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# Removal of chromium (III) by two-aqueous phases extraction

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## A B S T R A C T

Two-aqueous phase extraction of chromium (III) as a solute from their aqueous solutions was investigated using polyethoxylated alcohols (CiEj) as a biodegradable non-ionic surfactant in the presence of anionic sodium dodecylbenzene sulfonate (SDBS). First, the combined effects of chromium and surfactants mixture (anionic and non-ionic) on the cloud point temperature were determined. After this, the phase diagrams of binary systems water–surfactant (NW342 and C<sub>10</sub>E<sub>3</sub>) were traced. According to the given surfactants concentration, the extracted solute reached 98.5% and 60% for NW342 and C<sub>10</sub>E<sub>3</sub>, respectively at pH equal to 3. The addition of sodium chloride lowers the cloud point temperature of surfactant where the phenomenon of salting-out was pronounced. Under the optimal extraction conditions, the suggested extraction mechanism is based on chromium species-NW342 non-ionic surfactant micelles solvation. Since, the prevalence species (93.82%) were Cr(III)<sub>4</sub>(OH)<sub>6</sub><sup>6+</sup>, given by a theoretical calculation using CHEAQS V. L20.1. The first stage regeneration of NW342 surfactant was 27.82% at pH equal to 4.

2<sup>3</sup> factorial designs were employed for screening the factors that would influence the overall optimization of a batch procedure of sorption.

## 1. Introduction

Cloud point extraction (CPE) can constitute an interesting alternative to traditional liquid–liquid solvent extraction which is widely used in hydrometallurgy [1–3]. This method is based on supramolecular assemblies which result from the spontaneous association of a large number of components into a specific phase (i.e., micelles and vesicles), because the main advantage of micellar extraction is the achievement of high values of the concentrating factor using small-volume samples for analysis when compared with traditional extraction [1,2].

The solubility of non-ionic surfactants (NS) in aqueous solution is depressed above a well-defined temperature known as cloud point temperature ( $T_c$ ). By setting the solution at a temperature above  $T_c$ , the solution separates into a concentrated phase containing most of the surfactant (coacervate phase), which consists of large hydrated micelles, and a dilute aqueous phase of NS with a concentration level near the critical micelle concentration (cmc). The micellar phase is used for preconcentrating.

The NS chemistry showed that, NS dissolves in water due to hydrogen bond formation between oxygen atoms of polyoxyethyl chain and water molecules [1,4]. Heating of aqueous NS solu-

tions to a definite temperature ( $T_c$ ), results in destruction of these bonds and further separation of the system into two phases. Thus, CPE arises from the partitioning of a solute between the two water-based phases depending on its affinity towards the surfactant [2,5]. CPE can be used for the extractive preconcentration [2,6–12], separation and/or purification of metal ions [2,9,13–15], metal chelates [2,16–18], biomaterials [2,19,20] and organic compounds [3,21]. Currently, the use of surfactants grows rapidly in the daily needs for life and hygiene conditions. Nonetheless, the surfactants have a negative effect on surface and wastewater quality [3]. To reduce this shortcoming, the use of biodegradable surfactants turns out to be necessary. Many authors [3] proposed that the nature of the surfactants hydrophobic groups is determinant for their biodegradability, while the nature and position of hydrophilic groups displayed less effect. In this work, polyethoxylated and alkoxyated alcohols (Oxo-C<sub>10</sub>E<sub>3</sub> and NW342) have been used as non-ionic surfactants in the extraction of chromium (III) from nitrate medium due to their satisfactory biodegradable activities [3].

Possible synergy was also investigated by addition of sodium dodecylbenzene sulfonate (SDBS) anionic surfactant to these latter [22]. The effects of temperature, ionic-strength and surfactant concentration upon solute extraction extent were studied, beside the influence of solute and coacervate pH. Process modelling attempts were performed on the basis of the experimental data, in order to fully describe the individual effects of these parameters, along with their possible interactions.

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## 2. Experimental

### 2.1. Reagents

The surfactants used were obtained from fatty Oxo alcohol ethoxylation. The non-ionic surfactant triethylene glycol monodecyl ether (Oxo- $C_{10}E_3$ ) ( $T_c = 2^\circ\text{C}$  at 1 wt.% in water,  $M_w = 290$  g/mol) and polyoxyethylene 50-stearate (ethoxylated stearic acid, simulsol NW342) ( $T_c = 22^\circ\text{C}$  at 1 wt.% in water,  $M_w = 560$  g/mol) were kindly supplied by SEPPIC (Castres, France). Polyols-free Oxo- $C_{10}E_3$  compound was obtained by washing it with water at  $90^\circ\text{C}$ . Anionic sodium dodecylbenzene sulfonate and chromium salt ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) were provided by Fluka (Buchs, Germany). Potassium chloride salt was supplied by Merck (Darmstadt, Germany) and nitric acid (60%) was purchased from Cheminova (Madrid, Spain).

