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ABSTRACT: Polyoxometalates (POMs) are nanometric metal–oxide anions with an unmatched range of chemical and physical properties. During the past decade, significant efforts have been made to study POM surface activity and self-assembly properties that are essential for catalysis applications and for producing organic–inorganic hybrid materials. A previous work highlighted the tungstosilicate ($SiW_{12}O_{40}^{4-}$) and tungstophosphate ($PW_{12}O_{40}^{3-}$) Keggin POM anions' spontaneous and noncovalent adsorption at the micellar surface of non-ionic surfactants. In this study, the critical micelle concentrations (CMC) of two non-ionic surfactants, the n-octyl-β-glucoside (C_8G_1) and the tetraethylene glycol monooctyl ether (C_8E_4), were measured in the presence of POMs, and we propose herein thermodynamic models to explain an increase or a decrease of the CMC depending on the choice of the POM/surfactant couple.

INTRODUCTION

Polyoxometalates (POMs) are molecular oxo-clusters of the early transition metals in their highest oxidation states. They can be considered either small water soluble oxides or nano-ions (1-4 nm).[1] The variety of their chemical and physical structures at the atomic scale makes them a key nano-particle used in numerous applications including in the medical, analytical and material science fields[2-6]. Among these properties, the catalytic properties are well known and noteworthy.[7-8] Their significant development in the last twenty years is also related to their ability to self-assemble in large structures[9] with enhanced physical properties but also to make hybrid organic-POM building blocks for designing smart complex[10-12] or advanced functional materials and devices.[13] Nanometer-sized POM clusters, such as the ones of Kegging type, can be classified as super-chaotropic anions[14] and adsorb at neutral polar interfaces,[15-16] a property that was exploited to organize them into a lyotropic liquid crystal structure.[17-19] This latter property is particularly noteworthy, considering that the weak interactions taking place between the negatively charged POMs and neutral interfaces are of non-electrostatic origin and are sufficiently strong to promote adsorption. Indeed, most of the previous studies aiming at adsorbing POMs on interfaces used the more classical approach based on the electrostatic coupling between cationic interfaces, for instance covered by cationic surfactants, and the negatively charged POMs. Langmuir films were for example made at the water-air interface by using an electrostatic coupling method.[20-25] The electrostatic coupling approach between cationic surfactants and POMs was also used many times with other goals, for example to produce catalytic nano-particles[12] or POM self-assembly in non-aqueous solvents.[26] An alternative approach was proposed by using surfactants with POMs as polar heads covalently bound to alkyl chains.[11, 13, 27-28] POM-surfactants proved to be efficient in structuring POM building blocks in bulk and at interfaces by spontaneous self-assembly in 2D or 3D, playing with the wealth of amphiphilic structures and organization in liquid crystals or fluid phases, e.g. micelles or microemulsions.

It appears that the non-covalent approach has many advantages over the electrostatic and covalent ones: (i) it produces more flexible and liquid-like structures (micelles, lyotropic phases) compared to the electrostatic approach, and (ii) it is much less costly and time-consuming than the covalent approach that requires multiple-step synthesis. However, a key issue for the control of the adsorption and self-assembly properties of POMs in aqueous media is to understand their non-electrostatic interactions with polar non-ionic moieties at interfaces.

In the present study, we investigate how the POMs' adsorption on micelles influences the micellization process in order to go further in the understanding of the non-electrostatic interactions between POMs and non-ionic surfactants. The critical micellar concentration (CMC) values of the octyl-beta-glucoside (C_8G_1), and the tetraethylene glycol monooctyl ether (C_8E_4), two non-ionic surfactant systems with identical alkyl chain length and thus volume, were determined by the surface tension measurement at different POM concentrations with $PW_{12}O_{40}^{3-}$ (or $[PW_{12}]^{3-}$) and $SiW_{12}O_{40}^{4-}$ (or $[SiW_{12}]^{4-}$), two Keggin's POMs for which we already know that they adsorb on these micellar surfaces.[15] The determination of the CMC is therefore used here as a thermodynamic probe of the POM/surfactant interactions[29] and we propose a thermodynamic model of the micellization process to explain our observation.

EXPERIMENTAL SECTION

Materials. $H_4SiW_{12}O_{40}.12H_2O$ 99.9% and $H_3PW_{12}O_{40}.12H_2O$ 99.995% were obtained from Aldrich. n-octyl-β-D-monoglucoside (C_8G_1) 99% was obtained from Anatrace. Tetraethylene glycol monooctyl ether (C_8E_4) 95,5% was synthesized following the steps described in Naskar et al..[15]

All the chemicals were used as received unless otherwise stated. Doubly distilled water (κ= 5−6 μS.cm^{-1} at 25°C) was employed for solution preparation. *pH* values of the solutions were measured and were always below 4.0, i.e. in the range of stability of the POMs in water.

Methods. The surface tension (γ) was measured as a function of the surfactant concentration using a drop shape analyzer (Krüss DSA 100). The surface tension values are the average values of 5 measurements at least for each point. The absolute precision is typically 1%. The CMC was determined at the apparent break in the surface tension. An error bar is estimated from the error made in the higher γ-slope determination. Various solutions of POMs at fixed concentrations were prepared either in water or in brine (100 mM of NaCl). Stock solutions of concentrated surfactants were also prepared in the same media. The density of each solution was measured at 23°C using a vibrating tube densitometer (Anton Paar DSA 5000). The liquid/air surface tension was measured after injecting a fixed number of mother solution drops into the cuvette containing the POMs solution. The γ values were accurate within ± 0.1 mN.m^{-1}.

