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Separation of Neutral Red and Methylene Blue from Wastewater using Two Aqueous Phase Extraction Methods

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Abstract: The aim of this work was the two-aqueous phase extraction of neutral red and methylene blue from wastewater. This has been achieved on the basis of phase separation properties of non-ionic surfactants above the so-called cloud point curve and the solubilization phenomena of coacervate micelles (surfactant rich phase). Three commercial surfactants were used in this work; the Oxo-$C_{15}E_7$ which is an ethoxylate fatty alcohol (Dehydol LT 7), Triton X-114 (iso-C_8H_{17}-C_6H_4-$(OCH_2CH_2)_{7,5}OH$), and Triton X-100 (iso-C_8H_{17}-C_6H_4-$(OCH_2CH_2)_{9,5}OH$) which are alkyl phenol ethoxylate surfactants. The phase diagrams of binary water/surfactants systems were drawn and the effect of sodium sulphate on water-surfactant systems was therefore studied. Oxo-$C_{15}E_7$ and Triton X-114 were used for the cloud point extraction of neutral red and methylene blue from their aqueous solutions at 100 mg/L and 7 mg/L, respectively. The experimental extraction results were expressed by the following three responses: percentage of the extracted dye (E), residual concentrations of dye in the dilute phase ($X_{s,w}$), and the volume fraction of coacervate (ϕ_C) at the equilibrium. The results obtained for each parameter were also represented on three-dimensional diagrams using an empirical smoothing method. The empirical modelling data were in agreement with the experimental ones. The main advantage was sought between E, which has reached 99% in the case of neutral red, whereas in the case of mehtylene blue 92% was obtained with respect to (ϕ_C), which should have a minimum value. At the optimal conditions,

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neutral red and methylene blue concentrations in the effluent were reduced to about 500 times and 7 times, respectively.

Keywords: Cloud point, non-ionic surfactant, coacervate, extraction, dyes, neutral red, methylene blue

INTRODUCTION

The two aqueous phase extraction methods were found to include simultaneously cloud point and solubilization phenomenon of non-ionic surfactants medium. Thus, most of the polyethoxylated non-ionic surfactants in aqueous solutions formed two phases above the cloud point (T_c): a surfactant-rich phase (coacervate) and a dilute phase in which the concentration of the surfactant is close to its critical micelle concentration (1). Therefore, due to the micellar solubilization property of the surfactants, the hydrophobic, amphiphilic, or even ionic solutes has been extracted in the coacervate after increasing the temperature above T_c. This method was first applied to the separation of metals ions in the presence of a chelating agent (1). Moreover, this method has also been adopted for the extraction of many other chemical species, such as metal ions, small organic molecules, and biological molecules (2–16). In addition to their solubilization capacity of dissolved pollutants, micelles of non-ionic surfactants were able to desorb organic species, even when the insoluble ones were adsorbed on a solid. Such a technique of contaminated solid washing has also been based on the micellar solubilization of the pollutant, followed by its concentration in the coacervate. On the other hand, desorption has been achieved by diffusion of the molecules from the solid surface modified by the surfactant into the micelles (17, 18).

Dye containing waste stream was found to be one of the major toxic industrial effluents. Unless properly treated, the dyes present in wastewater have significantly affected photosynthetic-related activity due to reduced light penetration. Besides, they may also be toxic to certain forms of aquatic life. Various types of dyes were used in many industrial processes especially textiles, pulps, paper-making, and paints etc. The highly colored effluents constitute a major environmental problem. Hence, these colored wastes must be treated before disposal.

Due to low biodegradability of dyes, colored effluents can not be treated efficiently by a conventional biological wastewater treatment process (19). Physical or chemical treatment processes were also generally used for such effluents. Many investigators have studied different techniques for wastewater treatment: membrane separation process (20), ozonation, and oxidation process (21), as well as the adsorption on different adsorbents (22, 23). Each method can be criticized. For example, in membrane separation processes care is needed to avoid membrane fouling. In the case of the adsorption process, the adsorption capacity is highly affected by the pH of solutions depending on the type of adsorbent and adsorbate, cloud point extraction can be used for removing dye from aqueous solution (9, 12, 24). Such a method offers some advantages over conventional liquid-liquid extraction, including high extraction efficiency, ease of waste disposal, and the use of non-toxic and less dangerous reagents.