### 2.2. Apparatus

The determination of the cloud point was carried out using a Mettler FP 900 apparatus: temperature was measured for the sample introduced in a cell using a precise sensor incorporated in a small oven. At the bottom of the measurement cell there is a luminous source, and an optic driver which illuminates the sample. The crossed sample light was converted by photoelectric cell to an electric signal proportional to the transmitted light intensity. The transmission of light was measured continuously, while the cell temperature increases linearly according to the chosen heating rate. The cloud point designates the temperature of the unique limpid phase which becomes cloudy inducing transmission decrease.

Extraction experiments of chromium (III) were carried out using a Mettmer precise oven.

Chromium concentration was analyzed by means of a Jobin Yvon-ULTIMA 2R instruments inductively coupled to a Plasma spectrometer.

### 2.3. Extraction procedure

The initial chrome concentration used in water was 0.15 wt.%, which is higher than recommended by environmental laws in crude water treatment. For the extraction tests, 25 ml of solution containing the surfactant at different concentrations in wt.% and the solute (0.15 wt.% Chrome (III)) in demineralised water were poured into graduated cylinders and heated in a precise oven at  $40^\circ\text{C}$  for 24 h to reach equilibrium. The volumes of both phases were registered and the dilute phase was analyzed.

To study the experimental design, the Mathematica 5.0 software was used to calculate the equation coefficients.

## 3. Results and discussion

### 3.1. Combined effect of anionic and non-ionic surfactants on the cloud point

The variation of cloud point temperature (CPT) versus the surfactant concentration was studied within the range 1–15 wt.% of NW342 (Fig. 1). Low differences were observed in CTP when the non-ionic surfactant increases. The cloud point temperature was  $22.4^\circ\text{C}$  at 1 wt.%. Thus, NW342 was chosen for the extraction due to its low cloud point temperature and high density of the surfactant-rich phase, which facilitate phase separation.

The addition of SDBS anionic surfactant at 0.1 wt.% to NW342 shows that the CPT varies from  $22.4$  to  $46.3^\circ\text{C}$ . This difference in temperature was practically the same when NW342 ranges from 1 to 15 wt.%. This phenomenon is attributed to the ionization of the anionic surfactant in water [23]. The solvation of NW342 under

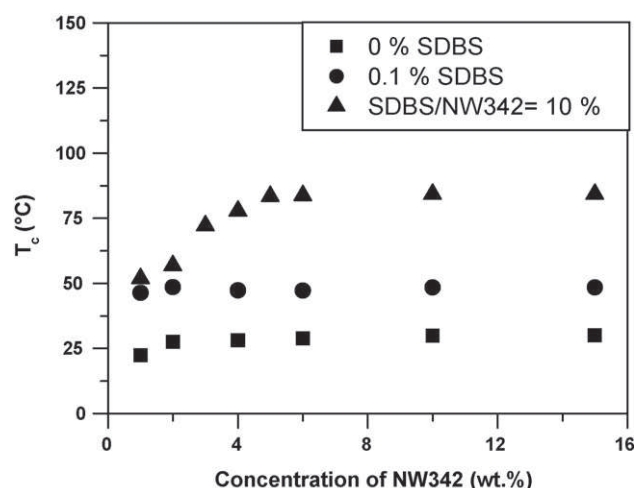


Fig. 1. Effect of SDBS on the cloud point temperature of NW342.

its molecular structure by SDBS increases the CPT. This temperature becomes higher when the concentration of SDBS increases. It achieves  $83.4^\circ\text{C}$  at SDBS-NW342 ratio equal to 10 in 15 wt.% of NW342.

Addition of SDBS at 1 wt.% of polyethoxy alcohol ( $C_{10}E_3$ ) induces a CPT increase from  $5.1$  to  $57.6^\circ\text{C}$  (Fig. 2). This can be explained in terms of autorepulsion tendency of non-ionic surfactants absence heads commissioned of anionic surfactants gathered to the surface [24]. It is only from the non-ionic surfactants site to the loaded head neighbourhood that the electrostatic repulsion is reduced encouraging the micellisation thus [25,26]. This one is distinctly bigger than in the case of NW342 (from  $22.4$  to  $46.3^\circ\text{C}$ ) but contrary to ethoxylated stearic acid surfactant (NW342), the cloud point temperature decreases while the concentration of  $C_{10}E_3$  increases. It can be assigned to the physico-chemical properties of this last.

