Research article

Use of aqueous two-phase PEG-salt systems for the removal of anionic surfactant from effluents

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A R T I C L E   I N F O

A B S T R A C T

Linear alkylbenzene sulfonates (LAS) are synthetic anionic surfactants that are extensively used in many industries. As a result, large volumes of effluents containing high levels of these compounds are discharged into water bodies, causing risks to aquatic flora and fauna. Then, there is a need for environmentally safe and economically viable technologies for the removal of LAS from aqueous matrices. The present work evaluates the use of aqueous two-phase systems (ATPS) composed of PEG and sulfate salts for this purpose, considering the effects of tie line length (TLL), molar mass of polymer, and type of cation-forming salt on the partitioning behavior of LAS. All the LAS partition coefficient (K_{LAS}) values were greater than unity, and the LAS extraction efficiencies ($\%E_{LAS}$) were higher than 97%. The system consisting of PEG 1500 + $(NH_4)_2SO_4$ + H_2O provided the highest K_{LAS} (1083.34) and $\%E_{LAS}$ (99.9%), indicating that the method provided good extraction of LAS to the top phase. This system was applied using a real effluent sample in laboratory-scale experiments as well as in bench-scale batch trials. The results obtained at the laboratory scale showed $\%E_{LAS}$ values greater than 98%, while the best K_{LAS} value obtained in the batch experiments was 8.50 ($\pm$1.75) ($\%E_{LAS} = 78.17\%$). These values demonstrated the potential of ATPS for the removal of LAS from industrial effluents.

1. Introduction

Surfactants are amphiphilic compounds that are preferentially concentrated at the interface in aqueous solutions. At relatively low molar concentrations, they form aggregates in the form of micelles in the bulk solution. These compounds are potent detergents with the ability to alter interfacial properties (Zhang and Somasundaran, 2006), and are therefore used in the textile, pharmaceutical, detergent, personal care product, oil recovery, and paper industries.

Among the most widely marketed surfactants are the linear alkylbenzene sulfonates (LAS), which account for 25–30% of the total global consumption of this class of surfactants (Okada et al., 2013) and are used primarily in the production of household and industrial detergents. These synthetic anionic surfactants contain a linear alkyl chain consisting of between 10 and 14 carbon atoms, which is connected to a sulfonated aromatic ring (Okada et al., 2013). Commercial LAS products consist of a mixture of homologues with different molar masses and the general chemical structure shown in Fig. 1.

Due to their widespread industrial use, the presence of LAS compounds in the environment is increasingly common and can lead to adverse impacts. Studies have found that LAS concentrations of around 16 mg kg^{-1} (dry weight basis) in soil can influence microbial and biological activity, while concentrations higher than 40–60 mg kg^{-1} have toxic effects in invertebrates (Mungray and Kumar, 2008). Additionally, this can result in the leaching of soluble salts to deeper soil layers and increase the absorption of toxic chemicals (Jensen, 1999). In water bodies, the presence of LAS can increase the concentrations of xenobiotic compounds, decrease the amount of dissolved oxygen, and cause foam formation, hence affecting photosynthetic activity (Mungray and Kumar, 2008).

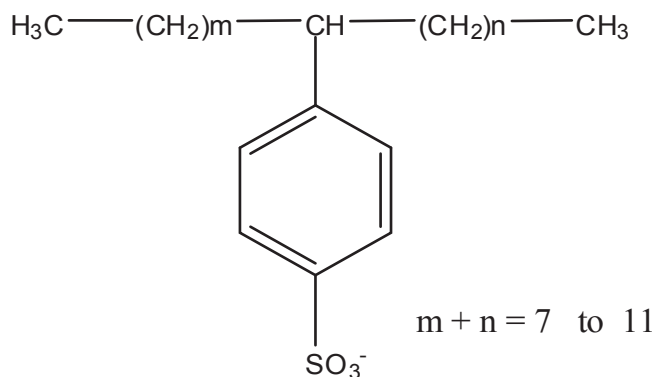The removal of LAS from wastewater is challenging because the