Neutral red and methylene blue were considered hazardous and classified as special waste and the disposal to such chemicals was covered by regulations which may vary according to location. On the basis of these findings, the cloud point extraction of neutral red and methylene blue from their aqueous solutions at 100 mg/L ($3.46 \cdot 10^{-4}$ M) and 7 mg/L ($2.18 \cdot 10^{-5}$ M), respectively was investigated in the present work. The effects of temperature, surfactant concentration, effluent pH solutions, as well as the addition of sodium sulphate (a strong salting-out electrolyte) on solutes extraction extent were also achieved. The initial dyes concentrations used were chosen to avoid samples analyses dilutions (dilute phase after extraction) which can induce inevitable errors. This work has been focused on the comparison between ethoxylated alkylphenols non-ionic surfactants type (EAP) and ethoxylated alcohols (EA) in dye extraction. Ethoxylated alcohols (EA) have been used as good alternatives to EAP, due to their satisfactory biodegradable activities (4, 5, 25, 26). Actually, EAP surfactants were no more used for detergence applications in many countries, and we are going to be superseded progressively because of the toxic intermediate substances generated from their biodegradation process such as alkylphenols molecules.

MATERIALS AND METHODS

Reagents

The Oxo-$C_{15}E_7$ used in this work was a commercial surfactant, obtained from fatty Oxo alcohol ethoxylation (Dehydol LT 7), the cloud point of this surfactant at 1 wt.% in water was 54°C and its critical micellar concentration was $4.8 \cdot 10^{-4}$ M. This sample was kindly supplied by Henkel (Ain-Temouchent, Algeria). Triton X-100 (iso-octyl phenoxy polyethoxy ethanol) and Triton X-114 (occtyl phenol polyethylene glycol ether) were supplied by Sigma-Aldrich. The critical micellar concentration of TX-100 and TX-114 are $3.0 \cdot 10^{-4}$ and $1.7 \cdot 10^{-4}$ M, respectively. The cloud point of TX-100 and TX-114 at 1 wt.% in water were 68 and 24°C, respectively. Neutral red (3-amino-7-dimethylamino-2-methylphenazine hydrochloride, $C_{15}H_{17}ClN_4$, molecular weight: 288.77, solubility in water: 50 g/L) and methylene blue (phenothiazin-5-ium, 3,7-bis (dimethylamino)-, chloride, $C_{16}H_{18}ClN_3S$, molecular weight: 319.85, solubility in water: 40 g/L) were supplied by ACROS. The wavelengths of the maximum absorption, were 460 nm for methylene blue and 660 nm for neutral red. For all experiments, the surfactants and the dye were used without further purification. The pH values of the solutions were adjusted between 2 and 13 by adding hydrochloric acid and sodium hydroxide as appropriate. The structure of neutral red and methylene blue in basic and in acidic medium are shown in Fig. 1.

Apparatus

The determination of the cloud point was carried out using a Mettler FP 900 apparatus: temperature of the sample placed in a cell was measured using a precise sensor placed in a small oven. At the bottom of the measuring cell, there is a luminous source and an optic driver which illuminates the sample. The crossed sample light was converted by photoelectric cell into an electric signal proportional to the transmitted light intensity. The transmission of light was measured continuously, while the cell temperature increased linearly according to the chosen heating rate. The cloud point designates the temperature of the unique limpid phase which becomes cloudy, inducing a transmission decrease. Dye concentration was determined using a spectrophotometer (SAFAS type MC2).

Procedure

For the extraction tests, 10 mL of solution containing the surfactant (at concentrations of 1, 4, 7, 10 or 13 wt.%) and the solute (100 mg/L for neutral red and 7 mg/L for methylene blue) in distilled water, were poured into graduated cylinders and heated in a precise thermostated bath for 2 hours, to reach phase separation (dilute phase and coacervate). The heating temperature range was from the cloud point temperature was about twenty degrees.

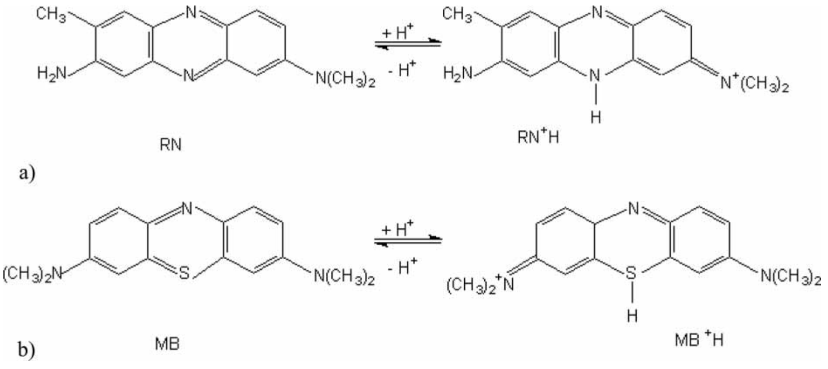


Figure 1. Structure of neutral red and methylene blue in basic and in acidic medium.