RESULTS AND DISCUSSION

The micellization of surfactants in water is a thermodynamic mechanism to minimize the free energy of the solution via the aggregation of the surfactants above a critical concentration (CMC).[29]

A) CMC as a function of POM concentration. CMC values of the two surfactant systems (C_8E_4 and C_8G_1) in water or in brine were determined via surface tension measurement as a function of the surfactant concentration and for different POM concentrations. Fig. 1A and 1C show the surface tension of C_8E_4 and C_8G_1 solutions respectively in the presence of 0, 5, 10 and 25 mM of $[SiW_{12}]^{4-}$. Fig. 1B shows the surface tension of C_8G_1 solutions in the presence of 2, 5, 10 and 25 mM of $[PW_{12}]^{3-}$. The critical micelle concentrations were determined from the point of intersection of two straight lines of surface tension vs logarithm bulk concentration curves above and below CMC. The averaged surface tension observed at and above the CMC is called γ_{CMC}. CMC and γ_{CMC} values were reported in Table 1 for both surfactants. The CMC variations as a function of POM concentration were also plotted in Fig. 2 to highlight the differences between the different surfactant/POM couples.

It was not possible to study the C_8E_4 / $[PW_{12}]^{3-}$ system, as the solution turns to turbid at lower concentration of C_8E_4 and becomes clear at higher concentration of C_8E_4 (observation for 2 mM $[PW_{12}]^{3-}$). It seems to be due to precipitation or coacervate formation at low concentration.[30] This indicates that $[PW_{12}]^{3-}$ interacts more strongly with C_8E_4 than $[SiW_{12}]^{4-}$.

The CMC values of C_8G_1 and C_8E_4 in water without POMs are in line with literature data, i.e. between 19 and 25 mM for C_8G_1[31-34] (titration calorimetry measurement which is known to be very accurate gave 27.1 mM)[35] and around 8 mM for C_8E_4[15, 36, 37] (the titration calorimetry value is 8.4 mM). In the presence of POMs, we determined a shift of the CMC to lower values in the case of $[SiW_{12}]^{4-}$ with C_8E_4 or $[PW_{12}]^{3-}$ with C_8G_1 as expected for an electrolyte effect with non-ionic surfactant. However this effect is significant at very low concentration of POM (below 10 mM) whereas it is observed with such amplitude above 100 mM for usual electrolytes.[33, 38-40] On the other hand we determined a slight increase of the CMC when $[SiW_{12}]^{4-}$ is added to a solution of C_8G_1.

