effects associated with PEG dilution.

2.3. Conductivity

Conductivity measurements were carried out at 298.15 ± 0.10 K with an Amel 160 apparatus. The cell constant (1.041 cm^{-1}) was determined with a 0.01 M KCl aqueous solution.

2.4. Viscosity

Viscosity measurements were performed by means of an Ubbelohde viscosimeter equipped with an optical system for flow detection. Details of the experimental procedure are reported elsewhere [2]. The results were expressed as relative viscosity ($\eta_{rel} = \eta/\eta_o$), where η and η_o are the viscosities of sample solution and solvent, respectively. Owing to the low concentration of the surfactant, and the consequent almost constant density of the solutions, the relative viscosity was approximated to the ratio of experimentally measured flow times: $\eta_{rel} = t/t_o$. The density actually changes monotonically up to less than 1% in the most concentrated solution: this does not bias the trend of the function $\eta_{rel} = f(m_S)$.

3. Results

3.1. Isothermal titration calorimetry

Fig. 1a shows typical enthalpy of dilution ($\Delta_{dil}H$) curves which were obtained by adding concentrated aqueous LiPFO, containing micelles, to water in the presence or absence of a given PEG polymer. In this and in the other figures that report experimental data as a function of the surfactant concentration, the lines are mere guide for eyes. The figure indicates the critical surfactant concentrations pertinent to polymer–surfactant systems: the critical micelle concentration (cmc) in the absence of the polymer, the critical aggregation concentration (cac) at which the interaction with the polymer begins, and the saturation concentration of the polymer, C_2.

The curve relative to the dilution in water can be used to determine a cmc value, 0.0276 mol kg^{-1}, which is a little lower than in the literature (see Table 2 in Ref. [2]). However, note that in our work the cmc was identified as the concentration at which the ITC curve indicates the beginning of the micellization process [4]. This choice is consistent with the analogous identification of the cac in the presence of polymers. If, as others have done [22,23], we identify the cmc at the maximum of the differential property being measured (in the present case $\Delta(\Delta_{dil}H)/\Delta m_S$), we can then calculate a value 0.0311 mol kg^{-1} in agreement with literature data.

By graphically evaluating the enthalpy of micellization from the dilution curve in Fig. 1a we can determine $\Delta_{mic}H = 8.48\ \mathrm{kJ\,mol^{-1}}$. This value changes to 8.36 kJ mol^{-1} when calcu-

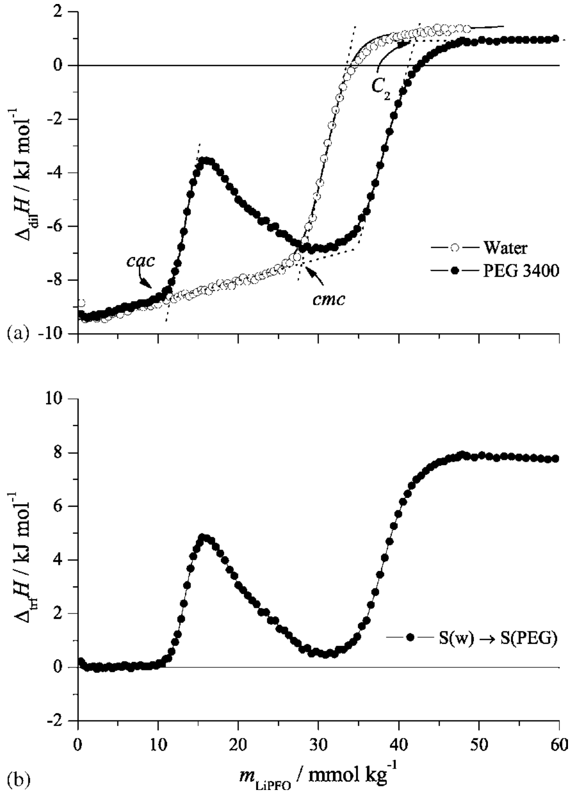

Fig. 1. (a) Typical curves of heats of dilution of a concentrated LiPFO aqueous solution in water and aqueous PEG. (b) Enthalpy of transfer (Eq. (1)) of monomeric surfactant (S) from water to 0.1% PEG 3400 solutions.