The volumes of both phases were registered. A small amount of the dilute phase was pumped using a syringe and analyzed by a spectrophotometer (SAFAS type MC2) to determine the dye concentration. To observe the effect of salts on dye extraction, sodium sulphate was selected.

RESULTS AND DISCUSSION

Phase Diagrams

The phase diagrams of the system water/surfactant/dye can not be plotted because the dye prevented the cloud point detection of such a system. Hence, it was not possible to study the solute effect on the surfactants cloud point curves. Nevertheless, as in the case of phenol and benzyl alcohol extraction (10, 11), it was necessary to first plot the phase diagrams of water/surfactant systems, which allowed to identify approximately the cloud point extraction domain (two-phase zone) for each surfactant (Fig. 2). In a homologous series of polyethoxylated non-ionic surfactants, the cloud point increases with the éthoxylation number (OE) and decreases when the carbon number of the hydrophobic chain increases (27). Thus, critical temperature of TX-114 was about 24°C, while that of TX-100 was located above 68°C (Fig. 2). The critical temperature of Oxo-$C_{15}E_7$ was about 54°C, and this surfactant does not belong to the same homologous series of TX-114 and TX-100. Organic solubilizates can interact with the surfactant polar head group or with its hydrophobic length after solubilization in micelles. According to their chemical nature, organic compounds can vary the surfactants cloud point (10)–(11, 28–30). In our case, as it can be seen in cloud point extraction test, the

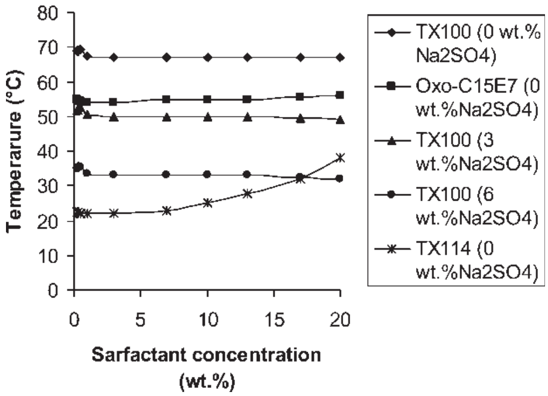


Figure 2. Effect of sodium sulphate on the cloud point temperature of Oxo-$C_{15}E_7$, TX-100 and TX-114.

phase separation of the system water/surfactant/dye, was possible at the cloud point temperatures of the system water/surfactant. Indeed, at low concentrations, neutral red and methylene blue, have a insignificant effect on the cloud point of the studied surfactants. Nevertheless, TX-100 was avoided in cloud point extraction test. With a relatively high cloud point temperature, these surfactants cannot allow to study the temperature effect on the extraction parameters.

When small amounts of sodium chloride were added (less than 0.01 M) to non-ionic surfactant solutions, the cloud point remained constant (28). Nevertheless, at high concentrations (higher than 0.1 M), sodium chloride lowered the cloud point (30). Figure 2 shows the cloud point decreasing TX-100 by sodium sulphate. This phenomenon was due to the salting-out of the surfactant which was induced by the solvated electrolyte. Figure 2 shows how 6 wt.% of Na_2SO_4 (0.42 M) was able to lower the cloud point of 1 wt.% TX-100 solution from 68°C to 35°C. Therefore, cloud point can be adjusted at room temperature by a simple control of surfactant and salt concentrations, and therefore reduces the heating energy cost in large-scale cloud point extraction processes. Salt addition can also have an application in the extraction of heat sensitive products. However, electrolyte does not contribute equally between the dilute phase and coacervate, and its addition increases the density of the dilute phase. This makes phases separation easier in some non-ionic surfactant systems (1, 31, 32).