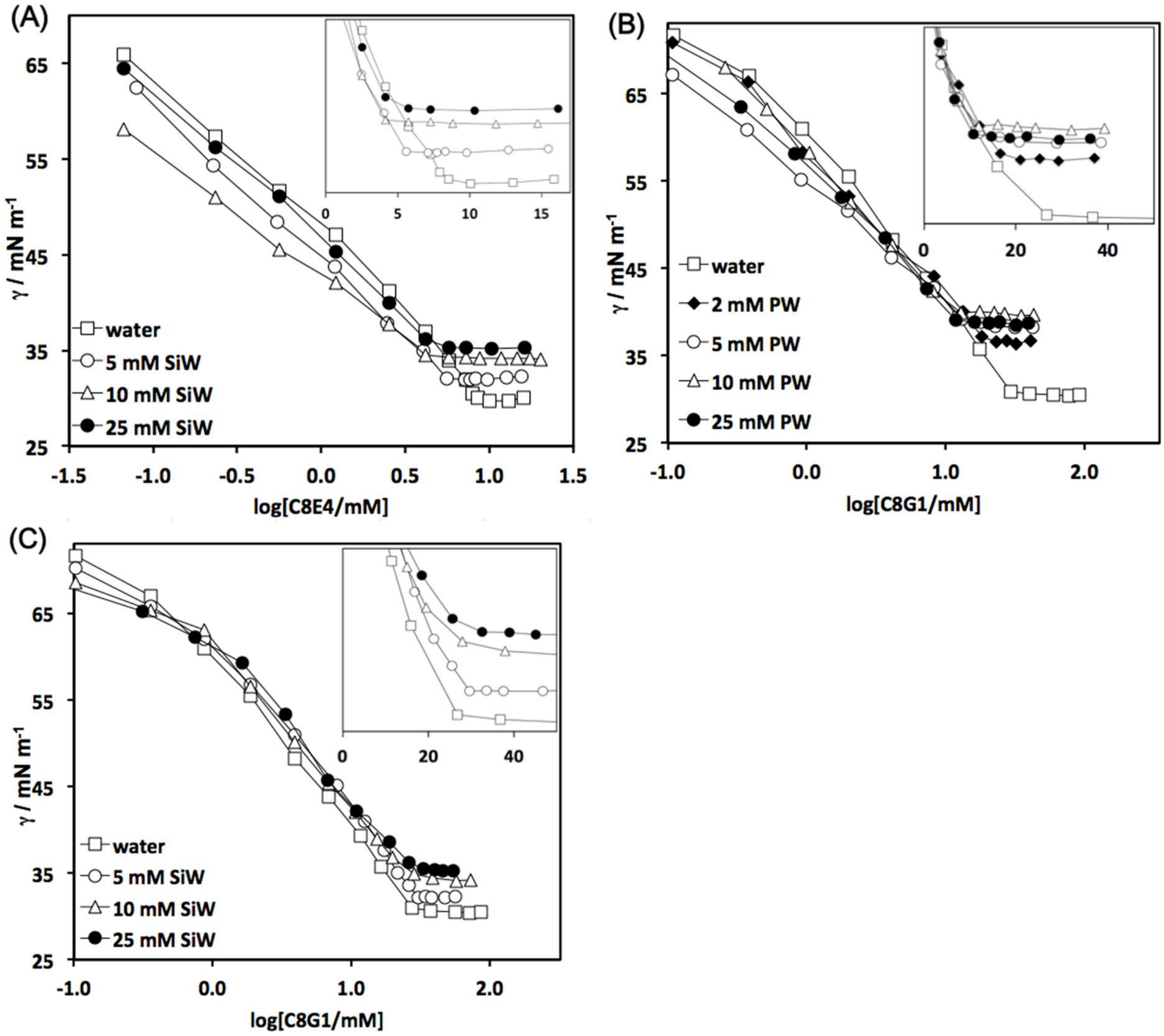

Figure 1. Surface tension as a function of logarithm of the surfactant concentration at various POM concentrations: A) C_8E_4 with $[SiW_{12}]^{4-}$, B) C_8G_1 with $[PW_{12}]^{3-}$, C) C_8G_1 with $[SiW_{12}]^{4-}$. The CMC were determined from the point of intersection between the highest slope when the surface tension decreases before the CMC and the regime where the surface tension is constant.

We have also observed that the higher the POM concentration, the higher the surface tension at the CMC, γ_{CMC}, whatever the surfactant/POM couple. This effect has already been observed if we refer to other published works.[41-43] It was indeed shown that γ_{CMC} increases for mixed non-ionic and ionic surfactants, increasing the concentration of ionic surfactants or when using a pH sensitive surfactant for which the ratio of charged and non charged polar heads can be tuned. In all these cases an increase of the surface tension at the CMC can be correlated to the concentration of charge at the water/air interface enhancing the surface energy.

The surface tension without surfactant and for different concentrations of POM in solution was measured (see Table 1). Small variations of surface tension were observed in the presence of POMs, which indicates a very weak adsorption at the bare water/air surface, which likely arises from the slight surface activity of protons.[44] The effect of background salt was also studied for comparison between the C_8G_1 system and C_8E_4, with 100 mM of NaCl and at 10 mM of $[SiW_{12}]^{4-}$ with 100 mM of NaCl. The background salt has a slight effect on the CMC of C_8G_1 and C_8E_4 without POM. Indeed for C_8G_1 the CMC in 100 mM of NaCl (25.7 mM) is slightly lower than the CMC in pure water, i.e. 27.6 mM (see Table 1). As mentioned previously, this is not surprising for a non-ionic surfactant for which CMC is usually not or only slightly affected by the presence of salt at low concentrations. Ion effect on the non-ionic surfactant CMC becomes indeed significant only at high salt concentrations, i.e. in the molar range or when they show specific effect, with the CMC's decrease much more pronounced for "salting-out" ions than for "salting-in" ions.[39-40, 45] On the other hand, a significant CMC decrease is observed for the $C_8G_1/[SiW_{12}]^{4-}$ (10 mM) system from 30.1 down to 23.5 mM when adding 100 mM of NaCl whereas an increase was determined adding only 10 mM of $[SiW_{12}]^{4-}$ POM to the pure system (from 27.6 up to 30.1 mM). This behavior is similar to the effect of the addition of salt to an anionic surfactant solution, which leads to a decrease of the CMC by a screening effect.[45] The same observation can be done for the $C_8E_4//[SiW_{12}]^{4-}$ (10 mM) system. This observation could be qualitatively explained by a screening effect of the charges of an "ionic surfactant" formed by the association of POMs and the non-ionic surfactants.

The affinity of the POMs for surfactants was previously shown by studying the POMs' adsorption onto micellar surfaces using the same surfactants at higher concentration.[15] SAXS data were indeed analyzed taking into account a strong adsorption of the Keggin-type POMs, $[PW_{12}]^{3-}$ and $[SiW_{12}]^{4-}$, at the surface of non-ionic micelles made either with C_8G_1 or C_8E_4. It was also shown that depending on the chemical nature of the surfactant polar head (glucose or PEG), the POMs were more or less embedded in the polar heads corona and without a direct bond involved between POMs and surfactants. The consequences of the adsorption of POMs on the micelles were a huge increase of the stability of the micellar solution and a change in the micelle shape from elongated to spherical. It was also shown that for C_8E_4 solutions, the cloud point (CP), i.e. the temperature above which a liquid-liquid phase separation takes place, was increased from 40°C to 90°C by the addition of Keggin POMs. This is a tremendous effect compared to the one of thiocyanate, SCN^-, one of the most salting-in anions in the Hofmeister series, for which the CP only increases by a few degrees. The salting-in effect and the adsorption propensity of POMs onto micelles were shown to be stronger for the more polarizable POMs, $[PW_{12}]^{3-}$ compared to $[SiW_{12}]^{4-}$ or other larger POM nanoions such as DAWSON type of polyoxometalates i.e. following the POM's charge density.[46] It was proposed that the driving force of the adsorption of POMs mainly originates from the gain of entropy brought about by the release of several hydration water molecules in the bulk. Indeed, a partial dehydration of both the POMs and the surface polar heads is expected along with the adsorption of POMs at the micelle surface.

