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Acidic surfactant solutions for tributylphosphate removal in nuclear fuel reprocessing plants: A formulation study

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ABSTRACT

The removal of tributylphosphate (TBP), an organic solvent widely used as a complexing agent for uranium and plutonium in nuclear plants, was investigated to understand and adapt the mechanisms involved in TBP detachment and solubilization in acidic surfactant solutions. Two well-known degreasing mechanisms, roll-up and emulsification, should be combined for maximum effect. These mechanisms were characterized with a CCD camera to measure contact angles between a solid substrate and a liquid drop. We measured the contact angles of a TBP drop deposited on a stainless steel plate immersed in an acidic surfactant solution, and quantified the amount of TBP solubilized in the micelles by turbidity measurements. Preliminary results of micelle size characterization by dynamic light scattering are presented. We formulated new acidic surfactant solutions associating two industrial surfactants, Pluronic P123 and Rewopal X1207L, with improvement factors in various fields (total organic matter content, oil detachment and solubilization efficiency, emulsion stability, etc.).

1. Introduction

In the coming decades the nuclear industry will have to meet the major challenge of dismantling the first-generation nuclear plants. This article focuses on nuclear fuel reprocessing plants. The contamination possibly present in these plants is caused by an organic solvent tributylphosphate (TBP), used in the Purex® process as a uranium and plutonium complexing agent. TBP exhibits high affinity for metal surfaces, and thus adheres to every stainless steel device, such as the vessels used in the Purex process in the UP2-400 plant at La Hague (France).

In this case, decontamination consists in rinsing the installations to remove the radioactive elements with the effluent. The rinsing solutions should contain surfactants, molecules operating at solid/liquid interfaces and able to detach the radioactive TBP from stainless steel surfaces. Surfactant solutions used in nuclear applications are subject to several limitations. As these solutions become nuclear waste, they are subject to special requirements. For example, the total organic concentration (surfactants) is limited to 1 wt%. Moreover, counterions such as Na^+, Cl^- or Br^- are not suitable for the nuclear waste conditioning in a glass matrix. This led us to choose nonionic surfactants as active molecules; otherwise, surfactant solutions must be prepared in acidic media to avoid plutonium and uranium hydroxide precipitation, which occurs when the pH becomes slightly basic. These requirements are, therefore, directly driven by the nuclear application.

The first studies concerning the use of acidic surfactant solutions as decontamination media were carried out in 2004 [1]. The authors concluded that nitric acid was the best solution with an optimum concentration of up to 0.5 mol/L. They also showed that the process was practicable at industrial scale. Their solution was an association of two industrial surfactants, Rewopal X1207L and Antarox FM33 with a total concentration of 1 wt% with a RewopalX1207L/Antarox FM33 ratio of 4:1. This formulation was defined as the reference solution (RS).

This paper deals with understanding the mechanisms involved in degreasing phenomena and the improvement brought by formulation science.

2. Degreasing phenomenon

A simplified model describes degreasing of liquid contamination in two separate stages. The oil is first detached from the surface, then the organic solvent molecules solubilize throughout the micelles of surfactant solution. The actual process is much more complicated with the simultaneous progress of these two steps

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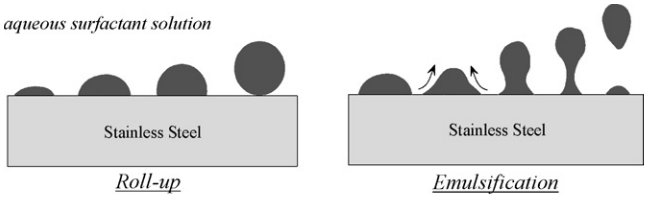

Fig. 1. Mechanisms of oil detachment from a solid surface under surfactant solution action.

[2]. However, in this study each step in the phenomenon was analyzed using different techniques to assess the effect of the solution formulation on both stages.

Oil detachment can follow different mechanisms. The two main ones, roll-up and emulsification, are well known and depend on the structure of the surfactant used in the formulation. The first occurs when a surfactant with high-wetting power is used (Fig. 1), and the second is indicative of a surfactant with high-emulsifying power. The differences observed between these mechanisms are attributable to the preferred location of surfactant adsorption in the three-phase system. The equilibrium contact angle θ of an organic liquid drop deposited on a substrate surface and immersed in an aqueous surfactant solution is given by Young's equation (1).

$$\cos\,\theta = \frac{\gamma_{\mathrm{ws}} - \gamma_{\mathrm{os}}}{\gamma_{\mathrm{wo}}} \tag{1}$$

where γ_{ws}, γ_{os} and γ_{wo} are the interfacial tensions between water and substrate, oil drop and substrate, water and oil drop, respectively.

The roll-up process requires surfactants with high-wetting power. Such molecules preferentially lower the water/substrate interfacial tension γ_{ws}, ensuring better wetting by the aqueous solution and allowing the surfactant solution to spread over the solid surface. This tends to reduce the contact line between the oil drop and the solid substrate. Consequently, the oil drop dewets the surface and $\cos\theta$ decreases, as shown by relation (1). In this case, the drop detaches spontaneously and no oil remains on the solid surface.

