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Two-Phase Extraction of Dye Eosine B Imperial Red Using Non Ionic Surfactant Triton X-100 Iso-octyl Phenoxy Polyethoxy Ethanol and Dehydol LT7

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Abstract: The objective of this work is the extraction by coacervate of Eosin B. Its extraction has been achieved in aqueous solution by using the extractant triton X-100 (iso-octyl phenoxy polyethoxy ethanol) and dehydol Lt7 which are easily and rapidly biodegradable. The experimental results of the extraction, as a function of the concentration of the surfactant and the temperature, are expressed by the following three quantities: percentage of dye extracted (E), residual concentration of dye in the phase dilute (Xs, w) and volume fraction of the coacervate (Φc) at equilibrium. The results obtained for each parameter are represented on three-dimensional diagrams by using the empirical smoothing method. The calculated values are consistent with the measurements. For OXoC15E7, the extraction yields achieved under optimal conditions with TX-100 surfactant are 99.18% and 98% successively. The results revealed that the reduction of the solute concentration in the dilute phase is about 48 and 88.5 times with Dehydol LT7 and TX-100, respectively. Besides, the addition of sodium sulfate is also investigated.

Keywords: cloud point, non ionic surfactants, eosin B dye, cloud point extraction

1. INTRODUCTION

Synthetic dyes are widely used in printing, textile industries food, cosmetic, clinical, metal coloring, photography (sensitization), biology (staining of microscopic preparations), color indicators and medical care therapy (antiseptic) [32]. The research work carried out on these dyes, has shown that these chemical compounds have carcinogenic effects for humans and animals [11, 24, 34]. Both, the coloured untreated or partially treated discharges in the ecosystem cause a dramatic source of pollution, eutrophication, inhibition of photosynthesis in aquatic plants by reducing the penetration of light [38].

Eosine B is an acid, anionic used as a dye in cytology, for laboratory microscopy, to stain cell cytoplasm (plant or animal), collagen, muscle fibers, lymphocytes and bacteria. It is also used to stain raw wood of a burgundy red before application of varnish, disinfectant and drying in dermatology, hydrogeological tracer and Photopolymerization [8].It is an irritant, harmful if swallowed and causes serious eye damage [19].

The degradation of such dyes often requires a physico-chemical process and also a biological treatment chain ensuring the elimination of the various pollutants in successive

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stages [46]. The physico-chemical treatments commonly utilized include adsorption [5], coagulation [44], flocculation, precipitation, ozonation [9], membrane processes [45] ultrafiltration and nanofiltration [1], filtration with coagulation [18], ozonation with coagulation. Although, they are successfully used for the treatment of the industrial effluents, these separation methods have proven to be ineffective given the standards required for these discharges. As a matter of fact, the cloud point extraction treatment is proposed in this work as an efficient and reliable alternative [2].

The present work concerns the extraction of the problem point (PCE) of the dye, and it has been observed that this method simultaneously includes the problem point and the phenomenon of solubilization of the medium of nonionic surfactants. Besides, most polyethoxylated nonionic surfactants in aqueous solution form two phases above the cloud point (T,): a rich-surfactant phase (coacervate) and a dilute phase in which the concentration of the surfactant is close to its critical micelle concentration [38]. Therefore, due to the micellar solubilizing property of surfactants, the hydrophobic, amphiphilic or even ionic solutes can be extracted into the coacervate after increasing the temperature above Tc. EPCs using micelles or mixed micelles. It is a promising method for setting up a new large-scale process in which the aqueous phase is used [2]. The small volume of the rich phase in biodegradable surfactants obtained by the cloud point method makes it possible to design an extraction strategy requiring low cost, extraction efficiency and good efficiency more than those using organic solvents. This fact is particularly interesting, as the concept of "green chemistry" is obyed. This novel process called liquid-coacervate extraction or cloud point extraction (CPE), was first time applied to the separation of metal ions in the presence of a chelating agent [41]. It has been largely utilized to remove organic [16, 43]. Really, surfactants suitable for the cloud point extraction process should be poorly soluble in water (to limit the loss of surfactants in the dilute phase), have a low cloud point (to reduce the need for heating), solubilize pollutants, form low toxicity and of course biodegradable.