Table 1. Micellization parameters at 23°C of C_8G_1 and C_8E_4 in water or in brine with various $[SiW_{12}]^{4-}$ or $[PW_{12}]^{3-}$ concentrations: CMC and surface tension at CMC.

Solvent (medium)		C_8G_1		C_8E_4	
	$\gamma_{solvent}$ /mN·m^{-1}	CMC /mM	γ_{CMC} /mN·m^{-1}	CMC /mM	γ_{CMC} /mN·m^{-1}
H_2O	72,6	27.6	30.5	9.2	29.9
100 mM NaCl	72.3	25.7	32.0	7.5	28.0
100 mM NaCl +10 mM $[SiW_{12}]^{4-}$		23.5	34.5	3.2	32.6
5 mM $[SiW_{12}]^{4-}$	72.5	29.4	32.3	5.9	32.1
10 mM $[SiW_{12}]^{4-}$	72.6	30.1	34.1	4.5	34.3
25 mM $[SiW_{12}]^{4-}$	69.3	31.5	35.4	4.7	35.2
2 mM $[PW_{12}]^{3-}$	72.2	20.2	36.3		
5 mM $[PW_{12}]^{3-}$	72.0	14.8	37.9		
10 mM $[PW_{12}]^{3-}$	71.2	11.0	39.7		
25 mM $[PW_{12}]^{3-}$	70.1	11.0	39.0		

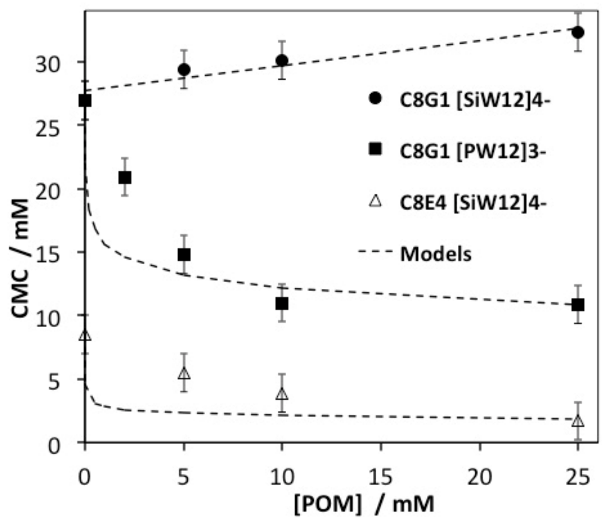

Figure 2. CMCs' variation as a function of POM concentration in water for the three couples $C_8G_1/[SiW_{12}]^{4-}$, $C_8G_1/[PW_{12}]^{3-}$ and $C_8E_4/[SiW_{12}]^{4-}$. Dashed lines correspond to the thermodynamic model presented later in the document.

The effect of the addition of POMs on the CMC is significant compared to the effect of classical salts.[47-48] Moreover, the CMC either increases with POM concentration, as for the $C_8G_1/[SiW_{12}]^{4-}$ couple or decreases for $C_8G_1/[PW_{12}]^{3-}$ and $C_8E_4/[SiW_{12}]^{4-}$ couples respectively, as observed in Fig. 2. This significant effect of POMs could be related to their super-chaotropic character or super "salting-in" property.

In the following section an explanation is proposed for the different effects of the addition of $[SiW_{12}]^{4-}$ and $[PW_{12}]^{3-}$ on the CMC of C_8G_1 and C_8E_4 using a thermodynamic approach based on the pseudo-phase model and thanks to a statistical mechanic calculation to determine the ΔG of POM adsorption onto the micelles.

B) Phase equilibrium model in micellar solutions of non-ionic surfactants in the presence of POMs.

The well-known pseudo-phase (see SI. 1) is used to describe the system as follows.[49] This model is generally considered to be valid at high aggregation numbers. In our case, the latter is between 25 to 45, depending on the adsorbed POMs. Thus pseudo-phase is a valid approximation as in that case, straightforward calculations show that the error on the Gibbs energy is around 1.3 % when the aggregation number is 30. Moreover, it has the big advantage that it does not depend on the aggregation number so that only one fitted parameter by equilibria is required.

As shown in Fig.2, we have observed two different behaviors for the CMC variation versus POMs concentration. We already know that two POMs studied here are adsorbed at the micelle surface of both surfactants.[15] A CMC increase indicates that the monomer form is stabilized. In order to explain this stabilization, the assumption is made that a fraction of surfactant molecules is not free but associated with POMs despite the fact that we have no direct or indirect evidence of the existence of these POM/monomer association and that the formation of this association is the predominant effect compared to the adsorption on POMs on the micelles. On the opposite, a decrease of the CMC can be explained by a stabilization of the micelles, which suggests that POMs' adsorption onto the micelles becomes the predominant effect compared to the POM/monomer interaction.