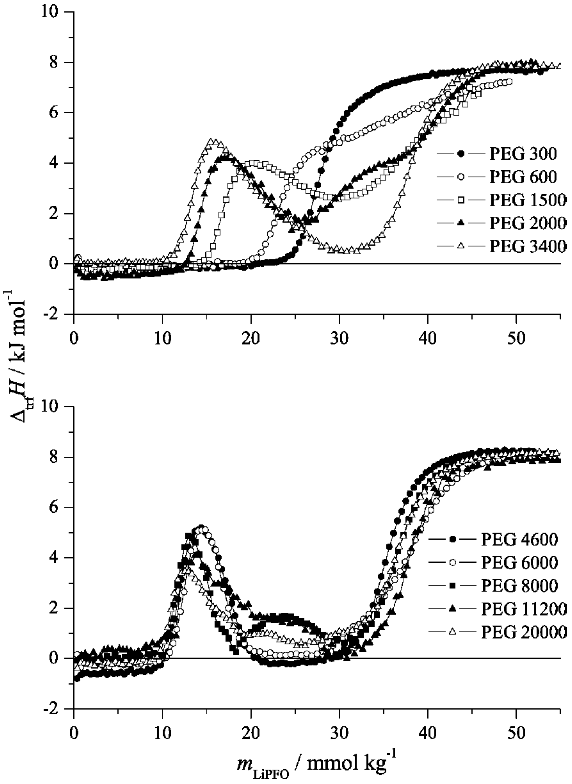

Fig. 2. Enthalpy of transfer, $\Delta_{trf}H$, of LiPFO from water to 0.1% PEG at 25 °C as a function of surfactant concentration for polymers of different molecular weight.

lated from the analytical deconvolution of the calorimetric curve at the flex point (0.0311 mol kg^{-1}). No $\Delta_{mic}H$ datum was found in the literature for the same surfactant. The above values are comparable with those measured for the sodium salt, while larger than for cesium salt (8–9 kJ mol^{-1} for NaPFO, 5.1 kJ mol^{-1} for CsPFO, see Table 2 in Ref. [2]).

Fig. 1b reports the enthalpy of transfer of one mole of monomeric LiPFO from water to 0.1% (w/w) PEG 8000 solutions ($\Delta_{trf}H(S,m)$) as a function of surfactant (S) concentration. Values of the transfer enthalpies were obtained by subtracting the dilution enthalpy of the surfactant in water from the dilution enthalpies in the PEG solutions, measured at the same S concentration, and adding a further term ($\delta_{mic}H$), which measures the heat effect due to micellization:

$$\Delta_{trf}H(S, m)_{W\rightarrow PEG} = \Delta_{dil}H(S)_{PEG} - \Delta_{dil}H(S)_{w} + \delta_{mic}H \tag{1}$$

For a complete definition of the quantity $\delta_{mic}H$ and its calculation see Ref. [2]. The function $\Delta_{trf}H(S,m)$ represents, over the whole surfactant concentration range, the heat associated with the process by which the surfactant is transferred from its monomeric form to an aggregated form, whether this is a complex with the polymer or a free micelle. This function reflects mainly the heat of aggregation on the polymer for S concentrations below the saturation of the polymer itself, while it approaches the micellization enthalpy for concentrations far exceeding saturation.

Fig. 2 reports the values of the transfer enthalpy defined by Eq. (1) (hereafter $\Delta_{trf}H$) as a function of surfactant concentration for all the polymers examined in this work. The enthalpies of transfer follow a very similar pattern to that observed for CsPFO [2]. Interaction with the polymer is already observed with PEG 300 and PEG 600, which exhibit a decrease of the cmc (0.0251 and 0.0208 mol kg^{-1}, respectively) as compared with the cmc in water (0.0276 mol kg^{-1}). For these short polymers, the trend of the dilution curve strongly resembles the dilution in pure water, and may imply that micellization occurs earlier through the formation of mixed micelles. On the other hand, the longer polymers display the typical endothermic peak at low surfactant concentrations attributed to the aggregation of the surfactant on the polymer [2,4,24,25]. As for CsPFO, this peak shifts to lower S concentrations and increases in magnitude for increasing PEG molecular weights up to about 4600 Da. Unlike CsPFO, the magnitude of the endothermic peak decreases for M_w values larger than 4600 Da, and is not followed by any exothermic effect.

Possible effects related to the distribution of molecular weights of the polymer samples were already found to be negligible in the case of other systems [2,25], through measurements with polymer samples characterized by a very low polydispersity index ($D < 1.07$), and were not expressly investigated in the present work.