Fig. 1. Molecular structure of commercial linear alkylbenzene sulfonate (LAS).

effluents often contain different types of surfactants and other substances, making it difficult to select a single effective removal method (Kaya et al., 2009). The methods most commonly described for LAS removal are adsorption (Kastrisianaki-Guyton et al., 2016), biological degradation (Okada et al., 2013), electrocoagulation/electroflotation (Jangkorn et al., 2011), and advanced oxidation processes (Rivera-Utrilla et al., 2008). However, such methods have certain disadvantages. Treatment by adsorption generates a surfactant-rich solid phase that needs to be disposed of or regenerated. Biological treatments are affected by the complexity of the effluent and can be inefficient. Advanced oxidation processes can result in the formation of toxic byproducts, while electrocoagulation/electroflotation is expensive to install and operate. There is therefore a need to develop low cost, environmentally safe, and efficient technologies for the removal of LAS from effluents.

One option is the use of aqueous two-phase systems (ATPS). These are ternary systems that under specific conditions of temperature and composition have two distinct phases in thermodynamic equilibrium (Murari et al., 2015). The different phases are usually formed by mixing aqueous solutions of a polymer and a salt, two incompatible polymers, or two electrolytes. The advantages of ATPS include low cost, scale-up ability, the possibility of recycling the components, fast phase separation, and elimination of the use of toxic solvents. The technique is environmentally safe and uses water as the main component (Glyk et al., 2014). ATPS have been used for the removal of various solutes including dyes (Mageste et al., 2012), organic pollutants (Rodrigues et al., 2011), metal ions (Cunha et al., 2016; de Lemos et al., 2012; Patricio et al., 2011), and proteins (Perez et al., 2015).

The use of ATPS as a strategy to remove surfactants from aqueous matrices emerges because it is very well established in the literature that anionic surfactants and polymers form composites used in a wide range of industrial applications, such as the production of agrochemicals (Wang et al., 2016), cosmetics (Bradbury et al., 2016), and pharmaceuticals (Arzhavitina and Steckel, 2010). Nevertheless, there have been few studies concerning surfactant partitioning behavior in ATPS. Drouin and Cooper (1992) investigated the partitioning of the surfactants cetylpyridinium chloride (CPC), Nonidet P-40, and dodecylbenzenesulfonic acid (DBSA), as well as some biosurfactants, in a PEG-dextran ATPS in the presence and absence of phosphate buffer. It was observed that the partitioning behavior of the surfactants was strongly influenced by their charge. Albertsson and Andersson (Albertsson and Andersson (1981) and Svensson et al. (1985) described the partitioning of Triton X-100 and/or octyl glucoside surfactants incorporated into a PEG-dextran ATPS, for the purpose of separating and isolating chlorophyll proteins of the chloroplast thylakoid membranes.

A review of the literature reveals that there is a lack of experimental data concerning the interactions responsible for the partitioning of surfactants in ATPS. To the best of our knowledge, there are no reports describing the partitioning behavior of LAS in a PEG-salt ATPS for the purpose of its removal from real industrial effluents. Therefore, the aims of the present study were to understand the main interactions responsible for LAS partitioning in this type of ATPS and to evaluate the possible use of this system for the removal of LAS from a real effluent.

2. Materials and methods

2.1. Materials

Polyethylene glycol (PEG) with average molar masses of 400, 1500, 6000, 10000, and 35000 g mol^{-1} (all with 100% purity), and the salts ammonium sulfate ((NH$_4$)$_2$SO$_4$, 99% purity), lithium sulfate monohydrate (Li$_2$SO$_4$H$_2$O, 99% purity), magnesium sulfate heptahydrate (MgSO$_4$7H$_2$O, 98–102% purity), and sodium sulfate (Na$_2$SO$_4$, 99% purity) were obtained from Synth (São Paulo, Brazil). PEG (average molar mass of 10000 g mol^{-1}) and LAS was obtained from Sigma-Aldrich (St. Louis, MO, United States). The effluent was kindly provided by an engine repair service in Belo Horizonte (Minas Gerais, Brazil). All reagents were analytical grade and were used without further purification. Distilled water was used to prepare the solutions in all the experiments.