Conversely, oil removal by emulsification requires a surfactant with high-emulsifying power that preferentially adsorbs on the oil/water interface [3]. The combined effect of this adsorption and oil buoyancy provokes a cohesive break into the drop, removing part of the drop from the surface. In this case, a small amount of oily soil remains on the solid surface. The removal, solubilization and transport of the soil in the surfactant solution is easier than in the roll-up process, but degreasing is not complete.

Once the oil has been removed from the solid support, it must be solubilized in the surfactant solution to facilitate elimination. This second degreasing step requires the surfactant to be in its self-associating form. These aggregate surfactant forms, or micelles, are capable of sequestering organic molecules in aqueous media. The surfactant concentration must be higher than the critical micelle concentration (cmc) for solubilization to occur. Emulsifying surfactants are more efficient for this stage because of their adsorption at the oil/water interface.

The surfactant type, therefore, very significant affects the degreasing efficiency. The active molecules must be chosen with regard to the nature of the oil and solid substrate. Surface cleaning processes require both wetting and emulsifying power to obtain the best results [4]. Maximum degreasing efficiency is obtained with the association of high-wetting and high-emulsifying power surfactants. This paper summarizes the studies carried out to identify the surfactants best capable of emulsifying TBP and of wetting stainless steel with the objective of improving the reference solution (RS) developed in the past without formulation studies.

3. Materials and methods

Aqueous surfactant solutions were all prepared in 0.5 mol/L nitric acid. The water used for sample dissolution was first deionized. Surfactant materials were industrial samples provided by vendors: Pluronics® P123 and P84 synthesized by BASF Corp., Antarox FM33® by Rhôdia, and Rewopal X1207L® or Ifralan B1286® by Ifrachimie (ex-Witco). The trade name of Rewopal X1207L has changed with the name of the company. They are all nonionic polyoxyethylenated surfactants. The hydrophilic part of the molecules consists of polyethylene oxide (PEO) polymer chains, and the hydrophobic part comprises alkyl chains for Rewopal X1207L, polypropylene oxide (PPO) chains for Pluronic type surfactants, and both chains for Antarox FM33. Industrial surfactants must be used to ensure availability for large-scale operation.

In order to make sure that all the stainless steel plates exhibited the same surface state, the metal was corroded in an oxidizing solution (0.11 mol/L $\mathrm{Ce^{IV+}}$; 3 mol/L $\mathrm{HNO_3}$) for 4 h and then abundantly rinsed with deionized water.

3.1. Contact angle measurements

Fig. 2 shows a schematic description of the experimental setup (Digidrop by GBX) allowing us to measure TBP detachment kinetics from a stainless steel plate. The classical sessile drop method was used, with data acquisition by a goniometer to record the contact angles. First, a TBP drop was deposited on the solid substrate with a microsyringe. The metal plate was then immersed in a surfactant solution to measure the oil detachment kinetics and plot the kinetic curves $\theta = f(t)$. At $t = 0$ s, the plate was immersed in the solution and $\theta = 0^\circ$ because of the affinity of TBP for stainless steel. The TBP/stainless steel contact angle θ increased with time. Degreasing was considered "effective" when θ reached a minimum of 90°.

This technique was also used to classify the surfactants according to the degreasing mechanism involved. A CCD camera was used to observe the TBP drop shape during removal so that simple image analysis can conclude whether a surfactant is high-wetting or high-emulsifying.

3.2. TBP/"aqueous solution" interfacial tension

The interfacial tension between TBP and aqueous surfactant solutions was determined using a Krüss K12 tensiometer equipped with a platinum–iridium DuNoüy ring. TBP (14 mL) was added to the surfactant solution (14 mL) 24 h before the measurement. After 24 h under steady-state conditions, the repeatability of the interfacial tension values indicated that equilibrium had been reached.

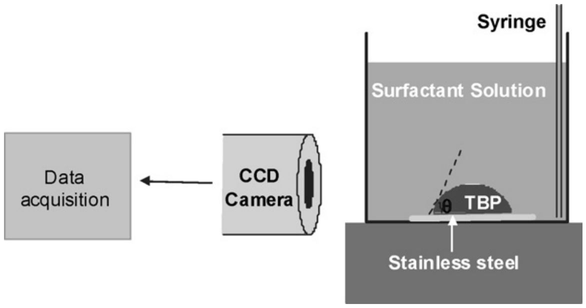

Fig. 2. Experimental setup for the measurement of TBP detachment kinetics.

3.3. *Turbidity measurements*

Light scattering was used to quantify the total amount of TBP sequestered in the micelles and to analyze the stability of the emulsions created when the TBP concentration was much higher. When TBP molecules penetrated into surfactant micelles, the system remained monophasic, optically clear until a concentration limit was reached ($C_{(TBP)MAX}$). At TBP concentrations exceeding $C_{(TBP)MAX}$, the system became diphasic, cloudy. From this concentration, the dispersion was an emulsion. The dispersed objects were no longer nanometric swollen micelles, but micrometric oil drops stabilized by surfactants. Whereas solutions containing swollen micelles are stable, emulsions are unstable and subject to phase separation. The time necessary for the system to reach phase separation depended on the oil drop size and the type of surfactant.