Thus, when POMs are added to the system, different species could be considered and the simplest ones are: the monomer m, the POM p, the micelle M, the POM associated with the monomer m_a and the micelle associated with the POM M_a, with respective fractions according the three following equilibria and as sketched in Fig. 3:

$$m \quad \overset{(1)}{\Leftrightarrow} \quad m \text{ in M}$$

the basic equilibrium as already sketched and described in SI. 1.

$$m + p \quad \overset{(2)}{\Leftrightarrow} \quad m_{\mathrm{a}}$$

and

$$m \quad \overset{(3)}{\Leftrightarrow} \quad m \text{ in } \mathrm{M_a}$$

The equilibrium constant K_1^0 of the Equilibrium (1) can be expressed as (See SI. 1):

$$K_1^0 = \frac{1}{c_{\mathrm{m}}} = \mathrm{e}^{-\frac{\mu_{\mathrm{M}}^0 - \mu_{\mathrm{m}}^0}{k_B T}} = \mathrm{e}^{-\frac{\Delta G_{\mathrm{mic}}^0}{k_B T}} \tag{1}$$

Likewise for the Equilibrium (2), we can write the chemical potential equilibrium as:

$$\mu_{\mathrm{m}}^0 + k_B T \ln c_{\mathrm{m}} + \mu_{\mathrm{p}}^0 + k_B T \ln c_{\mathrm{p}} = \mu_{\mathrm{m_a}}^0 + \mathrm{k}_B T \ln c_{\mathrm{m_a}} \tag{2}$$

where c_{p} and $c_{\mathrm{m_a}}$ are the POM concentration and the concentration of monomers associated with POM.

This new equilibrium constant K_2^0 can thus be expressed as:

$$K_2^0 = \frac{c_{\mathrm{m_a}}}{c_{\mathrm{m}} c_{\mathrm{p}}} = \mathrm{e}^{-\frac{\mu_{\mathrm{m_a}}^0 - \mu_{\mathrm{m}}^0 - \mu_{\mathrm{p}}^0}{k_B T}} = \mathrm{e}^{-\frac{\Delta G_{\mathrm{a}}^0}{k_B T}} \tag{3}$$

and depends on the energy of POM/monomer association, ΔG_{a}^0.

For the Equilibrium (3), the equality of the chemical potentials can be expressed as:

$$\mu_{\mathrm{m}}^0 + k_B T \ln c_{\mathrm{m}} = \mu_{\mathrm{M_a}}^0 \tag{4}$$

with the defined equilibrium constant K_3^0 as:

$$K_3^0 = \frac{1}{c_{\mathrm{m}}} = \mathrm{e}^{-\frac{\mu_{\mathrm{M_a}}^0 - \mu_{\mathrm{m}}^0}{k_B T}} = \mathrm{e}^{-\frac{\Delta G_{mic,a}^0}{k_B T}} \tag{5}$$

Equations (1) and (5) are not compatible, as the Equilibrium (1) cannot be present together with Equilibrium (3). In other words, only the most stable micellar aggregates, either the micelles without POMs (Equilibrium 1) or the one with POMs (Equilibrium 3) can be present as a pseudo-phase. Thus, on one hand, if $\mu_{\mathrm{M}}^{0} < \mu_{\mathrm{M_a}}^{0}$, the micelle without POMs is the most stable state for aggregation and Equilibrium (1) and (2) take place according to Eq. (1) and (3). On the other hand, if $\mu_{\mathrm{M}}^{0} > \mu_{\mathrm{M_a}}^{0}$, the micelle with POMs is the most stable pseudo-phase and Equilibrium (3) take place according to Eq. (5).

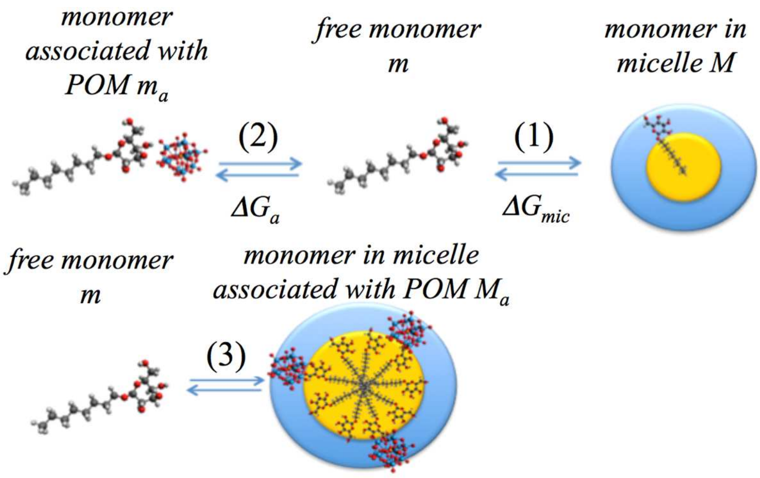

Figure 3. Sketch of the three equilibria of the surfactants taking into account the interaction of POM anions with the non-ionic surfactant in an aqueous medium: the surfactant monomers /micellar aggregation (equilibrium 1), the POM/surfactant association (equilibrium 2) and the surfactant monomers/micellar aggregation taking into account the adsorption of POM onto non-ionic micelles as already observed in reference (equilibrium 3).[15]

First case, the monomers are stabilized by the POMs (C_8G_1/$[SiW_{12}]^{4-}$ system).