2.2. Partitioning experiments

2.2.1. Preparation of stock aqueous two-phase systems (ATPS)

The solutions were prepared at different mass percentages using an analytical balance (Shimadzu AX 200, uncertainty of ±0.0001 g). Water, polymer, and stock salt solutions were mixed in defined amounts in order to obtain five TLL values for each ATPS, using the phase diagrams reported elsewhere (Murari et al., 2015; Martins et al., 2008a, 2008b; de Lemos et al., 2011; Carvalho et al., 2007). The systems were shaken for 3 min and then left to stand in a thermostatic bath (MA 184, Marconi, uncertainty of ±0.1 °C) at 25 °C for a minimum of 24 h, to allow the system to reach thermodynamic equilibrium. The phases were collected separately for use in the partitioning study.

2.2.2. Partitioning study

For each TLL, three ATPS were prepared by mixing about 3 g of each phase from the stock ATPS. Approximately 0.1 g aliquots of LAS solution (27%, w/w) were added to two of these ATPS, while the third system was used as a blank. The systems were shaken for 3 min and then left in a thermostatic bath at 25 °C for a minimum of 24 h. Subsequently, the top and bottom phases were collected separately and diluted for the quantification of LAS using a UV–Vis spectrophotometer (Evolution 60S, Thermo Scientific) at 223 nm (the maximum absorption wavelength of LAS).

The LAS partition coefficients (K$_{LAS}$) were obtained from the ratios of the analyte concentrations in the top and bottom phases of the systems. In accordance with the Beer-Lambert law, which states that the analyte concentration is directly proportional to its absorbance, K$_{LAS}$ could be calculated according to Eq. (Zhang and Somasundaran, 2006):

$$K_{LAS} = \frac{Abs_T \, f_{dT}}{Abs_B \, f_{dB}}, \tag{1}$$

where Abs_T and Abs_B are the absorbances of the top and bottom phases, respectively, and f_{dT} and f_{dB} are their dilution factors.

2.2.3. LAS preconcentration studies

The preconcentration of LAS was studied using the PEG 1500 + (NH$_4$)$_2$SO$_4$ + H$_2$O system with TLL of 25.56. The procedures adopted were the same as those used in the partitioning studies, although in these experiments the mass ratios of the phases were 1:9, 1:4, 1:2.5, 1:1.5, and 1:1.

2.2.4. Partitioning studies using a real effluent

The partitioning studies in the presence of a real effluent were carried out at the laboratory scale as well as in batch experiments at the bench scale. The effluent was previously filtered through qualitative filter paper (0.14 μm pore size) to remove suspended solids. The laboratory scale experimental procedures were the same as those described previously for the partitioning study, but using the effluent as solvent to prepare the stock solutions of polymer and salt. Furthermore, there was no addition of LAS solution to the systems, because the effluent already contained significant quantities of the surfactant.

For the experiments carried out at the bench scale, approximately 400 g of salt and 300 g of polymer were weighed out (BL3200H, Martei, uncertainty of ±0.01 g) and mixed in a glass vat with a capacity of 3.0 L. About 1900 g of the effluent was added to the system using a peristaltic pump (Quimis, flow 601 I, power 1/6 HP). The system was shaken by a jar test (Nova Ética) for 10 min at 200 rpm to ensure complete solubilization of the components. After this period, the system was allowed to stand for 30 min for phase separation. Samples were collected from both phases and were diluted prior to spectrophotometric quantification. After 24 h, during which the system remained closed, at rest, and at ambient temperature, samples were again collected for quantification.