(The results of the cloud point extraction of eosin B with TX-100 are consistent with the conclusions drawn from the experimental results found for eosin. Indeed, the cloud point extraction of the dye eosin Y can be successfully used to remove color from wastewater using TX-100 as a nonionic surfactant. The extraction efficiency increases with temperature, TX-100 and NaCl concentration. It has been observed that for a dye concentration up to 10 ppm, 100% eosin Y dye removal is possible using 0.2 M TX-100 at 95°C. For a higher dye concentration up to 200 ppm, 87.5-100% eosin Y removal can be achieved using 0.1 M TX-100 and 0.2 M salt concentration (NaCl) at 80°C [37]).

2. MATERIALS AND METHODS

2.1. Reagents

The non ionic surfactant used in this work, the Triton X-100 (iso-octyl phenoxy polyethoxy ethanol), belonging to the family of polyethoxylated alkylphenols (formula [iso-C_8H_{17}-C_6H_4-(OCH_2CH_2) $_{10}$OH]), was supplied by sigma-aldrich, its critical micellar mass concentration (cmc) is 0.162g / L, its surface tension at cmc ϒcmc is 37.7 Dyne / cm, a surface saturation concentration is 3.30 .10^{10} mol / cm2, head area polar S is 49.6 A ° ^{2} and its cloud point at 1% by weight in water was at 70°C.

LOxo-$C_{15}E_7$ belonging to the family of commercial polyethoxylated alcohols which is dehydol LT7 (oxo-$C_{15}E_7$) of formula [Oxo-$C_{15}H_{31}$- (OCH_2CH_2) $_7$OH] its critical micellar mass concentration, cmc is 0.01144g / L, its surface tension at cmc is ϒcmc is 31.60 dyne / cm a surface saturation concentration is 1.89. 10^{10} mol / cm^2, area of the polar head S is 87.72 A ° ^{2}. This sample was provided by Henkel (Ain Temouchent, Algeria).

Eosine B obtained from an Algerian pharmacy, in the form of a 2% aqueous solution of disodium eosine B (double-distilled water 100 cc Eosine disodium 2 g) contained in a plastic bottle, its volume is 60 ml. For all the experiments we prepared an eosin B solution with a concentration of $8.01.10^{-4}$ mol/L equivalent to 500 mg / L. surfactants were used without further purification.

2.2. Apparatus and procedure

2.2.1. 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 the 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 single limpid phase which becomes cloudy, inducing a transmission decrease.

The extraction efficiency of eosine B can be calculated by using (2.1):

$$E = (C_iV_i - C_dV_d) / C_iV_i \tag{2.1}$$

where C_i is initial concentration of eosine B, C_d is concentration of eosine B in dilute phase, V_i is initial volume of solution (10 mL), and V_d is volume of dilute phase. The phase separation was carried out in a memert-oven with good temperature control. The dye concentration in the diluted phase was measured at the wavelength 516 nm using the DR6000 UV-visible spectrophotometer.

2.2.2. Procedure

We prepared an aqueous solution of eosine B of concentration 500 mg/L equivalent to 8.10^{-4} mol/L, to which we added crude surfactant at different concentrations ranging from 1% up to 6% (by weight) and 4% (weight) of sodium sulphate salt Na_2SO_4. The mixture was then introduced into 10 mL test tubes, depending on the clouding temperature of the surfactant, the test tubes were then heated in a thermostatic oven at a desired temperature for two hours to allow a complete decantation of the two phases (diluted phase and coacervate). We waited until their compositions were stabilized reaching equilibrium, and then we recorded the values of the volumes of the two phases. Thence, we took a sample of the diluted phase using a syringe, for spectrophotometric analysis.