Table 1 lists the values of critical concentrations relevant to the various PEGs, together with an estimate of the enthalpy and free energy of formation of the LiPFO-PEG aggregate, which is initially formed at low surfactant concentrations. According to

Table 1
Thermodynamic data obtained from calorimetric titrations of 0.1% PEGs with LiPFO in water at 298.15 K

PEG M_w (Da)	cac[a] (mmol kg^{-1})	$\Delta_{trf}H_{max}$[b] (kJ mol^{-1})	$\Delta_{agg}G^o_m$[c] (kJ mol^{-1})	C_{max}[d] (mmol kg^{-1})	C_2[e] (mmol kg^{-1})
No PEG	27.6 (cmc)				
300	25.1	–	–	–	–
600	21.0	4.30	−39.1	26.6	58
1,500	15.1	4.06	−40.7	20.1	47
2,000	12.9	4.28	−41.5	17.2	45
3,400	11.6	4.86	−42.0	15.7	42.1
4,600	10.3	5.24	−42.6	14.3	39.7
6,000	11.1	5.17	−42.2	14.5	43.7
8,000	10.2	4.91	−42.7	13.1	40.8
11,200	10.8	4.20	−42.4	14.1	41.6
20,000	9.9	3.53	−42.8	12.7	41.0

[a] Critical aggregation concentration, uncertainty ±0.2 mmol kg^{-1}.

[b] Calculated through Eq. (2) at the maximum of the endothermic peak.

[c] Calculated as $\Delta_{agg}G^o_m = 2RT \ln \text{cac}$, standard state unit mole fraction.

[d] Concentration corresponding to $\Delta_{trf}H_{max.}$, uncertainty ±0.2 mmol kg^{-1}.

[e] Concentration of saturation of the polymer, uncertainty ±0.5 mmol kg^{-1} for $M_W > 3000$, but much larger for shorter polymers.

the charged phase separation model [26], values of the standard free energy of formation of this aggregate, starting from the free monomers, can be calculated as $\Delta_{agg}G^o_m = (2-\alpha)RT \ln \text{cac}$, where α is the counterion ionization degree. The data in Table 1 were evaluated assuming $\alpha = 0$, and in this paper are only used for internal comparisons. Under the hypothesis that the LiPFO that was added in the region of the maximum of the endothermic peak is 100% aggregated, the corresponding value of the transfer enthalpy ($\Delta_{trf}H_{max}$, see Table 1) can be identified with the enthalpy of aggregation of LiPFO monomers ($\Delta_{agg}H_m$).

3.2. Conductivity

The conductivity of aqueous solutions of LiPFO at 298.15 K was measured in water and water containing 0.1% PEG 8000. The experimental results are shown in Fig. 3. The values of the critical concentrations, which can be calculated from the intersections of the straight segments of the conductivity curves, are consistent with those determined by ITC. The ratios of the slopes of the straight lines allow us to determine the dissociation degree α of the counterions [27], which was $\alpha = 0.63$ for the free micelles, and 0.78 for the aggregate formed on PEG 8000. The ionic dissociation of the aggregate was larger than that of the free micelles, as already noticed for many other P–S complexes [28].

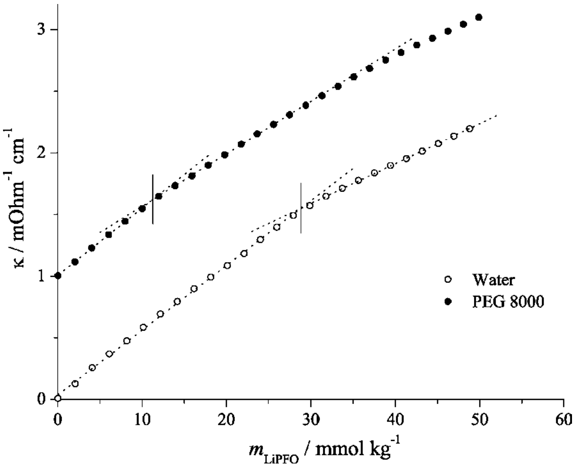

Fig. 3. Specific conductivity of aqueous LiPFO solutions at 25 °C. Vertical bars indicate critical concentrations. In order to increase readability the curves have been shifted from each other by 1 m Ω^{-1} cm^{-1}.