2.3. LAS extraction efficiency (%E$_{LAS}$)

The LAS extraction efficiency (%E$_{LAS}$), obtained as the ratio between the amount of surfactant extracted to the top phase of the ATPS and the total amount of LAS in the system, was calculated using Eq. (Okada et al., 2013):

$$\%E_{LAS} = \frac{Abs_T f_{dT} \times M_T}{(Abs_T f_T \times M_T) + (Abs_B f_{dB} \times M_B)} \times 100, \tag{2}$$

where Abs_T and Abs_B are the absorbances of the top and bottom phases, f_{dT} and f_{dB} are the corresponding dilution factors, and M_T and M_B are the weights of each phase.

3. Results and discussion

3.1. Effect of tie line length on LAS partitioning

The TLL is an important parameter that reflects the differences between the intensive thermodynamic properties of the phases in equilibrium in the ATPS, and significantly influences the partitioning behavior of solutes in ATPS (Mageste et al., 2012; Rodrigues et al., 2011; Cunha et al., 2016; de Lemos et al., 2012; Patricio et al., 2011). The TLL was calculated using Eq. (Mungray and Kumar, 2008):

$$TLL = \left[\left(C_P^T - C_P^B \right)^2 + \left(C_S^T - C_S^B \right)^2 \right]^{1/2}, \tag{3}$$

where C_P^T and C_P^B are the polymer concentrations and C_S^T and C_S^B are the salt concentrations in the top and bottom phases, respectively.

The effects of TLL on K$_{LAS}$ (Fig. 2(a)) and %E$_{LAS}$ (Fig. 2(b)) were evaluated at 25 °C using the systems composed of PEG 1500 and sulfate salts. For all TLL values, K$_{LAS}$ was greater than unity (Fig. 2),

indicating that LAS was preferentially concentrated in the top phase of the systems, and higher TLL values led to an increase in K$_{LAS}$. This behavior could be explained by the fact that a higher TLL results in an increase of the salt concentration in the bottom phase, with a corresponding increase of the polymer concentration in the top phase, hence increasing the degree of interaction between LAS and the component with which it interacts most strongly.

The interactions between anionic surfactants and PEG polymers have been extensively studied (Wang et al., 2016; Bradbury et al., 2016; Arzhavitina and Steckel, 2010), and the general picture of such interactions is well accepted. When the surfactant concentration is lower than the critical aggregation concentration (CAC), the surfactant does not interacts with polymer. When the concentration exceeds the CAC, the surfactant monomers start to bind cooperatively to PEG chains, and a structural-reorganization where the PEG chains are bound to the surface of micelles take place as the surfactant concentration increases (Dai and Tam, 2006). In all the experiments, the LAS concentration was higher than the CAC, so consequently the interaction between the surfactant micelle surfaces and the polymer induced the surfactant to move to the ATPS top phase.

In order to evaluate the efficiency of the ATPS in extracting LAS to the top phase, the %E$_{LAS}$ values were calculated and related to the TLL, as shown in Fig. 2(b). It can be seen that for all TLL values, the %E$_{LAS}$ values were greater than 99%. This finding confirmed the potential application of the ATPS, because at the first TLL, the lowest %E$_{LAS}$ value was 99.17%. Under such conditions, lower amounts of salt and polymer were required to form the ATPS, hence decreasing the cost of the process.

The results presented in this study are promising when compared to previous studies. Ozdemir et al. (2011) reported an efficiency of 99.63% for the removal of dodecylbenzenesulfonate (SDBS) from aqueous solutions using adsorption by polyaniline polymers. Zsilak et al. (2014) evaluated the use of photocatalysis combined with ozonization for LAS degradation and found removal efficiencies of 85% after 45 h. In addition to such physical and physical-chemical treatment techniques, other work by Duarte et al. (2015) evaluated LAS degradation in an anaerobic reactor. The reactor was fed with a synthetic substrate containing nitrate, and LAS was added at a concentration of 22 mg L^{-1}. After 104 days of operation, the maximum degradation of LAS was 87%.