Extraction of Neutral Red and Methylene Blue

The extraction results of neutral red and methylene blue (solutes) from their aqueous solutions at 100 mg/L and 7 mg/L respectively by different surfactants, were expressed by tree "responses" (Y): percentage of extracted solute (E), residual concentrations of solute ($X_{s,w}$) in the dilute phase and the coacervate volume fraction at equilibrium (ϕ_C) (10)– (11, 33). For each parameter determined, by considering central composite designs (34), the results were analyzed by an empirical fitting. In this method, the experimental values can be used to determine, the polynomial model constants which were adjusted. The models were checked by plotting computing data against experimental results. The quadratic correlation was chosen to give the slope and the regression coefficient (R^2) closer to unity.

$$Y = a_0 + a_1X_t + a_2T + X_tT + X_t^2 + T^2 \tag{1}$$

Such correlation allows building the response surface. However, one cannot allow physical significance to the portion of horizontal planes corresponding to the maximum value of the response.

Extraction of Neutral Red

The quadratic equations for the three properties (E, $X_{s,w}$, and ϕ_C), whose reliability was checked, are as follows:

$$\begin{aligned} E_{(TX\text{-}114)} &= 126.134 + 6.569X_t - 3.140T \\ &\quad - 4.167 \cdot 10^{4}X_tT - 0.326X_t^2 + 0.043T^2 \end{aligned} \tag{2}$$

$$\begin{aligned} E_{(Oxo\text{-}C_{15}E_7)} &= 172.373 + 7.762X_t - 3.301T \\ &\quad - 7.222 \cdot 10^{-3}X_tT - 0.345X_t^2 + 0.025T^2 \end{aligned} \tag{3}$$

$$\begin{aligned} X_{s.w(TX\text{-}114)} &= 24.240 - 6.483X_t + 0.252T \\ &\quad + 9.815 \cdot 10^{-3}X_tT + 0.284X_t^2 - 1.806 \cdot 10^{-3}T^2 \end{aligned} \tag{4}$$

$$\begin{aligned} X_{s.w(Oxo\text{-}C_{15}E_7)} &= 1.134 \cdot 10^{3} + 30.525X_t - 39.490T \\ &\quad - 0.557X_tT + 0.303X_t^2 + 0.345T^2 \end{aligned} \tag{5}$$

$$\begin{aligned} \phi_{c(TX\text{-}114)} &= (-0.416 + 0.083X_t + 0.025T + 5.556 \cdot 10^{-4}X_tT \\ &\quad - 3.611 \cdot 10^{-3}X_t^2 - 4.167 \cdot 10^{-4}T^2) \end{aligned} \tag{6}$$

$$\begin{aligned} \phi_{c(Oxo\text{-}C_{15}E_7)} &= (4.073 + 0.156X_t - 0.116T - 1.944 \cdot 10^{-3}X_tT \\ &\quad + 6.944 \cdot 10^{-4}X_t^2 + 8.333 \cdot 10^{-4}T^2) \end{aligned} \tag{7}$$

Figure 3 represents the three-dimensional isoresponse curves of the studied properties fitted to the quadratic model [equations (2)–(7)]. Figures 3a and 3b show that the extent of neutral red extraction, E, increases with X_t. In this work, E reached 99.2% for 13 wt.% of TX-114 and 98.32% for the same concentration of Oxo-$C_{15}E_7$ (Table 1). On the other hand, E decreases slightly with great raise of temperature above the cloud point (Table 1). This is probably due to the increase in the solubility of neutral red in water. This increase makes the neutral red extraction in the coacervate more difficult at high temperatures. In Figs. 3c and 3d, it is shown that the concentration of residual neutral red $X_{s,w}$ decreases as X_t increases, but slightly with T. Thus, beyond the cloud point, a significant rise in temperature has the opposite effect on the extraction (10, 11). Hence, at high surfactant concentrations ($X_t = 13$ wt.%) (Table 1), neutral red concentration in the effluent can be reduced to about 500 times with TX-114 and 172 times with Oxo-$C_{15}E_7$. In order to increase the concentration factor of solute, a minimum volume fraction of coacervate (ϕ_C) should be obtained when temperature increases. Hence, according to Figs. 3e and 3f, and Table 1, the value of ϕ_C is low at high temperatures and at low surfactant concentration. But, raising up the temperature is unfavorable for efficient extraction extent (Figs. 3a, 3b), while, high surfactant concentrations increase ϕ_C (Figs. 3e, 3f). So, the optimization of the process needs to compromise between the three studied parameters E, $X_{s,w}$, and ϕ_C.