3. RESULTS AND DISCUSSIONS

3.1. Phase diagram

3.1.1. Cloud point measurement

The cloud point (CP) of the water / surfactant / solute system refers to the temperature of a single clear phase, which becomes cloudy. Below this temperature a single phase exists, often called "pseudo phase". Really, beyond this point, cloudy solutions separate into two phases: one phase containing most of the surfactant called "coacervate" and another phase in which the concentration of the surfactant is near the critical micellar concentration [39] However, the solute (dye) in our case prevented the detection of the CP of such a system. It was therefore necessary to plot the phase diagrams of the binary water / surfactant systems in order to determine approximately the CP of the extraction domain for each surfactant.

3.1.2. Cloud point curve

The nonionic surfactants studied is the polyethoxylated alkylphenol (Triton X100) and the ethoxylated alcohol, dehydol LT7 (oxo-$C_{15}E_7$). We first established the binary water / surfactant diagrams as shown in Fig. 3.1.

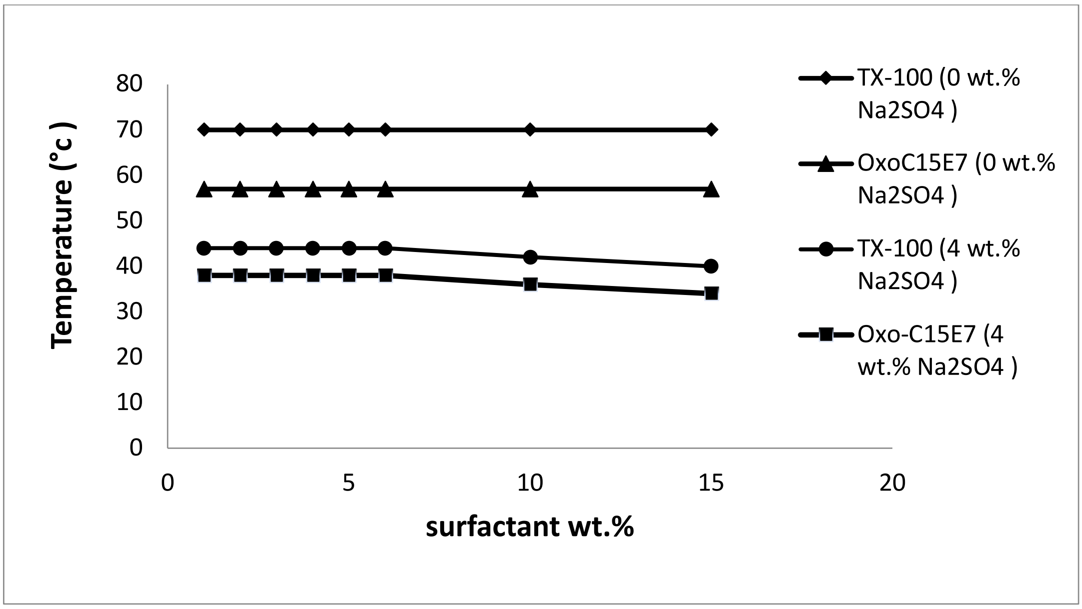

Fig. 3.1. Effect of sodium sulphate on the could point temperature of Oxo-C15E7 and TX-100

In a homologous series of polyethoxylated nonionic surfactants, the CP increases with the number (of ethoxylation (EO)) of ethylene oxides in the hydrophilic chain of the surfactant, due to the increase in the solubility of the surfactant in water. On the other hand, it decreases when the number of carbon in the hydrophobic chain increases. This is due to the reduction in the solubility of surfactants in water when the number of carbon in the hydrophobic chain increases. The CP of OXo-$C_{15}E_7$ surfactant 1% (wt.) was approximately 57°C lower than that of TX-100 at 1% (wt.) which was approximately 70°C (Fig. 3.1). This is due to the fact that TX-100 has one carbon atom less in the hydrophobic chain than OXo-$C_{15}E_7$ and counts three additional ethylene oxides in the hydrophilic chain [20].