3.2. Influence of cation-forming salt on LAS extraction

Several studies have investigated the effect of the cation on solute partitioning behavior in ATPS (Mageste et al., 2012; Rodrigues et al., 2011; Cunha et al., 2016; de Lemos et al., 2012; Patricio et al., 2011). Such studies are important in order to obtain information about the contribution of electrostatic interactions between the system components and the partitioned solute. Here, the effect of the cation was evaluated at 25 °C for the ATPS composed of PEG 1500 + sulfate salts + water. The results (Fig. 2) showed that the K$_{LAS}$ and %E$_{LAS}$ values followed the order: Na$^+$ < Mg^{2+} < Li$^+$ ≈ NH$_4^+$. This demonstrated that the nature of the cation salt influenced the PEG-micelle surface interaction, supporting the PEG-surfactant interaction mechanism proposed by Xia and Dubin (1992), whereby the salt cations act as mediators, interacting simultaneously with the polymer and the micelle surface.

3.3. Effect of polymer molar mass

The molar mass of the ATPS-forming polymer influences the solute partitioning behavior (Khayati et al., 2015). This effect was evaluated and the results are presented in Fig. 3. It can be seen that
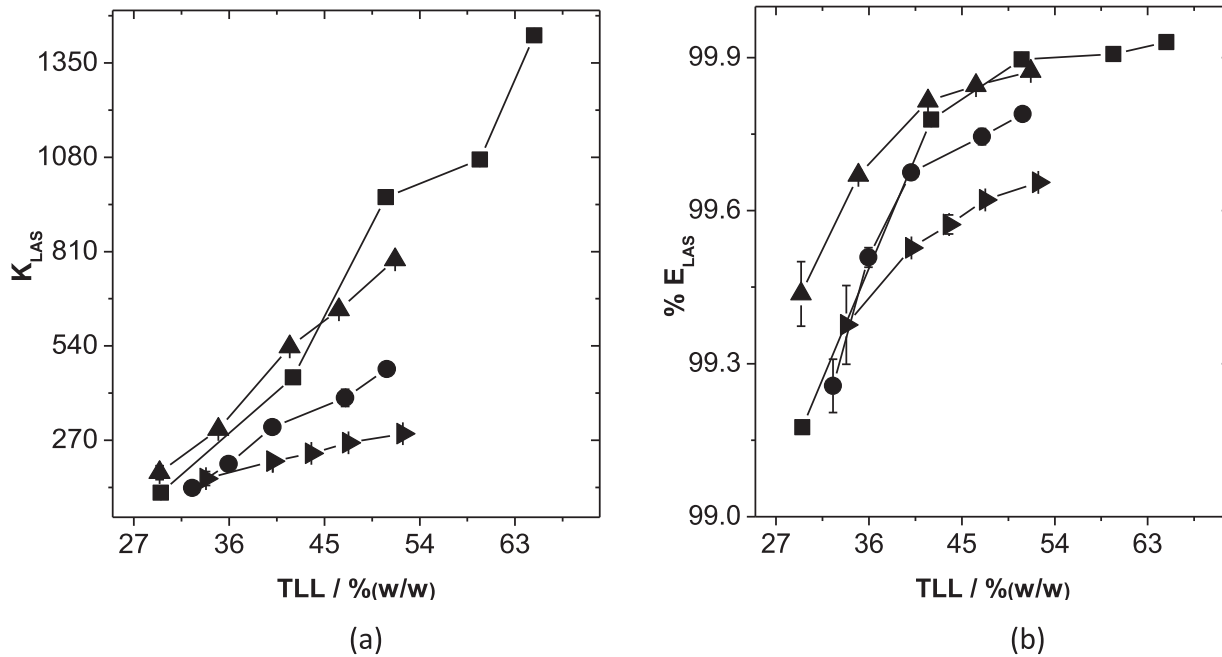
Fig. 2. TLL effect on the LAS partition behavior at 25 °C. ATPS: (■) PEG 1500 + $(NH_4)_2SO_4$ + H_2O; (▲) PEG 1500 + Li_2SO_4 + H_2O; (●) PEG 1500 + Na_2SO_4 + H_2O; (▶) PEG 1500 + $MgSO_4$ + H_2O.
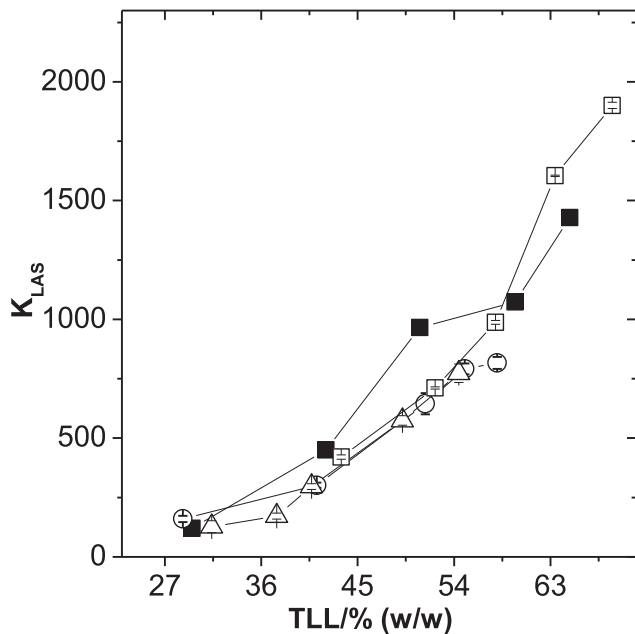