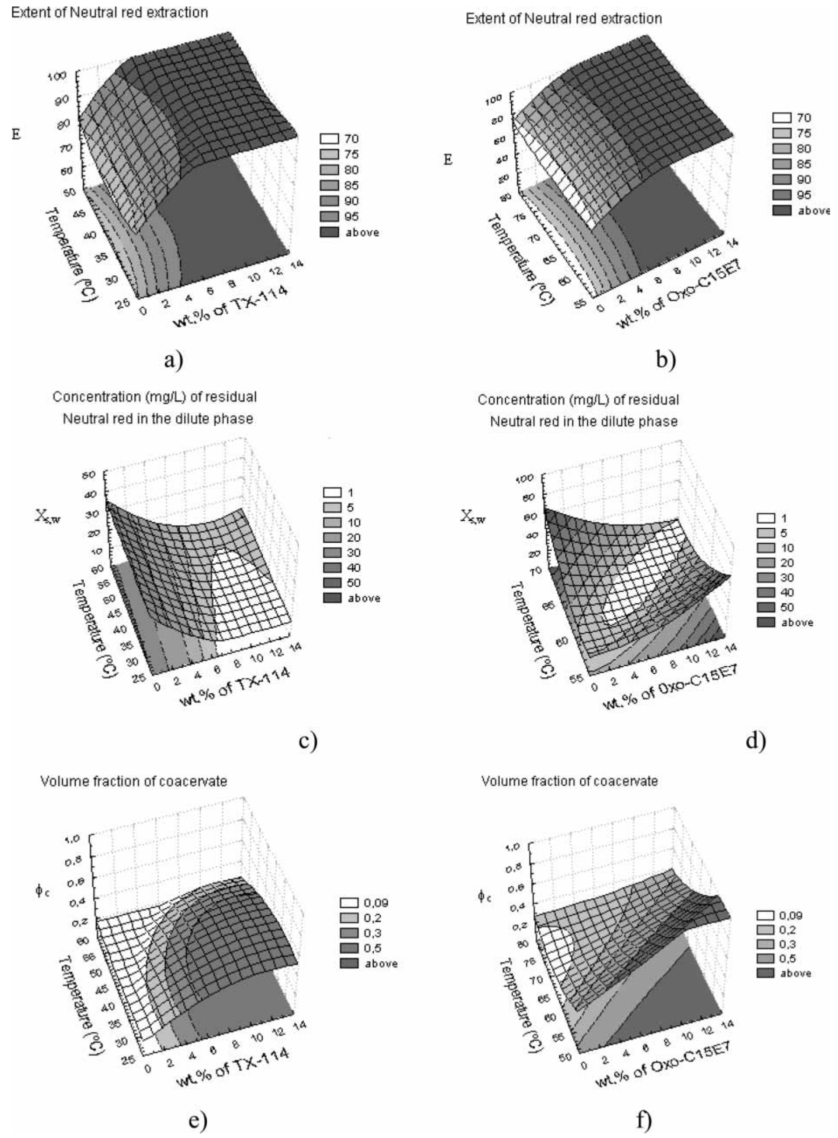


Figure 3. Three-dimensional isoresponse curves smoothed by a quadratic model Eqs. (2) to (7): a) $E_{(TX\text{-}114)} = f(X_t, T)$; b) $E_{(Oxo\text{-}C_{15}E_7)} = f(X_t, T)$; c) $X_{s,w\ (TX\text{-}114)} = f(X_t, T)$; d) $X_{s,w\ (Oxo\text{-}C_{15}E_7)} = f(X_t, T)$; e) $\phi_{C(TX\text{-}114)} = f(X_t, T)$; f) $\phi C_{(Oxo\text{-}C_{15}E_7)} = f(X_t, T)$.

Extraction of Methylene Blue

For E, $X_{s,w}$, and ϕ_C properties concerning the extraction of Methylene blue with TX-114 and Oxo-$C_{15}E_7$, the quadratic model provides the following

Table 1. Some experimental results of the extraction parameters (E, $X_{s,w}$, ϕ_C and $X_{s,w}/X_{s,0}$)

	(X_T, T)	E (%)	$X_{s,w}$ (mg/L)	ϕ_C	$X_{s,w}/X_{s,0}$[a]
N R, TX-114	(4, 31)	92.00	9.55	0.29	10.47
	(4, 37)	86.43	14.57	0.22	6.86
	(13, 40)	99.20	0.20	0.40	500
N R, Oxo-$C_{15}E_7$	(4, 57)	90.20	4.11	0.35	24.33
	(4, 66)	85.29	10.41	0.15	9.60
	(13, 66)	98.32	0.58	0.51	172.41
M B, TX-114	(4, 50)	74.20	2.09	0.15	3.35
	(13, 55)	92.52	0.92	0.38	7.60
M B, Oxo-$C_{15}E_7$	(4, 61)	44.45	3.97	0.09	1.76
	(4, 70)	34.91	3.45	0.025	2.02
	(13, 73)	45.24	2.68	0.10	2.61