In this first case, the association POM-monomer is non negligible and results in an increase of the surfactant solubility and thus of the CMC. From Eq. (1) and (3), we get the concentration of monomers associated with POM:

$$c_{\mathrm{m_a}} = CMC_0 c_{\mathrm{p}} \mathrm{e}^{\frac{-\Delta G_{\mathrm{a}}^{0}}{k_B T}} = \mathrm{c_p} \mathrm{e}^{\frac{-\Delta G_{\mathrm{a}}^{0} + \Delta G_{\mathrm{mic}}^{0}}{k_B T}} \quad (6)$$

with the micellar critical concentration CMC_0 without POM into the system:

$$CMC_0 = \mathrm{e}^{\frac{\Delta G_{\mathrm{mic}}^{0}}{k_B T}} \quad (7)$$

The total concentration of monomers not involved in a micelle reads:

$$CMC = c_m + c_{\mathrm{m_a}} = CMC_0 + c_{\mathrm{m_a}} \quad (8)$$

Then, using Eq. (6), the CMC can be written as:

$$CMC = CMC_0\left(1 + c_\mathrm{p}\mathrm{e}^{\frac{-\Delta G_\mathrm{a}^0}{k_B T}}\right) = CMC_0\left(1 + c_\mathrm{p}K_2^0\right) \qquad (9)$$

Thus, the model predicts a linear increase of the CMC versus the POM concentration in solution. This expression (Eq. 9) can be compared with the experiments if we express CMC as a function of the total POM concentration:

$$[\mathrm{POM}] = c_\mathrm{p} + c_{\mathrm{m_a}} \qquad (10)$$

From Eq. (6) we obtain:

$$[\mathrm{POM}] = c_\mathrm{p}\left(1 + \mathrm{e}^{\frac{-\Delta G_\mathrm{a}^0 + \Delta G_\mathrm{mic}^0}{k_B T}}\right) \qquad (11)$$

and finally

$$CMC = CMC_0\left(1 + [\mathrm{POM}]\frac{K_2^0}{1 + K_2^0 CMC_0}\right) \qquad (12)$$

By fitting in Fig. 2 the CMC variation versus $[SiW_{12}]^{4-}$ concentration for C8G1 system, we obtain:

CMC = 0.196 $[POM]$+27.706 (in mmol.L^{-1}). Then, we deduce ΔG_{mic}^0, ΔG_a^0 and the constant $K_2^0 = \frac{c_{\mathrm{m_a}}}{c_\mathrm{p} c_\mathrm{m}}$ for the equilibrium $m + p = m_\mathrm{a}$ and we find (for details see SI. 2.):

$\Delta G_\mathrm{mic}^0 \approx -9$ kJ.mol^{-1} , $\Delta G_\mathrm{a}^0 \approx -5$ kJ.mol^{-1} and $K_2^0 = 8.8$ L·mol^{-1}, values that indicate a lower Gibbs energy of micellization compared to the basic system without POM[50] but a non negligeable POM/surfactant energy of complex formation.

The association constant can be simply expressed as a function of the proportion α of association of surfactant with POM and the total initial concentration of POM and monomers, c^{init}:

$$K_2^0 = 8{,}8\ \mathrm{L.mol^{-1}} = \frac{\alpha\, c^{init}}{(1-\alpha)\, c^{init}(1-\alpha)\, c^{init}} \qquad (13)$$

If we consider c^{init} = 25 mM, then α = 16 %, which means that about 1/6 of surfactants would be associated with POM for concentrations close to the CMC. Even if the fraction of POM/monomer complexes is weak, it is sufficient to slightly increase the CMC.

Second case, the micelles are stabilized by the POMs ($C_8G_1/[PW_{12}]^{3-}$ and $C_8E_4/[SiW_{12}]^{4-}$ systems).

As mentioned above, a plausible alternative to explain a decrease of the CMC is that POMs adsorption onto the micelle becomes the predominant effect in comparison to the

POM/monomer dimeric complex, which is negligible here. $\mu_{M_a}^0$ is now lower than μ_M^0. Thus only Equilibria (3) has to be considered:

$$m \overset{(3)}{\Leftrightarrow} m \text{ in } \mathrm{M_a}$$

and characterized by the equilibrium constant K_3^0 that depends on the free energy of micellization ($\Delta G_{\mathrm{mic,a}}^0$) with POMs. Due to the charges of the POMs adsorbed onto the micelles, the previous method based on the equilibrium between the species cannot be solely applied and an approach based on the specific calculation of the free energy of micellization ($\Delta G_{\mathrm{mic,a}}^0$) with POMs has to be used by establishing a lateral equation of state (EOS).[51-57] This equation quantifies the different interactions between the surfactant heads within the aggregates (whatever their shape) and also the interactions between the charged adsorbed species (POMs) onto the micelles. For a non-ionic micellar system without POMs, the total free energy of micellization ($\Delta G_{\mathrm{mic}}^0$) is considered to be the sum of two terms that represents i) the hydrocarbon-water free energy, proportional to the water/alkane surface tension γ and ii) the short-range steric repulsion energy of the surfactant head groups, inversely proportional to the variation of the polar head surfaces $(a - a_0)$.