Fig. 3. Molar mass polymer effect on the LAS partitioning behavior at 25 °C. ATPS: (□) PEG 400 + $(NH_4)_2SO_4$ + H_2O; (■) PEG 1500 + $(NH_4)_2SO_4$ + H_2O; (○) PEG 6000 + $(NH_4)_2SO_4$ + H_2O; (△) PEG 10.000 + $(NH_4)_2SO_4$ + H_2O.

the values of K_{LAS} did not vary significantly according to the molar mass of the polymer, indicating a balance between two different effects: i) As the molar mass of the polymer increased, there was a decrease in the number of hydroxyls for the same mass percentage polymer, which increased the hydrophobicity of the phase rich in this component (Khayati et al., 2015). This increase in hydrophobicity favored interaction between polymer and surfactant, so the

surfactant micelles moved to the top phase; ii) As the molar mass of the polymer increased, the number of different ways that the solute can be ordered relative to components of the polymeric phase decreased, with lower configurational entropy of the top phase favoring migration of the LAS micelles to the bottom phase of the ATPS.

3.4. LAS preconcentration study

Science and industry have increasingly sought methods for the removal/separation of pollutants or added-value compounds that provide minimal waste generation. Preconcentration studies are important because they enable evaluation of the capacity of an ATPS to promote preconcentration of the solute in a small quantity of a phase. Investigation was therefore made of LAS preconcentration and the $\%E_{LAS}$ values obtained using the ATPS composed of PEG 1500 + $(NH_4)_2SO_4$ + H_2O, with TLL of 29.56, as shown in Fig. 4. The $\%E_{LAS}$ values were greater than 97%, indicating that in an industrial application it would be possible to treat large quantities of wastewater, generating smaller top phase volumes with high concentrations of surfactant. In addition to having to handle smaller top phase volumes, the fact that LAS is concentrated in this phase would assist its recovery for further processing and enable reuse of the bottom phase in a new ATPS.