[a] $X_{s,0} = 100$ mg/L for neutral red (NR) and 1 mg/L for methylene blue (MB).

equations:

$$E_{(TX-114)} = 169.982 + 18.405X_t - 7.604T - 0.229X_tT - 0.284X_t^2 + 0.104T^2 \quad (8)$$

$$E_{(Oxo-C_{15}E_7)} = -53.174 + 16.134X_t + 2.742T - 0.180X_tT - 0.080X_t^2 - 0.024T^2 \quad (9)$$

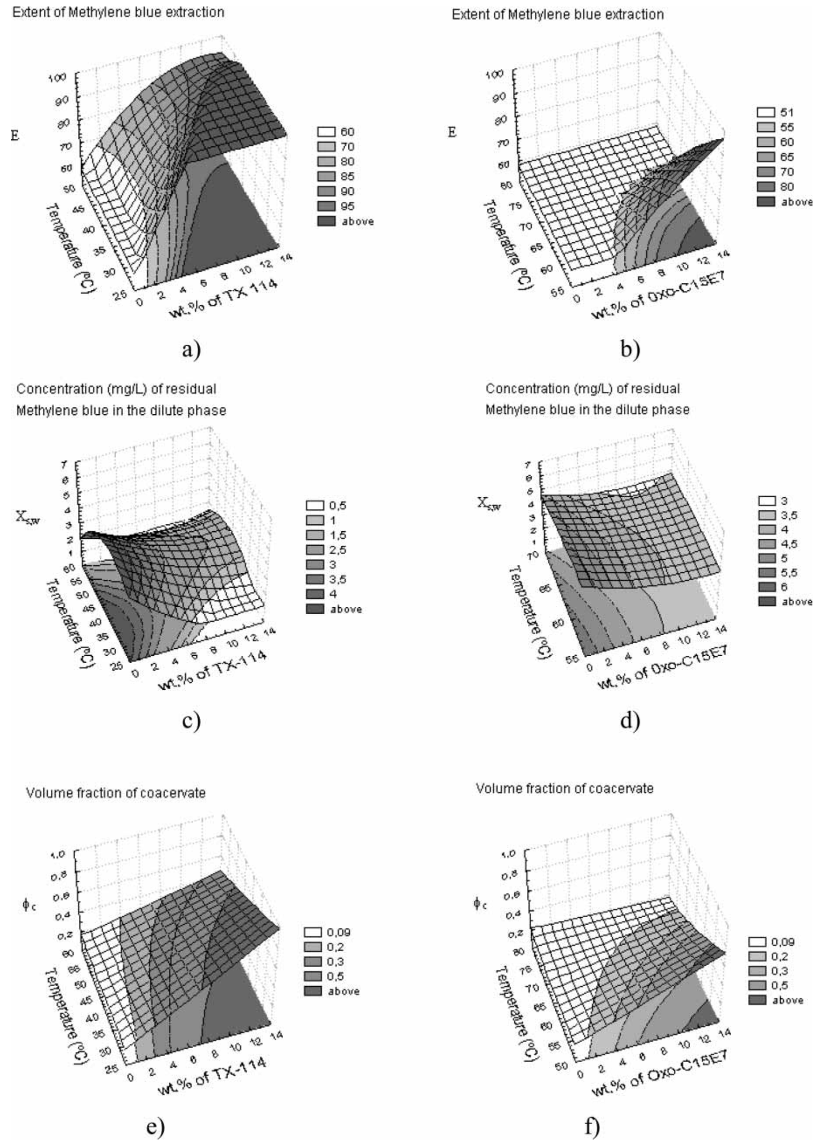
$$X_{s.w(TX-114)} = -4.481 - 0.956X_t + 0.519T + 0.011X_tT + 0.018X_t^2 - 0.714 \cdot 10^{-2}T^2 \quad (10)$$

$$X_{s.w(Oxo-C_{15}E_7)} = -7.851 - 0.653X_t + 0.501T + 5.556X_tT + 0.014X_t^2 - 4.722 \cdot 10^{-3}T^2 \quad (11)$$

$$\phi_{c(TX-114)} = -0.101 + 0.098X_t - 4.750 \cdot 10^{-3}T - 1.250 \cdot 10^{-3}X_tT + 1.389 \cdot 10^{-4}X_t^2 + 5 \cdot 10^{-5}T^2 \quad (12)$$

$$\phi_{c(Oxo-C_{15}E_7)} = 1.093 + 0.127X_t - 0.035T - 1.667 \cdot 10^{-3}X_tT + 1.389 \cdot 10^{-4}X_t^2 + 2.778 \cdot 10^{-4}T^2 \quad (13)$$