$C_{(TBP)MAX}$ could be identified by light scattering analysis, because light is fully scattered throughout the solution in a cloudy system. A "spectrode" electrode emitted a beam of light and analyzed the light scattering ratio in the solution as TBP was added in the vessel.

3.4. *Dynamic light scattering (DLS)*

This scattering technique was used to assess the size increase of micelles with different amounts of TBP. DLS was performed at 298 K using a Malvern Zetasizer NanoZS instrument, fitted with a 532 nm laser at a fixed scattering angle of 90°. The surfactant micellar solutions were adjusted with a suitable quantity of TBP and filtered through a 0.45 μm cellulose membrane filter before analysis. An average micelle size distribution was determined using the program CONTIN (Provencher) [5].

4. Results and discussion

Table 1 presents some physico-chemical properties at 298 K and the structures of the surfactants used in this study. The critical micellar concentration and the surface tension at 1 and 0.1 wt% are listed for the four industrial surfactants and for the reference solution (80/20 Rewopal X1207L/Antarox FM33 at 1 wt%). In this table, exceptionally, the surfactants are considered in pure water without nitric acid so that comparison is possible with prior studies, including numerous papers by Alexandridis concerning Pluronics [6–9]. Each subsequent solution contained 0.5 mol/L of nitric acid.

4.1. *Reference solution (RS) degreasing performance evaluation*

Surface tension values provide information about the wetting power of aqueous surfactant solutions. Generally, the more the surfactants decrease the surface tension, the more the aqueous solutions will spread onto the solid surface. Table 1 shows that the two surfactants in the reference solution are high-wetting power surfactants. Originally, Antarox FM33 was chosen as a wetting surfactant and Rewopal X1207L as an emulsifying surfactant on the basis of property descriptions on vendor datasheets.

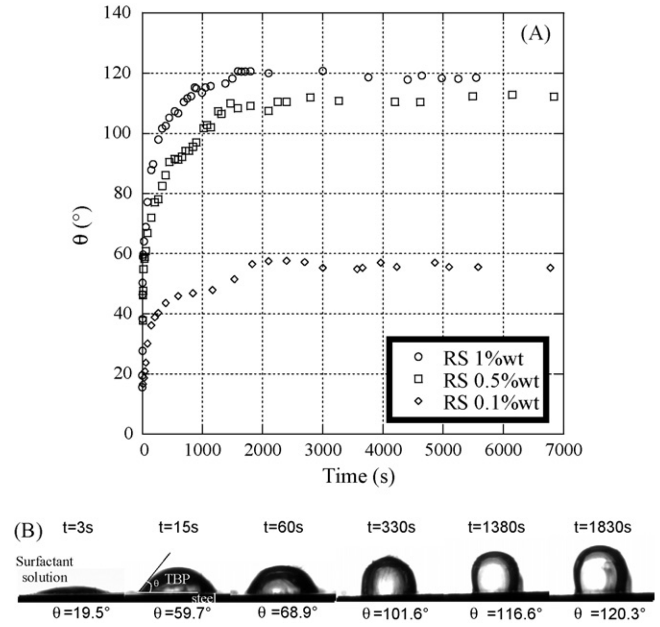

Fig. 3. (A) Degreasing kinetics of a TBP drop for various concentrations of reference solutions (RS) at 298 K; (B) roll-up phenomenon for RS, 1 wt% and 298 K.

Fig. 3A shows the TBP degreasing kinetics obtained with the reference solution at various concentrations. It appears that the long-term angle (θ_{eq}) is directly related to the oil detachment efficiency of each solution. The time necessary to reach equilibrium is quite short, around 2000 s, and is independent of the solution concentration. The two more concentrated solutions exhibit better degreasing power with θ_{eq} exceeding 90°, up to 120° and 110°, respectively, for the 1 and 0.5 wt% solutions. These results are quite positive as experimental conditions driven by an industrial approach are unfavorable. Several studies have examined oil detachment from solid surfaces in the past. The solid substrates considered included silica [10], gold [11], or glass [12,13]. For a stainless steel surface, the results are different whether the surfactant used is ionic or nonionic. Anionic, zwitterionic and nonionic surfactants proved to be more effective cleaners at high pH, whereas cationic surfactants are most effective at low pH [14–16]. At low pH, the stainless steel surface is positively charged, and the most favorable case to optimize oil drop detachment is to provide an oil/water interface presenting the same charge, using cationic surfactants. Because nonionic polyoxyethylenated surfactants like Triton X-100 [14] maintain a slightly negative charge at low pH, optimal oil detachment cannot be obtained with HNO_3 concentrations up to 0.5 M.