3.5. Partitioning studies using a real effluent

The presence of LAS is commonplace in effluents and water resources, and the undesirable effects of these compounds in the environment are widely acknowledged. It is therefore important to conduct LAS partitioning studies using real effluent samples in order to evaluate the feasibility and potential application of this technique in industry. LAS partitioning using a real effluent was performed using the ATPS composed of PEG 1500 and $(NH_4)_2SO_4$. Fig. 5 shows the K_{LAS} and $\%E_{LAS}$ values, as a function of TLL, for experiments conducted at the laboratory scale.
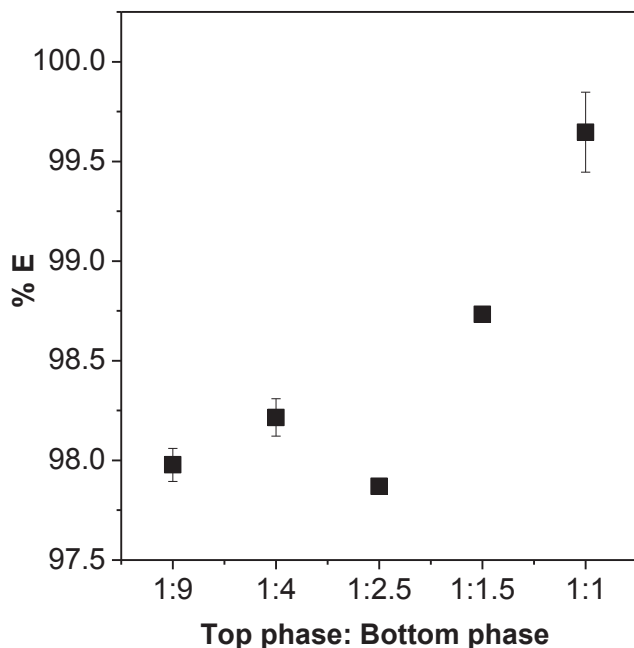
Fig. 4. The % E_{LAS} values in LAS pre-concentration studies in top phase at 25 °C. ATPS: (■) PEG 1500 + $(NH_4)_2SO_4$ + H_2O.

For all the TLL values studied, the K_{LAS} values were greater than unity (Fig. 2(a)). As discussed previously, these values were indicative of preferential distribution of LAS in the PEG-rich top phase. The K_{LAS} values were lower than obtained in the experiments carried out with distilled water, because the effluent was a complex matrix containing other pollutants that competed with LAS for the PEG phase. As a result, the LAS partitioning behavior was influenced by the other components present and their interactions with the constituents of the ATPS. Nonetheless, even using a real effluent, % E_{LAS} values above 98% were obtained, confirming the potential of

this method for the treatment of effluents containing LAS.

For comparison, Table 1 shows the efficiencies of removal/extraction of LAS from wastewater reported in the literature for different methods. Large differences in efficiency can be seen, and the most efficient method (achieving 98% removal) required the combination of two techniques. This information highlights the potential application of ATPS as an environmentally safe technique that is both inexpensive and highly efficient.

In the batch experiments carried out in this study, the effluent was pumped into a tub containing salt and polymer. Values of K_{LAS} of 6.19 ($\pm$5.5) and %E_{LAS} of 65.43% were obtained in the first analysis after the phase separation process. After 24 h, the values obtained for K_{LAS} and %E_{LAS} were 8.50 ($\pm$1.75) and 78.18%, respectively. These data indicated that the process was spontaneous and that LAS was concentrated in the PEG-rich top phase. In this experiment, the ATPS was produced using the first TLL value. The extraction efficiencies showed that the process occurred rapidly, because there was little difference between the %E_{LAS} values for the samples collected immediately after phase separation and after 24 h.

Considering possible applications of this system, the results obtained here are promising, since there was 78.17% removal of LAS to the top phase in the batch experiments. Furthermore, the kinetics of LAS recovery using the ATPS was favorable, with a fast separation process. However, further studies will be needed to improve the system before its implementation in a pilot plant.