3.3. Viscosity

Fig. 4 reports the change in relative viscosity ($\eta_{rel} = \eta/\eta_o$, where η is the viscosity of the sample solution and η_o the viscosity of the solvent) observed in a titration with LiPFO of a 0.5% PEG 8000 solution. The viscosity increases up to the cac, then it decreases, reaches a minimum and, at larger surfactant concentrations, it increases steeply and monotonically. No such viscosity minimum was observed when adding LiPFO to 0.1% PEG aqueous solutions. This is probably due to the low contribution by the diluted polymer to the overall viscosity of the medium.

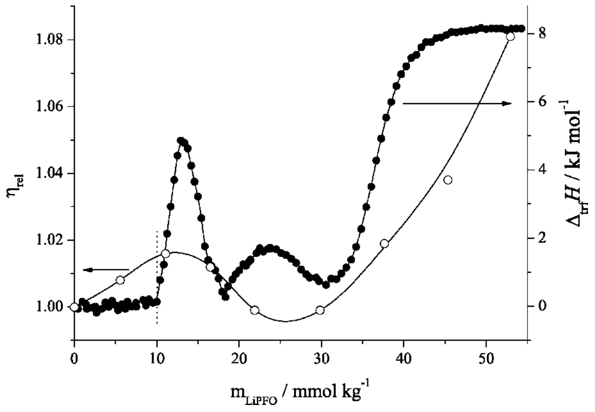

Fig. 4. Relative viscosity (η_{rel}) for 0.5% PEG 8000 aqueous solutions as a function of LiPFO concentration. Comparison with surfactant transfer enthalpy, $\Delta_{trf}H$.

Table 2
Thermodynamic data for the micellization of perfluorooctanoates in water at 298.15 K

S	cmc (mol kg^{-1})	$\Delta_{\mathrm{mic}}G^{\circ}$[a] (kJ mol^{-1})	$\Delta_{\mathrm{mic}}H$ (kJ mol^{-1})	$\Delta_{\mathrm{mic}}S$ (J K^{-1} mol^{-1})	$\Delta_{\mathrm{mic}}C_p$ (J K^{-1} mol^{-1})	$\Delta_{\mathrm{mic}}V$ (cm^3 mol^{-1})	α
LiPFO[b]	0.0276	−26.02	8.48	116	−502[c]	10.2[c]	0.62
NaPFO[d]	0.0325	−27.49	8.93	122	−555	12.4	0.51
CsPFO[e]	0.0234	−30.44	5.10	119	−392	9.9	0.42

[a] $\Delta_{\mathrm{mic}}G^{\circ} = (2-\alpha)\,RT\ln \mathrm{cmc}$, standard state unit mole fraction.
[b] This work.
[c] Preliminary results from our laboratory.
[d] Data averaged among values reported in Ref. [2].
[e] Ref. [2].

4. Discussion

Table 2 summarizes the thermodynamic data of micellization of the three perfluorooctanoates for which most experimental properties were determined. The table shows that the nature of the counterion only slightly affects the values of many properties: for instance, very similar values are observed for the entropy, volume and heat capacity of micellization. The main differences are observed in the free energy of micellization and in the dissociation degree of the counterion. The larger stability of CsPFO micelles appears to be mainly due to enthalpic effect, which in this case is less unfavourable. The smaller dissociation of the Cs^+ ion may be related to its smaller hydrated radius, which favours the interaction with the micellar head groups. The change in the dissociation degree of the counterion seems to account for the trend of the micellization free energies. In fact, the calculation of the micellization free energy under the hypothesis of zero counterion dissociation ($\Delta_{\mathrm{mic}}G = 2RT\ln \mathrm{cac}$), as often done, would strongly bias the comparison leading to almost constant values (−37.71 kJ mol^{-1} for LiPFO, −36.90 kJ mol^{-1} for NaPFO and −38.53 kJ mol^{-1} for CsPFO).

We will now discuss the data on the aggregation of the surfactant on the PEG polymers following the line adopted in our previous work on cesium perfluorooctanoate [2]. The aggregation process of LiPFO on PEG oligomers exactly parallels the process already observed for CsPFO. The values of critical concentrations and of the thermodynamic properties of aggregation are plotted in Fig. 5 as a function of the molecular weight of the polymers. The almost constant value of these thermodynamic parameters at large M_{W} values was taken as an indication of a constant composition and thermodynamic stability of the P–S aggregates. The trends of the functions in Fig. 5 show that the binding of the surfactant molecules on the PEG chains reaches an almost stable condition after M_{W}~2400 Da. This probably means that a chain of about 55 PEG monomeric units is able to bind the first fully formed micellar cluster of surfactant molecules. The above minimum value of M_{W} appears to be consistent with the analogous value of ~2600 Da already found for CsPFO [2].