Fig. 3B shows the roll-up phenomenon observed with 1 wt% RS. The solution being prepared with two wetting surfactants, "roll-up" is the expected degreasing mechanism. At $t = 1830$ s, the TBP drop is almost totally detached with a contact angle equal to 120.3°. The drop does not detach spontaneously owing to the too small difference in density between the surfactant solution (~1) and tributylphosphate (0.9727). The buoyancy force is thus too weak compared with gravitation and Van der Waals forces.

Table 1
Physico-chemical properties of the surfactants used in this paper [1,6,7]

Surfactant	Hydrophobic part	Hydrophilic part	CMC (wt%) 298 K	γ (mN/m) 1 wt%, 298 K	γ (mN/m) 0.1 wt%, 298 K
Pluronic P84	$(PPO)_{43}$	$(PEO)_{19}$	2.600	36	40
Pluronic P123	$(PPO)_{70}$	$(PEO)_{20}$	0.030	34	34
Antarox FM33	C_{10} + PPO	(PEO)	0.020	30	30
Rewopal X1207L	C_{11-13}	$(PEO)_{6-15}$	0.023	26	26
Reference solution	–	–	0.100	27	27

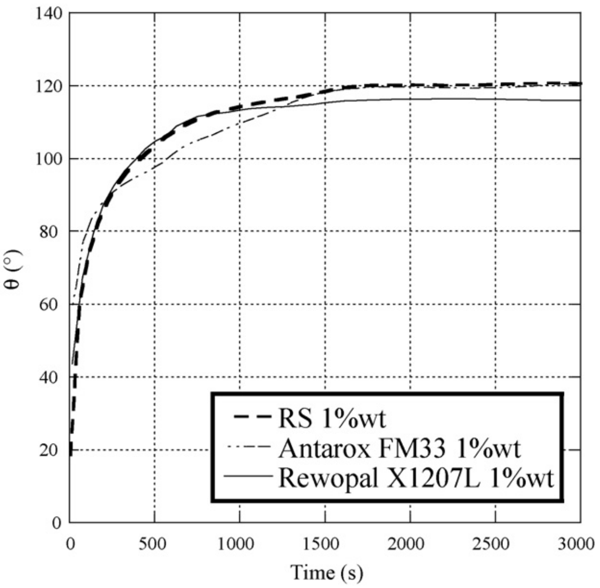

Fig. 4. Degreasing kinetics for the reference solution and each surfactant separately at 298 K.

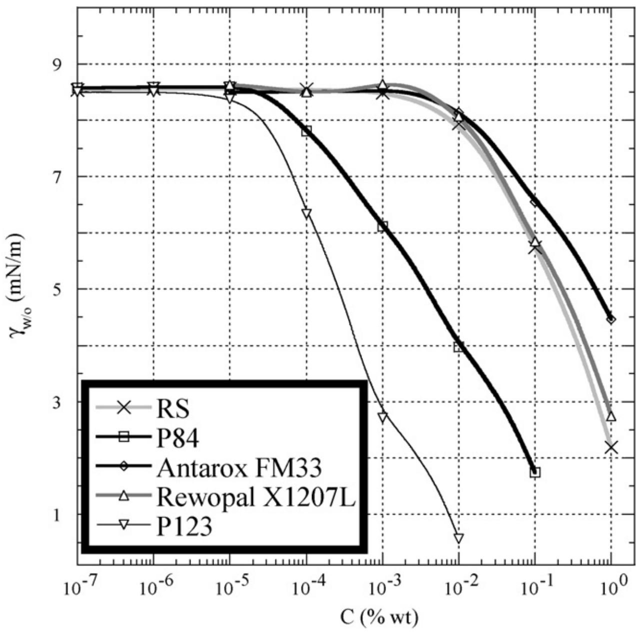

Fig. 5. Interfacial tension values of TBP/water medium line as a function of various surfactant concentration.

Fig. 4 provides a more detailed analysis of the TBP detachment mechanisms by the RS. It shows degreasing kinetics obtained separately with Antarox FM33 and Rewopal X1207L. The curves are quite similar to RS. Antarox FM33 and Rewopal X1207L result in TBP removal by a roll-up mechanism. The timescales are very similar. This result confirms the that both surfactant components of the RS are high-wetting power surfactants favoring roll-up mechanisms. This means RS contains two wetting surfactants with very weak emulsifying power. A formulation improvement would thus involve the use of a specific TBP emulsifying surfactant. Pluronic amphiphilic triblock copolymers are known to emulsify TBP [17,18]. The next section deals with the experiments conducted to assess the high-emulsifying power surfactant most suitable for this application.

4.2. High-emulsifying power surfactants

The technique we used to evidence the emulsifying power of surfactants was to measure the interfacial tension of the TBP/water midline. The more the surfactant lowers the interfacial tension, the more emulsifying it is. Moreover, past studies showed that oily soil removal from a solid substrate is directly related to the oil/water interfacial tension [19]. The authors claimed that removal of oil droplets was easier with low interfacial tension, at a constant contact angle.