In the other hand, when the NW342 and  $C_{10}E_3$  surfactants concentrations were fixed at 2 wt.% and the SDBS concentration ranges from 0 to 1 wt.%, the results showed that the CPT increase too from 5 to  $125^\circ\text{C}$  in the case of the  $C_{10}E_3$  surfactant. This variation is less marked in the case of NW342, while CP varies from 27 to  $80^\circ\text{C}$  (Fig. 3). Therefore the combination of SDBS with the extractant (NW342 or  $C_{10}E_3$ ) is interesting to achieve an adequate CPT of extraction.

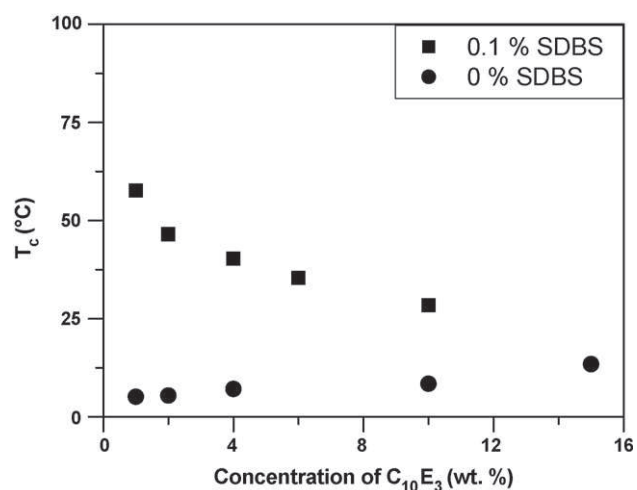


Fig. 2. Effect of SDBS on the could point temperature of  $C_{10}E_3$ .

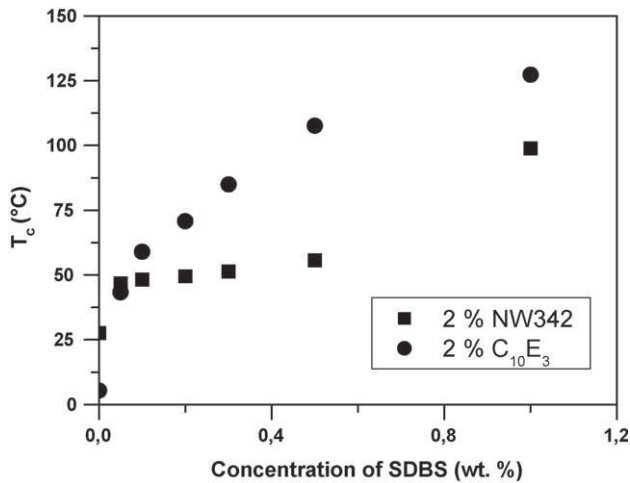


Fig. 3. Effect of anionic sodium dodecylbenzene sulfonate on the cloud point temperature of NW342 and  $C_{10}E_3$  solutions.

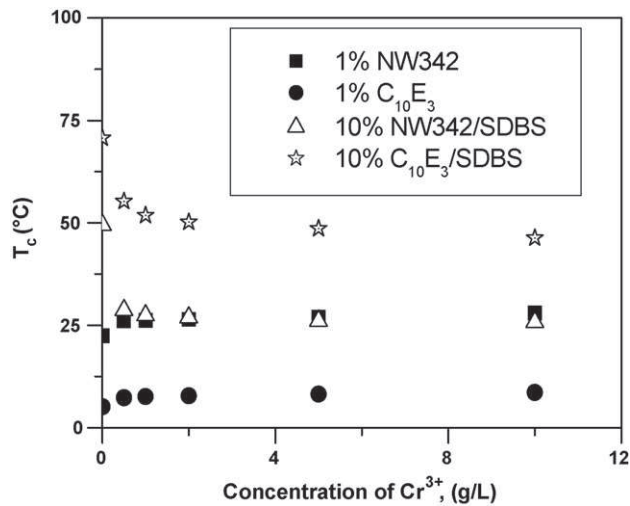


Fig. 4. Effect of  $Cr^{3+}$  concentration on the cloud point temperature of NW342 and of Oxo- $C_{10}E_3$ .

### 3.2. Chromium effect on the cloud point

Fig. 3 represents typical cloud point data for aqueous surfactant solutions as a function of the chromium concentration. At temperature above the extraction CPT ( $40^\circ C$ ), the solution is in the state of clouding and ready to be phase separated. For each surfactant