The solubilisates can interact with the polar head of the surfactant or with its hydrophobic length after solubilization in micelles. Owing to their chemical nature, the organic compounds can vary the CP of the surfactants [20, 21]. In our case, as it can be seen in the extraction test, the phase separation of the water / TA / dye system was possible at that of the water / TA system because 0.5g / L of eosin has insignificant CP value.

3.2. Effect of Na_2SO_4 on cloud point

It is well known that the presence of electrolytes causes a decrease in the solubility of an organic compound in water [40].

In Fig. 3.1, we can clearly see that the electrolyte (Na_2SO_4) lowers the cloud temperature of the nonionic surfactants used. This is due to the dehydration of the ethylene oxide links which weakens the hydrogen bond between the water molecule and the polar head of the surfactant causing by the solvation of the ions [40] Electrolytes have the structuring properties of water, making it less available to hydrate micellar aggregates. This phenomenon, known as the salting-out effect, therefore imposes a weakening of the hydrogen bonds between the ethylene oxide units of the nonionic surfactants and the water of hydration, as it has been previously noticed by [24].

The release phenomenon is mainly due to the anion of the electrolyte. In effect, the anion SO_4^{2-} has twice as much effect on the CP as Cl^- [16, 17]. In contrast, the results demonstrated by [40] suggest that the effect of the cation does not appear to be significant compared to that of the anion. The cation has thus less influence although some of them can form complexes with the oxygen atoms of the ethylene oxide members of the surfactant.

Fig.3.1 shows the CP reduction of the Water / TX-100 and Water / OXo-$C_{15}E_7$ systems by the addition of amount of the electrolyte Na_2SO_4. Despite the drop in the temperature caused by the electrolyte, there was no change in the shape of the demixing curve. It is consequently suggested that the solvated electrolyte slightly weakens the hydrogen bond between the water molecule and the polar head of the surfactant due to the change in the continuous medium.

Fig.3.1 displays how much 4% (by weight) of Na_2SO_4 could lower the CP of 5% (by weight) of TX-100 solution from 70°C down to 44°C and 5% (by weight) of oxo $C_{15}E_7$ solution, the CP decreased from 57°C to 38°C after the addition of 4% (by weight) of Na_2SO_4 [21]. The cloudy temperature (T_c) is sensitive to external agents such as electrolytes, alcohols, organic additives and ionic TA [3].

In our case, the extraction of the dye was achieved in the presence of 4% (by weight) of Na_2SO_4 and the experimental study region for the extraction extends to a wider temperature range between 38 ° C and 51 ° C for dehydol LT7 (OXo-$C_{15}E_7$) and between 45°C and 54°C for triton X-100 (TX-100). The surfactant concentration range was from 2 to 6% (mass.) for dehydol LT7 and 1 to 5% (mass.) for triton X-100.

4. EXTRACTION OF EOSIN B

Surfactants are used in many industrial and domestic activities, for the formulation of detergents, shampoo, maintenance product, machining product, metal cleaning agent, mineral flotation agent, and textile auxiliaries.

In the present section, the nonionic surfactants are advantageous in the removal of the dye. In effect, the results of extracting eosin B from its aqueous solution at 500 mg/L with the surfactants TX-100 and oxo$C_{15}E_7$, are expressed by the answers are:

- mass percentage of solute extracted (E)
- concentration in mg/L of solute remaining in the diluted phase after extraction ($x_{s,w}$)
- volume fraction of coacervate phase (Φc) to be balanced [29, 30, 32].

The results are expressed by the smoothing method which consists in determining the mean of the experimental values, the polynomial constants which fit better the constants of a polynomial which best adjust the variation of the studied property. The verification of the relevance of the identification is carried out by comparison in plotting the calculated values against the experimental results. Besides, the quadratic empirical correlation is chosen to give the slope and the (R^2)-coefficient close to unity. Such a correlation allows the construction of response surfaces:

$$y = a_0 + a_1xt + a_2T + a_{12}x_tT + a_{11}x_t^2 + a_{22}T^2 \tag{4.1}$$

where “y” is the physico-chemical response of the studied property; T is the temperature; x_t is the mass percentage of the surfactant and a_i (i=0, 1, 2, 12, 11, 22) are the fitting parameters of the mathematical model used thoughout.