Fig. 5 shows the effect of various surfactants on the TBP/water interfacial tension. These values can be compared for a given concentration. For example, Rewopal X1207L is more efficient than Antarox FM33. This mainly explains why suppliers classified it as an emulsifying surfactant. However, for the specific TBP/water/stainless steel system, it acts more like a wetting surfactant and removes TBP by a roll-up mechanism.

Pluronics appear to be more efficient than classical nonionic surfactants such as Antarox FM33 and Rewopal X1207L. For example, the first P123 surfactant molecules at the TBP/water interface are detected for a concentration of approximately 10^{-5} wt%, or about 100 times less concentrated than Antarox FM33 and Rewopal X1207L. Pluronic P84 is also a good TBP emulsifier, but its cmc is too high for all the degreasing process stages (see Table 1). At 1 wt% and 298 K, P84 is not self-associating, but is soluble as free unimers. This form cannot sequester TBP molecules and is unsuitable for TBP elimination. Finally, Pluronic P123 is the emulsifying surfactant most suitable for the TBP degreasing process.

CCD camera analysis confirmed these conclusions. The images (Fig. 6) show the effect of a 1 wt% P123 solution on a TBP drop deposited on a stainless steel plate. The surfactant molecules adsorb onto the TBP/water interface and lower the interfacial tension. The TBP drop is less cohesive, and the organic solvent buoyancy gives rise to the extraction of part of the TBP drop. Here, the slight difference between TBP and aqueous surfactant solutions is sufficient to produce a cohesive break of the TBP drop.

Pluronic P123 was selected as the emulsifying surfactant in a new acidic formulation. As shown in Table 1, the surfactant with

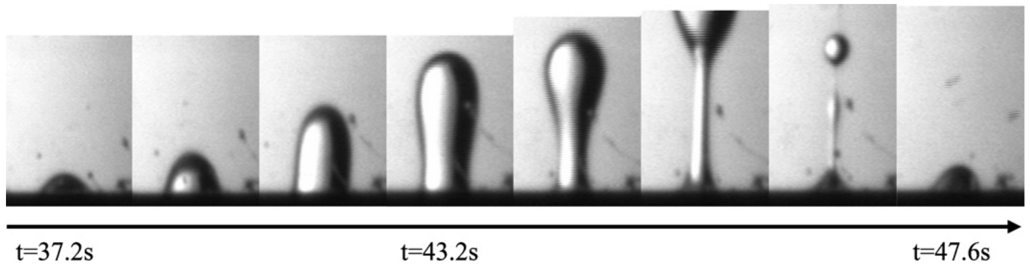

Fig. 6. TBP drop removal by a 1 wt% P123 solution at 298 K—the mechanism involved is emulsification.

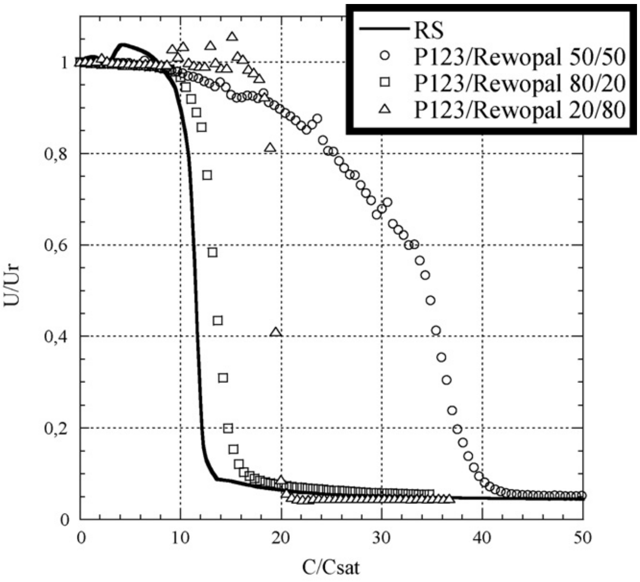

Fig. 7. Turbidity measurements of the acidic surfactant solutions as a function of normalized TBP concentration for various formulations (C = 1 wt%, 298 K).

the lowest surface tension was chosen as the wetting surfactant, hence the association of Pluronic P123 with Rewopal X1207L.

4.3. Association of Pluronic P123 with Rewopal X1207L

Fig. 7 summarizes the turbidity measurements of various acidic surfactant formulations. The Y-axis represents the turbidity index, defined by the ratio between the tension read by the spectrode at a given TBP concentration (U) and the tension when no TBP is present in solution (Ur). When this index is near 1 the system is optically clear and when it is close to 0 the three-phase system is a cloudy emulsion. The X-axis represents the TBP concentration normalized by the maximum TBP concentration in water (1.6×10^{-3} mol/L or 0.4 g/L). The maximal TBP solubilization, $C_{(\mathrm{TBP})\mathrm{MAX}}$, is related to the rough decrease of the curves. All the P123/Rewopal X1207L associations solubilize more TBP than the reference solution: RS solubilizes about 4.8 g/L, and P123/Rewopal X1207L 50/50, 80/20 and 20/80, respectively 14, 6 and 7.6 g/L. This increased efficiency is essentially due to the higher emulsifying properties of the formulations containing Pluronic P123. These curves reveal a synergistic effect at a given P123/Rewopal X1207L ratio. The 50/50 P123/Rewopal X1207L solution is about twice as efficient as the other formulations with 80/20 and 20/80 ratios. These results allow us to envisage much less concentrated solutions with efficiency similar to the reference solution.