4. Conclusions

The results showed that effective LAS removal was achieved using the ATPS technique applied to both synthetic and real effluent samples. The transfer of LAS to the ATPS top phase was attributed to interaction between the polymer and the micelle surface, mediated by the salt cation. The highest K_{LAS} and %E_{LAS} values were obtained for the ATPS composed of PEG 1500 + $(NH_4)_2SO_4$ + H_2O. This system was used in preconcentration studies in which it was possible to extract > 97% of the LAS, with generation of smaller volumes of waste. This system was also applied to remove LAS from
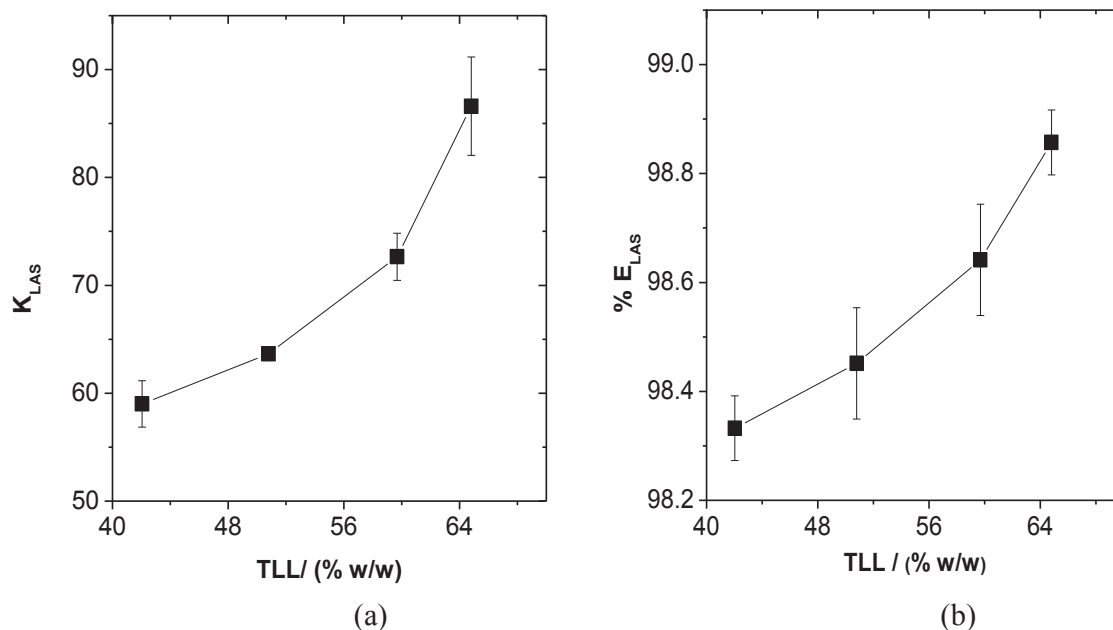

Fig. 5. LAS partition behavior using a real effluent in experiments on laboratory scale at 25 °C. ATPS: (■) PEG 1500 + $(NH_4)_2SO_4$ + effluent.

Table 1
Different methods for LAS removal from effluents with their highest reported efficiency.

Method	Maximum Efficiency of removal/extraction (%)	Used chemicals	Ref.
Fenton-like system	90%	$Fe^{2+}/Fe^0/H_2O_2$	(Zhu et al., 2015)
Biodegradation in anaerobic fluidized bed reactor	57%	Sucrose, sodium bicarbonate, NaCl, $MgCl_2$, $CaCl_2$	(Braga et al., 2015)
High-frequency ultrasound	42%	None	(Gallipoli and Braguglia, 2012)
Coagulation combined with Fenton oxidation	98%	$FeSO_4$, H_2O_2, polymeric aluminum ferric chloride sulfate.	(Han et al., 2012)
Aqueous two-phase system	98.85%	Poly(ethylene)glycol, ammonium sulphate	(This work)

real effluent samples, in experiments carried out in bench scale, with %E_{LAS} values greater than 98% demonstrating the potential industrial application of ATPS for the removal/recovery of this surfactant from effluents.

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