Expressed here per mole of surfactant, the free energy of micellization without POM is usually described by the eq. (14) as followed:

$$\Delta G_{\mathrm{mic}}^0 = F_{\mathrm{L}/\mathrm{W}} + F_{\mathrm{head-rep}} = \gamma(a - a_0) + \frac{c}{\mathrm{a - a_0}} \qquad (14)$$

with a_0 is the minimal head group area and which is fixed, from pure steric considerations, at 0.36 nm^2 for C_8G_1 and 0.23 nm^2 for C_8E_4. We assume that the aggregation numbers, the size parameter and the surface tension do not depend on the POMs. Experimentally, the dependence is actually weak and steric effects only slightly depend on the surrounded associations.

The factor c is calculated in the absence of POMs when the function is minimal thus with $c = \gamma(\mathrm{a - a_0})^2$ with a the surface per polar head within the micelles taken from literature and fixed at 0.49 nm^2 for C_8G_1 and 0.45 nm^2 for C_8E_4.[34, 58]

In the presence of POMs, an additional contribution to the free energy is considered that can be split into two terms and accounts for (i) the adsorption process of the POM, $\left(\frac{F_{\mathrm{ads}}}{N_{\mathrm{agg}}}\right)$ and (ii) the repulsions between the POMs adsorbed onto the micelles, $\left(\frac{F_{\mathrm{elec}}}{N_{\mathrm{agg}}}\right)$. N_{agg} is the aggregation number which have to be taken into account to model the curvature of the system (N_{agg} C_8G_1 = 25 to 45 and N_{agg} C_8E_4 =33 as obtained for a spherical model in presence of POMs[15]) :

$$\Delta G^0_{\text{mic,a}} = F_{\text{L}/\text{W}} + F_{\text{head-rep}} + \frac{(F_{\text{ads}}+F_{\text{elec}})}{N_{\text{agg}}} \quad (15)$$

The first contribution related to the POM adsorption onto the micelle can be written as

$$F_{\text{ads}} = N_{\text{ads}}(\Delta G_{\text{ads}} - k_B T \ln C^*_{\text{POM}}) \quad (16)$$

where ΔG_{ads} denotes the variation of the Gibbs energy for one POM during the adsorption. C^*_{POM} is the POM concentration in the solvent.

For the second term, F_{elec} explicitly stands for the electrostatic energy of the ions adsorbed to the surface and can be expressed as:[57]

$$F_{\text{elec}} = \frac{(\text{z}e)^2 {N_{\text{ads}}}^2}{8\pi\varepsilon_0\varepsilon_\text{r} R_{\text{coll}}} \quad (17)$$

with z = 3 or 4 the charge number of the POM, e the elementary charge, ε_0 and ε_r the vacuum and relative permittivities of the solvent, respectively. R_{coll} is the radius of the micelle ($4\pi {R_{\text{coll}}}^2 = \text{a}N_{\text{agg}}$) and N_{ads} is the average number of adsorbed POMs onto the micelles.

For the electrostatic formula, eq. (17), we should consider that the charges onto the micelle are uniformly distributed and that no correlation between the adsorbed ions is explicitly taken into account. This assumption remains valid when the ion adsorption is strong enough and when their distribution can be considered as a uniform shell of charges around the aggregates. However, in our case the number of POMs adsorbed is rather low (typically between 4 and 7 [15]) so that charge correlations have to be taken into account for ε_r (for details see SI. 3).

Finally the total free energy of micellization with POM adsorbed onto micelles can be written as:

$$\Delta G^0_{\text{mic,a}} = \gamma(a - a_0) + \frac{c}{a-a_0} + \frac{\left(\frac{(ze)^2 {N_{\text{ads}}}^2}{8\pi\varepsilon_0\varepsilon_\text{r} R_{\text{coll}}} + N_{\text{ads}}(\Delta G_{\text{ads}} - k_B T \ln C^*_{\text{POM}})\right)}{N_{\text{agg}}} \quad (18)$$

This total free energy is minimized versus N_{ads} and a in two steps (for details see SI. 4).

From previous fitting of SAXS spectra,[15] the ratio [surfactant]/[POM] on the micelle was estimated to be 4.3 ($3 < N_{\text{ads}} < 6$ roughly depending on N_{agg} and the POMs concentration) for a solution of C_8G_1 with of $[PW_{12}]^{3-}$ and 5.3 ($4 < N_{agg} < 6$) for a solution of C_8E_4 with $[SiW_{12}]^{4-}$.

ΔG_{ads} has been fitted to find a value for N_{ads} close to the experimental value for the same POM concentrations (10 mM).