Fig. 8A presents turbidity results with 1 wt% RS and 0.5 wt% P123/Rewopal X1207L (50/50). Although the latter system is less concentrated, the solubilized TBP amount is greater. This tendency is very interesting with regard to the industrial process. Indeed, effluent mineralization treatment, following decontamination operations, requires a minimum quantity of organic matter. Effluents are mineralized before final waste conditioning in a glass matrix. A two-fold reduction in the total amount of organic matter would decrease the long and expensive effluent mineralization step.

Moreover, the lower concentration does not result in a major drop in the degreasing kinetics. Fig. 8B indicates the TBP drop removal efficiency of a 0.5 wt% P123/Rewopal X1207L solution. Over short time scales, TBP removal appears to be slower than for the reference solution. This is due to the decreased wetting power of the solution. However, the long-term θ_{eq} value is equivalent to that of 1 wt% Antarox FM33/Rewopal X1207L 20/80, up to 118°. θ_{eq} is the most suitable value for degreasing solutions in an industrial approach. Indeed, the process involves static surfactant solution baths of several hours to remove TBP. The extended time behavior is, therefore, more representative of the industrial context.

Finally, this formulation study demonstrates the remarkable properties of the 50/50 P123/Rewopal X1207L solution. The degreasing behavior is enhanced in every aspect of performance. It is generally acknowledged that nonionic surfactants have little or no interaction with nonionic polymers [20,21]. Indeed, synergistic phenomena between surfactants and nonionic polymers often occur with ionic ones. Couderc-Azouani et al. studied strong interactions between anionic sodium dodecyl sulfate (SDS) and Pluronic L64 [22]. The authors described the formation of supramolecular aggregates constituted by SDS micelles surrounded by four L64 molecules, for a sufficient SDS concentration. However, they also evidenced uncommon interactions between nonionic surfactant, $C_{12}EO_6$ or hexaethylene glycol mono-n-dodecyl ether, and nonionic copolymer Pluronic L64. Whereas L64/SDS system formed special aggregates, L64/$C_{12}EO_6$ presented mixed micelles with strong interactions between the surfactants in all the concentration ranges investigated. Other studies showed synergistic interactions between Pluronic F127 and $C_{12}EO_6$ [23]. The decrease of the cmc of the mixture below the cmc of the single systems indicated sta-

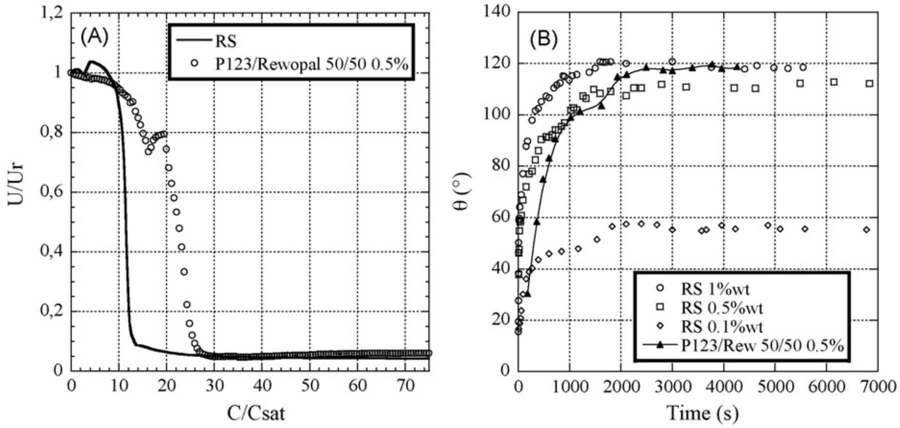

Fig. 8. (A) Turbidity measurements for the 1 wt% reference solution and 0.5 wt% P123/Rewopal X1207L (298 K). (B) Degreasing kinetics of a TBP drop for 0.5 wt% P123/RewopalX1207L 50/50 in comparison with references solutions.