4.1. Cloud point extraction using polyethoxylated alcohol, oxo-$C_{15}E_7$ (dehydol lt7)

The quadratic equations for the three quantities (E; xs,w and Φc) whose reliability, have been verified are as follows:

$$E\ (oxoc_{15}E_7,\ eosine\ B) = -351{,}05-32{,}34X_t+21{,}78T+0{,}93X_tT-1{,}21X_t^2-0{,}27T^2 \tag{4.2}$$

$$Xs,w\ (Oxo\text{-}c_{15}E_7,\ eosine\ B) = 1734{,}36-24{,}15X_t-73{,}76T+0{,}41X_tT-1{,}37X_t^2+0{,}81T^2 \tag{4.3}$$

$$\Phi c\ (Oxo\text{-}c_{15}E_7,\ eosine\ B) = 0{,}673+0{,}394X_t-0{,}027T-0{,}003X_tT-0{,}055x^2_t+0{,}0003T^2 \tag{4.4}$$

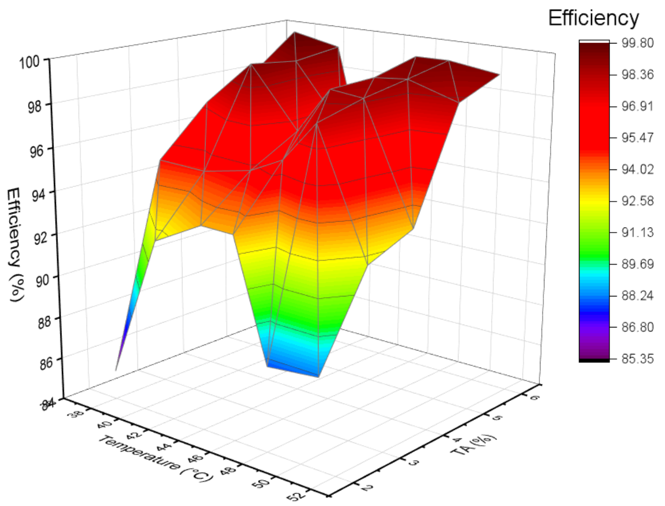

Fig. 4.1. Three-dimensional iso-response curve E = f (X_t,T) calculated by the quadratic model (4.2) for the system H_2O / Oxo-$C_{15}E_7$ / eosine B

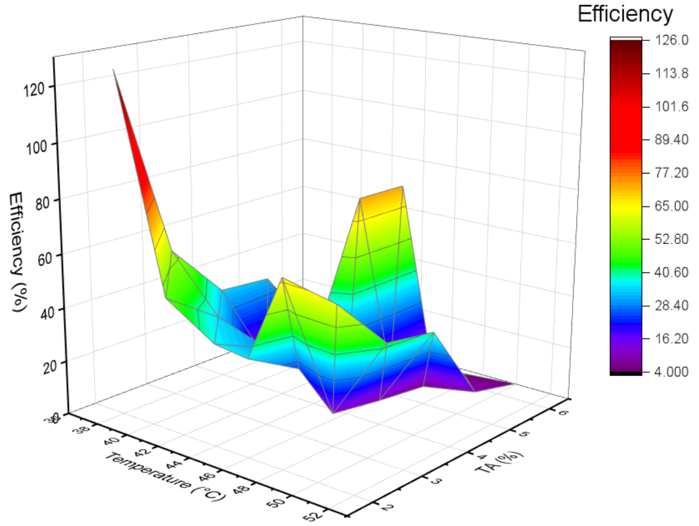

Fig. 4.2. Three-dimensional iso-response curve $X_{s,w}$ = f (X_t,T) calculated by the quadratic model (4.3) for the system H_2O / Oxo-$C_{15}E_7$ / eosine B