The behavior of the three properties with respect to X_t and T, was generally similar to that observed for neutral red extraction (Fig. 4). In fact, although the initial concentration of the neutral red in the effluent is higher than that of methylene blue, and the solubility was less, the extracted quantity of the neutral red with both the surfactants was higher than that of Methylene blue (Figs. 3 and 4 and Table 1), especially when Oxo-$C_{15}E_7$ was used (Figs. 3b–4b). Consequently, the values of $X_{s,w}$ for methylene



a) b) c) d) e) f)

Figure 4. Three-dimensional isoresponse curves smoothed by a quadratic model (Eqs. (8) to (13)): a) $E_{(TX\text{-}114)} = f(X_t, T)$; b) $E_{(Oxo\text{-}C_{15}E_7)} = f(X_t, T)$; c) $X_{s,w\ (TX\text{-}114)} = f(X_t, T)$; d) $X_{s,w\ (Oxo\text{-}C_{15}E_7)} = f(X_t, T)$; e) $\phi_{C(TX\text{-}114)} = f(X_t, T)$; f) $\phi_{C(Oxo\text{-}C_{15}E_7)} = f(X_t, T)$.

blue were lower than that for neutral red (Table 1). In this case, at high surfactant concentrations ($X_t = 13$ wt.%), methylene blue concentration in the effluent was reduced to about 7.6 times less with TX-114 and 2.61 times less using Oxo-$C_{15}E_7$ (Table 1).

Effects of Salt Concentration on Extraction

Figure 5 shows the variation of the extraction extent of methylene blue (7 mg/L) against surfactant concentrations (for TX-114 at 35°C or Oxo-$C_{15}E_7$ at 55°C) at different amount of sodium sulphate. It is clear from the figure that the extraction extent of methylene blue with TX-114 is higher than that obtained with Oxo-$C_{15}E_7$. Since both surfactants have nearly the same ethoxylate number (OE $\approx$ 7), one can conclude that this phenomenon was due to the surfactant hydrophobic length form. Indeed, after solubilization into micelles, methylene blue seems to interact with the surfactant hydrophobic length of TX-114 more than with Oxo-$C_{15}E_7$ one. This allows us to suggest that this solute was dissolved manly in the hydrocarbon core of micelles (close to the hydrophobic length). Whilst the extraction extent of neutral red with both surfactants (TX-114 and Oxo-$C_{15}E_7$) was similar (Figs. 3a and 3b). Hence, this solute seems to be less hydrophobic than methylene blue, and may be incorporated in the polyoxyethylene exterior of the micelles (35).

It may be observed from Fig. 5 that the extraction of methylene blue increases significantly when the electrolyte was added to the system water/surfactant/methylene blue. As mentioned above, the salting-out effect resulting from the solvated electrolyte depends upon the hydrogen bonding between water molecules and the surfactant polar head group as well as with the dye hydrophilic part. According to Saito and Shinoda (29), the addition of 0.17 M of NaCl (equivalent to 1 wt.%) to non-ionic surfactant solutions increases their hydrocarbon solubilization capacity, by lowering the surfactant cmc. This behavior may be the result of an increase in the micellar number within the concentration region. Hence, in the presence of electrolyte, dye and surfactant molecules were less soluble in water. Therefore, in the presence of 3 wt.% of the sodium sulphate solution, the surfactant and methylene blue solubilized in micelles were pushed out towards

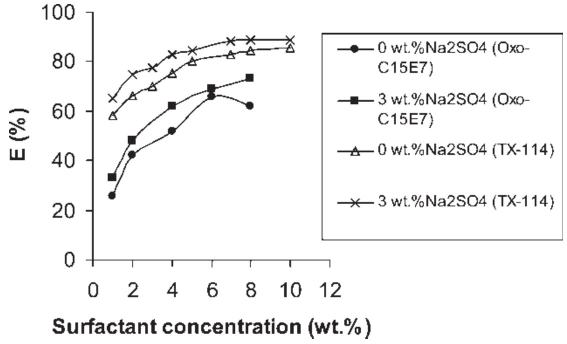


Figure 5. Effect of sodium sulphate on the extraction extent in the systems. H_2O/TX-114/methylene blue and H_2O/Oxo-$C_{15}E_7$/methylene blue (T = 35°C for TX-114; T = 55°C for Oxo-$C_{15}E_7$; 7 mg/L of methylene blue).

the coacervate phase. Thereby, the small coacervate volumes with high surfactant and dye concentrations were obtained with these conditions (10, 11, 33).