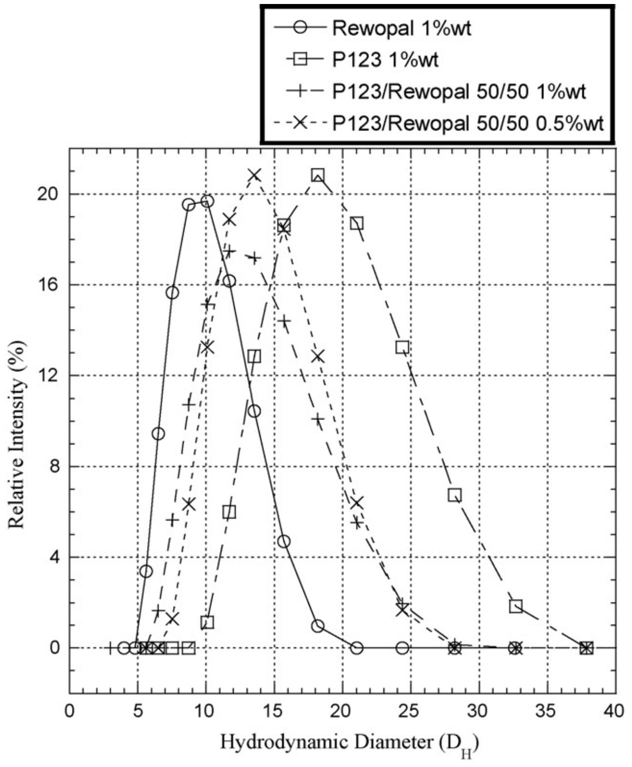

Fig. 9. Hydrodynamic diameter (D_H) distribution for pure and mixed micelles free of TBP.

bilization of the mixed micelles due to the strong interactions taking place between the surfactants. Moreover, the surfactants are assumed to be totally miscible in the mixed micelles, since each hydrated part presents the same ethoxylated chemical structure.

Thus, although nonionic surfactants are generally known not to interact with nonionic polymers, some articles describe strong interactions taking place in specific systems constituted by $C_{12}EO_6$ and a wide range of Pluronics [22–24]. The $C_{12}EO_6$ structure is quite similar to Rewopal X1207L and this synergistic behavior may be extrapolated to our system.

4.4. Swollen TBP micelle size

Dynamic light scattering (DLS) measurements were carried out as a preliminary approach to monitor the hydrodynamic diameter (D_H) of the micelles. Fig. 9 shows that the micelle size of the two-surfactant system is intermediate between those of the single systems. D_H reaches 12.5 nm for the mixed micelles, compared with 9.3 and 18.2 nm for the single systems of Rewopal X1207L and P123, respectively, at 1 wt% and 298 K. Several previous studies gave similar results for the hydrodynamic diameter of P123 micelles in water under different environmental conditions. D_H values of 18 and 19 nm were reported at 298 K [25,26], 17.2 and 18.2 nm at 303 K [27,28], and 20 nm near 313 K [29]. The temperature variation of does not significantly modify the hydrodynamic size of the P123 micelles. However, a temperature rise progressively leads to the dehydration of PEO and PPO moieties [30]. Although PPO is the hydrophobic part of the copolymer, it is known that some water molecules remain in the micelle core, mainly due to the polarity induced by the presence of an O atom [8,31]. Polymer–polymer interactions are facilitated and the aggregation number increases without affecting the hydrodynamic diameter.

Moreover, to the best of our knowledge, only one paper deals with a systematic study of diluted mixed P123/$C_{12}EO_6$ micelles [32]. The authors worked with different molar ratios between P123 and $C_{12}EO_6$. At a similar molar ratio (8.1), our system presents an equivalent hydrodynamic diameter, about 12.5 nm. The smaller mixed micelles could be due to the intercalation of $C_{12}EO_6$ surfactants between Pluronic molecules at the EO/PO interface.