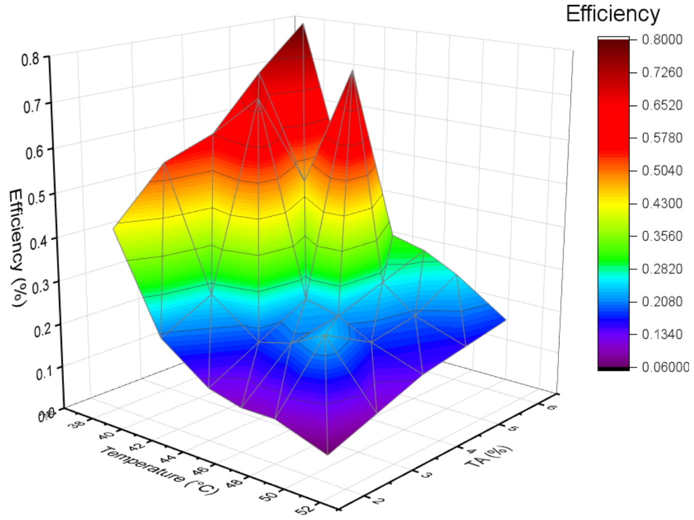

Fig. 4.3. Three-dimensional iso-response curve Φ_c = f (X_t,T) calculated by the quadratic model (4.4) for the system H_2O / Oxo-$C_{15}E_7$ / eosine B

The percentage of extracted dye (E) increases progressively, when both the initial mass percentage of the surfactant xt and temperature rise. The micelles of nonionic surfactant in which the dye has been solubilized, becoming more hydrophobic and concentrated in the coaceravat, when the temperature has risen above the CP causing an increase in the extraction. The extraction (E) decreases slightly with a strong increase in temperature above the CP and at low concentration of surfactant. Then the rise in temperature beyond the CP had a negative effect on the extraction power. Thus, the percentage of extraction of the eosine solute by dehydol lt7 (oxo-$C_{15}E_7$) is high in the region with a higher concentration of TA and at a temperature close to the CP. Indeed, at 5% by weight of oxo- $C_{15}E_7$ and 41°C, E reaches 98%.

Fig. 4.2, illustrates that the lowest residual concentration of the dye is obtained at high concentration of surfactant (X_t) and temperature close to the CP and $X_{s,w}$ decreases slightly with temperature. In practice at 5% in weight and 41 °C, the concentration of eosin in the effluent has been reduced from 500 mg L down to 7.67 mg/L (i.e. 65 times).

A minimum volume fraction of coacervate (Φ_c) must be obtained when the temperature increases for the treatment of the maximum effluent. The values calculated from the quadratic model (4.4), the Φ_c value is low at high temperature and at low concentration of the surfactant (X_t). However, a low Φ_c is unfavorable for the efficiency of the extraction (Fig.4.3); while in high concentration of surfactant, Φ_c increases due to the progressive enrichment of the coacervate in micelles. Then the optimization of the process must make a compromise between the three studied parameters E, $X_{s,w}$ and Φ_c.

Table 4.1. Experimental results of the extraction parameters E, $X_{s,w}$ and Φ_c

	(X_T,T)	E(%)	$X_{s,w}$(mg/L)	φ_C
eosine B; Oxo-$C_{15}E_7$	(2,38)	85.37	125.93	0.42
	(3,38)	94.88	55.51	0.54
	(2,46)	93.38	35.59	0.10
	(3,46)	96.04	24.70	0.20
	(2,51)	88.15	62.93	0.06
	(3,51)	92.23	43.08	0.10
	(5,51)	98.20	10.40	0.16
eosine B; TX-100	(2,45)	24.23	378.54	0.00
	(3,45)	68.54	206.77	0.24
	(2,48)	84.66	78.22	0.12
	(3,48)	96.35	22.23	0.18
	(2,51)	96.65	21.45	0.08
	(3,51)	98.22	11.39	0.12
	(5,51)	99.19	5.65	0.20