The saturation concentration of the polymer, C_2, points to an average value of 0.0415 mol kg^{-1} for the larger M_{Ws}. With this value we can estimate the ratio of surfactant molecules bound per PEG monomeric unit at the saturation, calculated as $R_{\mathrm{C2}} = (C_2 - \mathrm{cac})/m_{\mathrm{EO}}$. A value $R_{\mathrm{C2}} = 1.35$ was calculated for LiPFO aggregates, in close agreement with the average value of 1.33 calculated for the same PEG M_{ws} in the case of CsPFO [2].

The present data also indicate that when the polymer binds a small surfactant aggregate at low surfactant concentrations, it undergoes a conformational change analogous to the one observed in the case of CsPFO. In fact, Fig. 4 shows that the relative viscosity of 0.5% PEG 8000 solutions decreases as the concentration of the surfactant slightly exceeds the cac, and then reaches a minimum before displaying a final monotonic increase. For the sake of comparison, the figure also shows the transfer enthalpy data of the ITC titration performed with a 0.1% PEG 8000 solution. The viscosity and calorimetric data, though

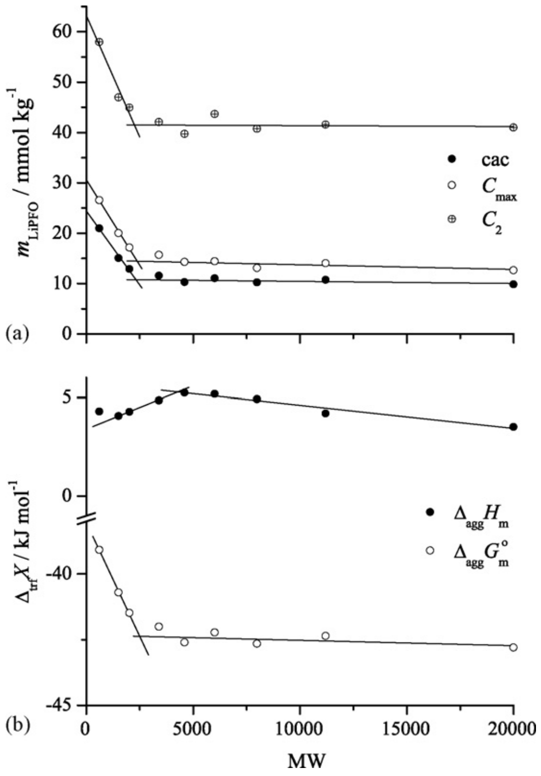

Fig. 5. Thermodynamic parameters for LiPFO aggregation on PEG as a function of PEG molecular weight at 25 °C: (a) surfactant concentrations at the critical aggregation (cac), at the maximum of the endothermic peak ($C_{\max}$) and at the saturation of the polymer (C_2); (b) $\Delta_{\mathrm{agg}}G^{\circ}_{\mathrm{m}} = 2RT\ln(\mathrm{cac}/55.51)$; $\Delta_{\mathrm{agg}}H_{\mathrm{m}} = \Delta_{\mathrm{trf}}H_{\max}$ (Table 1).

Table 3
Thermodynamic data for the aggregation of perfluorooctanoates in 0.1% PEG 8000 in water at 298.15 K

S	cac	α'	Aggregation of monomeric surfactant			Aggregation of preformed micelles[a]		
			$\Delta_{agg}G^{o}_{m}$ [b] (kJ mol^{-1})	$\Delta_{agg}H_{m}$ [c] (kJ mol^{-1})	$\Delta_{agg}S_{m}$ (J K^{-1} mol^{-1})	$\Delta_{agg}G^{o}_{M}$ (kJ mol^{-1})	$\Delta_{agg}H_{M}$ (kJ mol^{-1})	$\Delta_{agg}S_{M}$ (kJ mol^{-1})
LiPFO[d]	0.0102	0.78	−26.01	4.91	104	0.01	−3.57	−12
CsPFO[e]	0.0094	0.72	−27.55	3.93	106	2.89	−1.17	−13