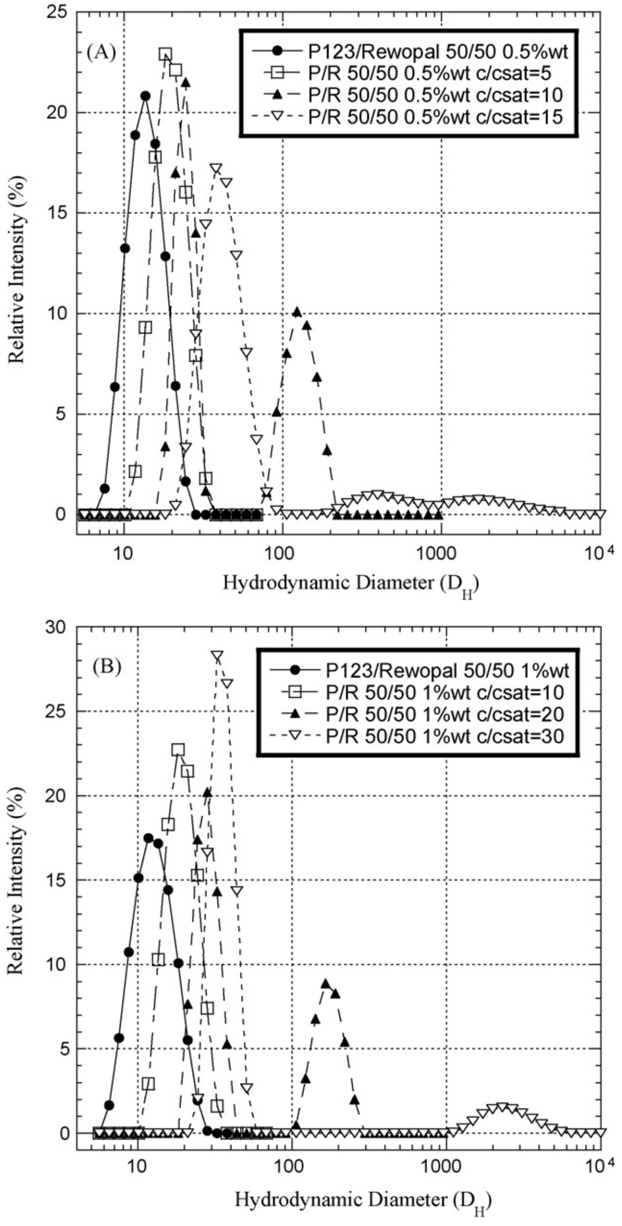

Fig. 10. Hydrodynamic diameter (D_H) distribution for mixed micelles solutions with various concentrations of TBP and surfactants.

Fig. 10 shows the size distribution of mixed micelles swollen by TBP molecules. Two systems are presented to assess the influence of the amphiphile concentration. The results are listed in Table 2.

Comparative experiments were carried out with a 1% P123/Rewopal X1207L solution at given concentrations of TBP (C/C_{sat} = 10, 20, 30) and a twice diluted 0.5 wt% P123/Rewopal 1207L (C/C_{sat} = 5, 10, 15). Dilution does not appear to have a significant effect on the micelle hydrodynamic sizes. For the samples with lower TBP concentrations the micelle diameter reaches 19.5 and 19.6 nm, respectively, for 1 wt% (C/C_{sat} = 10) and 0.5 wt% (C/C_{sat} = 5). Thus, the micelle size remains constant but the number of micelles decreases with dilution. The geometric arrangement of the micelles

Table 2
Evolution of hydrodynamic diameter (D_H) of mixed P123/Rewopal X1207 (or P/R) micelles with TBP content

Solution	D_H (nm) population 1	D_H (nm) population 2
P123 (P) 1%	18.2	-
Rewopal X1207L (R) 1%	9.3	-
P/R 50/50 1% C/Csat=0	12.5	-
P/R 50/50 1% C/Csat=10	19.5	-
P/R 50/50 1% C/Csat=20	27.3	164.2
P/R 50/50 1% C/Csat=30	34.6	Broad around 2μm
P/R 50/50 0.5% C/Csat=0	13.5	-
P/R 50/50 0.5% C/Csat=5	19.6	-
P/R 50/50 0.5% C/Csat=10	23.2	122.4
P/R 50/50 0.5% C/Csat=15	40.5	Broad around 1μm

is identical for these two samples, with the TBP equally distributed within the surfactant aggregates. The more concentrated samples present results of the same order, although the constant size with dilution is not so marked. This is probably due to the multiple sizes evidenced at these concentrations. This tends to render the correlation data more difficult to analyze with a single-angle apparatus. To conclude on the multiple-size analysis, a sharper technique such as small-angle neutron scattering (SANS) is required [33].

Moreover, the micelle size increases with addition of TBP, regardless of the dilution. The systems with higher TBP concentrations present micelle hydrodynamic radii up to three times larger than systems free of TBP. The volume increase, therefore, reaches 27. This capacity to extend the inner volume of the micelles to accommodate TBP molecules allows this formulation with a specific P123/Rewopal X1207L ratio of 50/50 to solubilize the organic solvent up to 14 g/L.

5. Conclusion

This paper shows the role of detergent formulation in nitric acid media for removal of oily tributylphosphate from metallic solid surfaces. The various techniques used highlight the necessity of adapting the surfactant composition and mixture to the targeted contamination. The selection of a molecule specifically adsorbing on the oil/water interface is crucial. This influences the oil removal mechanism and TBP solubilization in the surfactant micelles. An amphiphilic triblock copolymer known as Pluronic P123 was shown to favor maximum surfactant adsorption on TBP/water. This molecule was, therefore, included in a new formulation specifically for TBP removal (P123/Rewopal X1207L 50/50). The higher efficiency allowed us to reduce the surfactant concentration, and thus the total organic matter present in the waste effluent. The surfactant concentration was lowered from 1 to 0.5 wt%. This progress is very significant with regard to the final waste conditioning in a glass matrix.

Moreover, the stability of emulsions prepared with an excess TBP phase is enhanced by the physico-chemical properties of Pluronic P123 (results not shown in this paper). A TBP-rich phase possibly containing uranium and plutonium may lead to safety problems. High emulsion stability is, therefore, required to avoid phase separation and to ensure safety during the cleaning process. A 10 g/L ($C/C_{sat} = 25$) TBP-rich solution remains stable for several months when the surfactant solution is 50/50 P123/Rewopal X1207L at 0.5 wt%; the solution remains cloudy throughout the experiment. Conversely, when the surfactant solution is RS, the solution reverts to a two-phase system after only 10 h. This result is attributable to the high stability of the TBP/water interface through the presence of P123 in the new formulation.

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