4.2. Cloud point extraction using polyethoxylated alkylphenol, Triton x-100

So, by using a polyethoxylated alkylphenol surfactant, Triton x-100 for the properties E, XS, w and Φc, the extraction of Eosin with TX-100, the quadratic model gives the following equations E, $X_{S,w}$, Φ_c:

$$E(\text{Tx-100, eosine B}) = -31{,}61+108.73x_t - 2{,}26T - 1.39x_tT - 4.61x^2 + 0.066T^2 \quad (4.5)$$

$$X_{s,w}(\text{Tx-100, eosine B}) = 9263{,}25 - 499{,}03x - 325{,}24T + 7.43x_tT + 17.24x^2 + 2.88T^2 \quad (4.6)$$

$$\Phi_c(\text{Tx-100, eosine B}) = -7.48 + 0.38x_t + 0{,}302T - 0{,}006x_tT + 3.10^{-18}x_t^2 - 0{,}0030T^2 \quad (4.7)$$

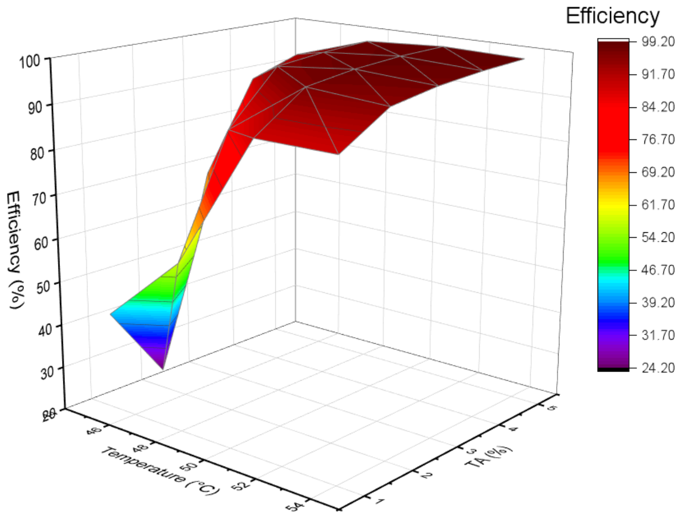

Fig. 4.4. Three-dimensional iso-response curve $E = f(X_t,T)$ calculated by the quadratic model (4.5) for the system H_2O / TX-100 / eosine B

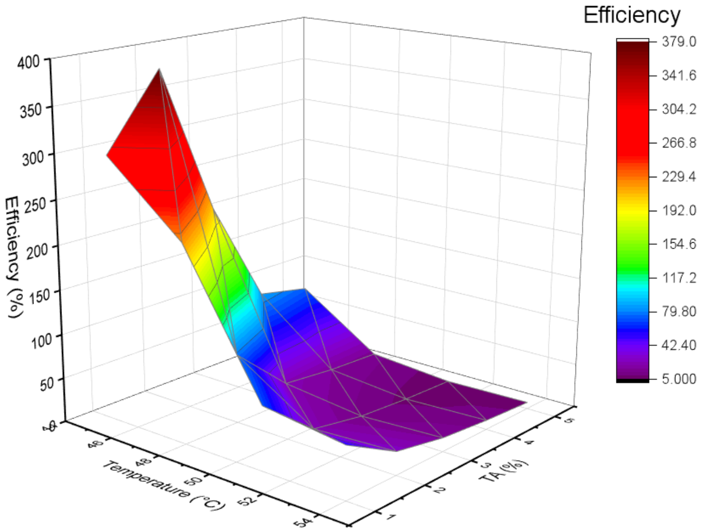

Fig. 4.5. Three-dimensional iso-response curve $X_{s,w} = f(X_t,T)$ calculated by the quadratic model (4.6) for the system H_2O / TX-100 / eosine B