[a] $\Delta_{agg}X_{M} = \Delta_{agg}X_{m} - \Delta_{mic}X$, $X = G, H, S$.
[b] $\Delta_{agg}G_{m}^{\circ} = (2 - \alpha')\, RT \ln \text{cac}$, standard state = unit mole fraction.
[c] $\Delta_{agg}H_{m} = \Delta_{trf}H_{max}$ (Table 2).
[d] this work.
[e] Ref. [2], changing the free energy standard state from 1 mol kg^{-1} to unit mole fraction.

collected at different polymer concentrations, can be compared since the position of the cac, was found to be independent of the polymer concentration for aggregates formed by PEG with SDS [24,25,29] and with perfluoroalkanoates [2,3]. The viscosity decrease is located soon after the endothermic peak exhibited by the corresponding transfer enthalpy curve. We have already pointed out [2] that the extrema of these two experimental properties are the probe of the same phenomenon, and their relative displacement on the concentration axis is due to their different nature. In fact, it is to be expected that a partial molar property, like the dilution enthalpy measured along a calorimetric titration, proves sensitive to any specific interaction in solution much earlier than a bulk property such as viscosity. Therefore, as in our previous work [2,3], we deduce that the endothermic peak observed at low surfactant concentration, originally attributed only to the dehydration of the PEG chain [24,30], is also partly caused by a conformational change of the polymer. In fact when the PEG wraps itself around a small surfactant aggregate, its chain would take on a strained, high energy conformation whose more compact structure is responsible for the decrease in viscosity.

A more quantitative comparison between the two systems is presented in Table 3. This table compares the values of the thermodynamic parameters relative to the formation of the first P–S complex formed by PEG 8000 with the two perfluorinated surfactants at low concentrations. The PEG 8000 polymer was chosen as being representative of the general behaviour of all larger molecular weight polymers. The knowledge of the value of the dissociation degree of the counterion, α', measured through conductivity for the P–S complex of this polymer, enabled us to calculate the free energy of aggregation of S on the polymer according to the complete charged phase separation model ($\Delta_{agg}G^{o}_{m} = (2 - \alpha')RT \ln \text{cac}$) [26]. The values of the corresponding entropy changes were calculated by the Gibbs equation.

Table 3 shows comparable thermodynamic data for the aggregation of surfactant monomers on the polymer chain ($\Delta_{agg}X_{m}$). A very similar α' value is exhibited by the two P–S aggregates, indicating the clear balancing role of the electrostatic screen provided by the polymeric chain. The comparable α' values would lead to an unbiased comparison of the standard free energy of aggregation of these two systems even when assuming $\alpha' = 0$.

The values of $\Delta_{agg}G_{m}^{\circ}$ indicate that the complex with PEG formed by CsPFO is more stable than that formed by LiPFO by 1.5 kJ mol^{-1}. However, if the LiPFO and CsPFO systems are compared with reference to the process of aggregation on the polymer of a preformed surfactant micelle (see $\Delta_{agg}X_{M}$ data in Table 3), the LiPFO micelles display a stronger tendency for aggregation on the polymer by ~3 kJ mol^{-1}. This derives from the much lower stability of the latter free micelles as compared with those of CsPFO ($\Delta_{mic}G^{\circ} = -26.02$ kJ mol^{-1} against -30.44 kJ mol^{-1}, see Table 2).

In summary, the two systems only show a slightly different behaviour in the micellization process. In fact they have the same pattern, and practically the same thermodynamic parameters, in the process of complex formation with the PEG polymers, provided these data refer to the reaction starting from monomeric surfactant. However, we have only focused on the aggregate that is initially formed at low surfactant concentrations, without applying a complete model, which would have been necessary in order to characterize the further aggregates that are probably formed by rearrangement at larger surfactant concentrations.

5. Conclusions

The calorimetric, conductivity and viscosity data relative to the aggregation of LiPFO on PEG oligomers of increasing molecular weight were found to be, as expected, very similar to those of CsPFO previously studied in our laboratory. The different nature of the counterion was found to affect only a few properties of micellization, particularly the dissociation of the counterion. When the monomeric surfactants aggregate on the PEG polymers, the electrostatic screen provided by the latter buries the possible effects related to the different size and different electrostatic field of the counterion. This leads to P–S complexes that are characterized by the same thermodynamic stability and by substantially the same thermodynamic parameters.

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