Effects of pH on Extraction

Generally solute-micelle interactions are strongly influenced by solute ionization (36). Therefore, the metallic chelates sharing between the dilute phase and coacervate vary with the pH of the non-ionic surfactant solutions (5, 12). After the deprotonation of a weak acid or the protonation of a weak base, slight interactions may occur with the surfactant. In these conditions, a small amount of those species may be solubilized, unlike neutral molecules. Consequently, a small amount of ionized solute can be extracted. The effects of the pH of the solution on the extent of neutral red and methylene blue extractions are shown in Fig. 6 for 70 mg/L and 7 mg/L of feed dye respectively using 4 wt.% of surfactant (TX-114 at 35°C or Oxo-$C_{15}E_7$ at 55°C). Extractions of Neutral red and Methylene blue were less in acidic pH and were increased with pH. The pK_a values of dyes were found to be about 6.8 for neutral red and 8.2 for methylene blue. At lower pH, the studied dyes were protonated, as shown in Fig. 1 and their ionic characteristics increase leading to less solubilization of both dyes in the hydrophobic micelles. In contrast, at higher pH, the dyes were deprotonated and their behaviors were like a hydrophobic molecule and easily solubilized into micelles. Thereby, dyes solubility is more important at basic pH leading to an increase in dyes extraction. One can notice that the effect of the pH solution was more significant on methylene blue extraction extent, and allows to suggest that the dissociated form of methylene blue is more hydrophilic than the neutral red cation.

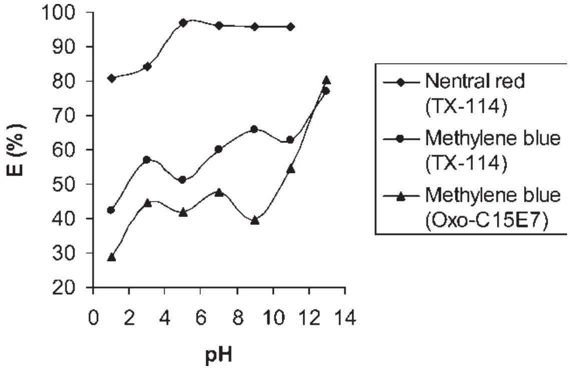


Figure 6. Effect of pH on the extraction percentage, E, in the systems. H_2O/TX-114/Neutral red; H_2O/TX-114/methylene blue; H_2O/Oxo-$C_{15}E_7$/methylene blue (4 wt.% of surfactants; 70 mg/L of neutral red; 7 mg/L of methylene blue; T = 35°C for TX-114; T = 55°C for Oxo-$C_{15}E_7$).

CONCLUSION

In the favourable conditions of (X_T, T), a first contact between the surfactant and neutral red solutions gave extraction percentages, around 99% for TX-114 and 98% for Oxo-$C_{15}E_7$, provided that the surfactant concentration should be higher than 10 wt.%. Hence, the neutral red concentration in the effluent was highly reduced with Oxo-$C_{15}E_7$ and even more with TX-114, in the first extraction process. Although, the solubility of methylene blue in water was less than that of neutral red, it was more difficult to be extracted than neutral red. Consequently, methylene blue concentration in the effluent was reduced no more than 7 times with TX-114 and twice using Oxo-$C_{15}E_7$. This was probably due to its weak interaction with the surfactant. In all cases, the extraction extent of both dyes, using TX-114 were higher than that obtained with Oxo-$C_{15}E_{7.}$ But this latter is more biodegradable (10, 11). On the other hand, an excessive rise of temperature beyond the cloud point is unfavorable for efficient extraction extent. However, in order to increase the concentration factor of the solute, a minimal volume fraction of coacervate (ϕ_C) should be obtained when the temperature increases. The sodium sulphate reduces the coacervate volume fraction because of the low cloud point of the surfactant solution, and also the increase of the extracted solute percentage. Both of the solutes, neutral red and methylene blue, were less extractible in acid pH solutions. The effect of pH is more significant on the methylene blue extraction extent. Indeed, the pH can be a key-parameter for surfactant regeneration in dyes extraction. The surfactant recycling in a cloud point extraction process seems to be possible for methylene blue extractions.

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