The first minimization $\frac{\mathrm{d}\Delta G^0_{\text{mic}}}{\mathrm{d}N_{\text{ads}}} = 0$ (see Fig. S4 in SI. 4) leads to:

$$N_{\text{ads}} = \frac{(k_B T \ln C^*_{\text{POM}} - \Delta G_{\text{ads}}) 4\pi\varepsilon_0\varepsilon_r R_{\text{coll}}}{(ze)^2} \quad (19)$$

Taking into account the results of the first step minimization, $\Delta G^0_{\text{mic,a}}$ can be expressed now as follows:

$$\Delta G^0_{\text{mic,a}} = \gamma(\mathrm{a} - \mathrm{a}_0) + \frac{C}{\mathrm{a}-\mathrm{a}_0} - \delta\sqrt{\mathrm{a}} \quad (20)$$

$$\text{with } \delta = \frac{k_B T\left(\ln C^*_{\text{POM}} - \frac{\Delta G_{\text{ads}}}{k_B T}\right)^2}{4L_B\sqrt{N_{\text{agg}}}\pi \mathrm{z}^2} \quad (21)$$

The second step of $\Delta G^0_{\text{mic,a}}$ minimization versus *a* was obtained by the Newton Raphson method (for details see SI. 4) and makes it possible to get its minimum value at each POM's concentration as well as the micellar characteristics i.e the N_{agg} and *a*, the surface per polar head.

We found ΔG_{ads} to be -16 k_BT and -22 k_BT for $C_8G_1/[PW_{12}]^{3-}$ and $C_8E_4/[SiW_{12}]^{4-}$ respectively (see dotted lines in Fig. S5 in SI. 5). These values cannot be compared directly as they concern two different POMs adsorbed on different surfactant molecules. Nevertheless, these values confirm the strong interaction of the POM with the polar interface of the non-ionic micelles, whether the sugar heads or the EO chains. The ΔG_{ads} values may appear rather high but are not so surprising when we consider some recent results concerning the POM crystal formation in aqueous phase using EO oligomers.[59] Indeed, EO oligomers/POM crystals can be formed spontaneously at low concentration and increasing the ionic strength, which imply strong attractive interactions between both species in solution. The adsorption of a polarizable anion on a polar surface implies that a few water molecules are released from the hydration shells of both the surface and the ion.[60] This partial dehydration process has an enthalpy cost which is higher for small salting-out anions compared to large salting-in or chaotropic anions of low charge density. Moreover, the entropy gain associated to the release of many water molecules into the bulk phase is supposed to be prominent over the enthalpy cost for POMs, owing to their large size and large water shell. $[PW_{12}]^{3-}$ anion is then expected to interact more strongly than $[SiW_{12}]^{4-}$ with the surface of non-ionic micelles that are highly hydrated. This adsorption mechanism stabilizes the micelles and results in a decrease of the CMC. This effect is stronger when the POM is adsorbed into the hydrated micellar shell with the release of a large number of water molecules, as for the $C_8E_4/[SiW_{12}]^{4-}$ system with a ΔG_{ads} of -22 k_BT (as the polyethoxylated chains are more hydrated that the sugar heads). This interaction can even be so strong that POM may become a "sticky anchorage" between two micelles leading to the formation of a coacervate[30] or a demixion as observed in the case of $C_8E_4/[PW_{12}]^{3-}$ system. On the other hand, the lower ΔG_{ads} value obtained for the $C_8G_1/[PW_{12}]^{3-}$ system can be explained by the (rigid) sugar head that prevents the penetration of $[PW_{12}]^{3-}$ in the polar corona of the C_8G_1 micelle. This model does not take into account that the aggregation number can vary as a function of number of adsorbed POM. However, to check this effect, it will require synchrotron radiation to exploit weak scattering data at the CMC.

CONCLUSION

In this study, we have shown that the variation of the non-ionic surfactant CMC in presence of Keggin POM can be positive or negative as a function of the choice of the polar head/POM couple. Indeed, we observe either a stabilization of the micelle for $C_8G_1/[PW_{12}]^{3-}$ and $C_8E_4/[SiW_{12}]^{4-}$ system, a stabilization of the monomeric form for $C_8G_1/[SiW_{12}]^{4-}$ and even a coacervate for $C_8E_4/[PW_{12}]^{3-}$. Thermodynamic approaches were used to quantitatively describe the CMC increase and decrease. A classical pseudo-phase model was used when the surfactant monomer form was stabilized (CMC increase) whereas a lateral equation of state was applied when the POM adsorption onto the micelles was the dominant effect (CMC decrease). This work contributes to the general understanding of the non-electrostatic interactions taking place in water between POMs and non-ionic amphiphilic molecules and can be extended to different kinds of hydrophilic surfaces or interfaces. It represents a keystone for the future development of innovative materials with original nanostructures and functional properties. Considering also that polyoxometalates (POMs) have been previously investigated for their antimicrobial, anti-tumoral properties,[61-64] to prevent amyloid plaque formation[5, 65] and more generally to adsorb on phospholipid membranes,[66-68] this work will help to understand their physicochemical properties in a biological medium.

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Notes

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SUPPORTING INFORMATION

Supporting Information Available: The following information is given in the supplementary file: description of the monomer micelle equilibrium using the pseudo phase model; determination of $\Delta\mathrm{G}^0_{\mathrm{mic}}$, $\Delta\mathrm{G}^0_{\mathrm{a}}$ and the constant K_2^0 for the $C_8G_1/[SiW_{12}]^{4-}$ system; determination of ε_{r} and electrostatic energy for a number of POMs adsorbed on the micelle; first minimization of $\Delta G^0_{\mathrm{mic,a}}$ as a function of N_{ads}; second minimization of $\Delta G^0_{\mathrm{mic,a}}$ as a function of a .

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