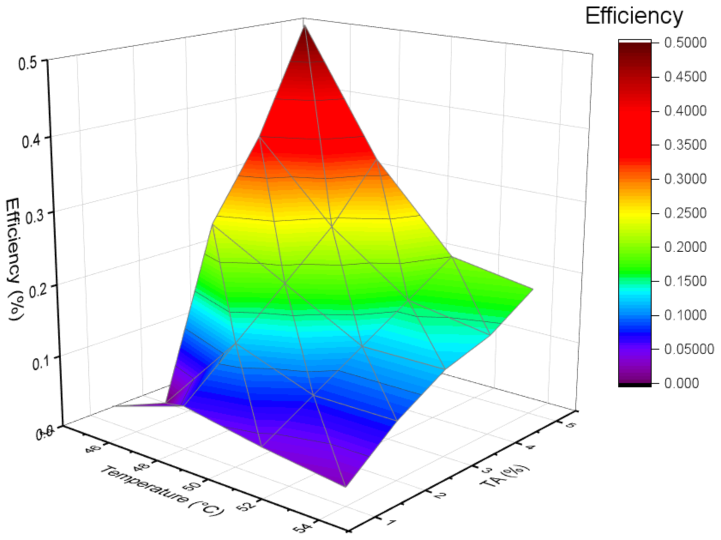

Fig. 4.6. Three-dimensional iso-response curve $\Phi_c = f(X_t,T)$ calculated by the quadratic model (4.7) for the system H2O / TX-100 / eosine B

The extracted amount of dye with TX-100 was higher than that achieved with Oxo $C_{15}E_7$ (Table 4.1 exp.). Therefore, the values of $X_{s,w}$ obtained with TX-100 were low compared to that given by oxo-$C_{15}E_7$ (table exp). Indeed at 5% oxo-$C_{15}E_7$ and 51°C, the Eosine B concentration in the effluent drops from 500 mg/L to 10.40 mg/L, i.e. 48.07 times less under the same conditions; the eosine B concentration in the effluent decreases drastically from 500 mg/L to 5.65 mg/L i.e. 88.49 times less using the TX-100.

5. CONCLUSION

Under optimal experimental conditions of (X_t, T), the percentages of extraction of the eosine B with the TX-100 surfactant are 99.19% and 98% for the Oxo-$C_{15}E_7$ at higher concentration of the surfactant (i.e. 5 % mass). On the other hand, in order to increase the concentration factor of the solute, a minimum of the volume fraction of the coacervate (Φ_c) should be obtained when X_t decreases. In addition, a minimum volume fraction of coacervate (Φ_c 0.1 for OXo-$C_{15}E_7$ and 0.08 for TX-100) was obtained at higher temperature. However, this latter has a slight effect on the extraction of the dye; the concentration of eosine B in the effluent was greatly reduced with OXo-$C_{15}E_7$ and even more with TX-100.

These two surfactants have almost the same number of ethoxylates (EO * 7). The results of the extraction show that the metylene blue (MB) is solubilized thanks to hydrophobic interactions with the micelles of the surfactants in the hydrophobic chain. Really, the solubilization of MB in the micelles seems to interact with the hydrophobic chain of TX-114 which is higher than that of OXo-$C_{15}E_7$. This allows to identify the solubilization site of the solute, namely the core of the micelles. Similar results were obtained from the CP of orange II with TX-100 and OXo-$C_{15}E_7$. In consequence, the results obtained in this study confirm the solubilization of the eosine B solution in the core of the micelles (close to the hydrophobic chain) of TX-100. The solubility of orange G is 50 g/L in water, whereas eosine B is 53.22%. Under the same operating conditions, the solubility of eosine B is 300 g/L (i.e. 98%), showing that the solubility of the pollutant in water cannot be a criterion indicative of the extraction yield.

On the other hand, the TX-100 is unfavorable from an energy point of view since it has a higher CP than that of OXo-$C_{15}E_7$. Hence it is possible for extracting with high energy input and less biodegradable surfactant than OXo-$C_{15}E_7$.

The comparison of the extraction yields by coacervate using the surfactant Oxo$C_{15}E_7$ with a concentration of approximately 4% of the dyes treated are as follows: NR (85.29%); MB (34.91%); orange G (51 %); orange II (98%) and eosin B (98%). It can be concluded that orange II and eosin B display strong interaction with Oxo$C_{15}E_7$.

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