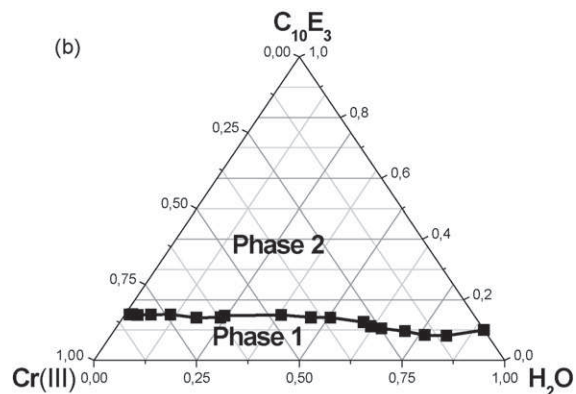
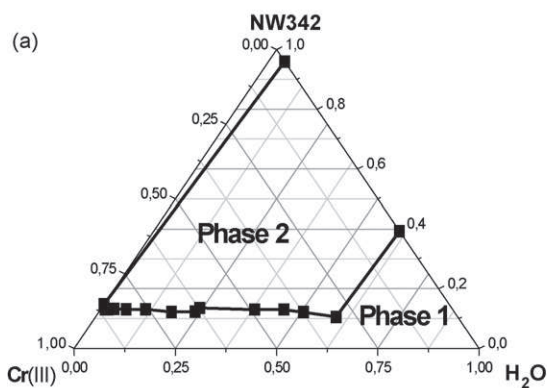


Fig. 5. Isothermal phase diagrams at  $40^\circ C$ : (a)  $Cr^{3+}/H_2O/NW342$  and (b)  $Cr^{3+}/H_2O/C_{10}E_3$ .

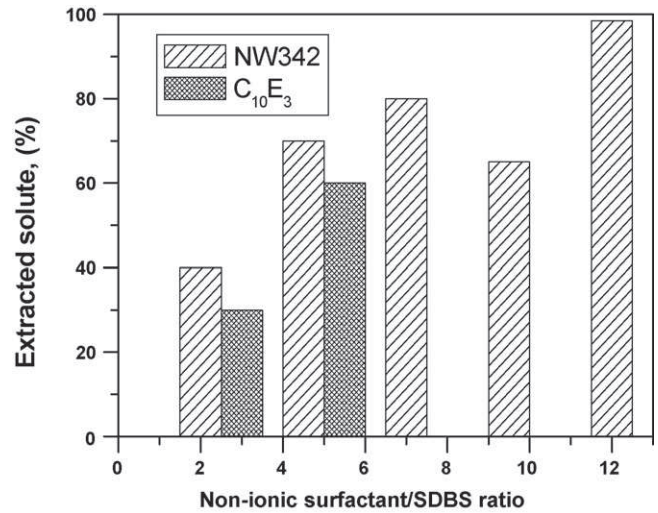


Fig. 6. Effect of non-ionic and anionic surfactants on the extraction extent in  $H_2O/NW342/SDBS/Cr^{3+}$  at  $40^\circ C$ .

(NW342 and  $C_{10}E_3$ ) taken separately, the cloud point increases partially in the first time then remains constant when the concentration of  $Cr(III)$  increases. In the case where each surfactant is combined with the SDBS (0.2 wt.%), the cloud point decreases from  $70$  to  $45^\circ C$  in the case of NW342 and from  $50$  to  $25^\circ C$  with  $C_{10}E_3$  initially remains constant beyond one of  $2\text{ g/l}$  of  $Cr^{3+}$  (see Fig. 4). One concluded that the addition of anionic sodium dodecylbenzene sulfonate exerts a significant effect on the CPT [24]; 0.2 wt.% of this last made it possible to increase the cloud point of the  $C_{10}E_3$  from  $5$ – $25^\circ C$  and from  $27$ – $45^\circ C$  with NW342.

### 3.3. Phase diagrams (isothermal diagrams)

By analogy with solvent extraction, chromium (III) being the “solute”, water and surfactant are considered as the “diluent” and the “solvent”, respectively (Fig. 5). At  $40^\circ C$ , the diagrams belong to type II (two of the binary systems partially miscible). In all cases, the second one-phase zone, near the  $H_2O$  apex, is too narrow to be visible on this scale (the aqueous solutions get cloudy as soon as the first drop of surfactant is added).

### 3.4. Extraction of soluble pollution

Fig. 6 shows the results obtained for chromium (III) with non-ionic surfactant/ SDBS ratio as surfactant after 24 h at the settling temperature.

The extractions carried out using C<sub>10</sub>E<sub>3</sub> were less efficient than those using NW342. The extraction efficiency even using C<sub>10</sub>E<sub>3</sub> never exceeds 60%. In contrast, CPE using NW342 as extractant, in the presence of fixed SDBS concentration equal to 0.2 wt.%, displayed an extraction effectiveness of 98.5%. Under these conditions, C<sub>10</sub>E<sub>3</sub> produced enhanced emulsion, and its separation becomes difficult even by changing the temperature, likely due to its high solubility in water, in correlation with its hydrocarbon hydrophilic chain.

### 3.5. Electrolyte effect on extraction

#### 3.5.1. Effect of sodium chloride on cloud point

For a concentration at 0.17 M (1 wt.%) of sodium chloride added to non-ionic surfactant solutions, the cloud point remains constant (Fig. 7). Beyond this concentration (higher than 0.17 M), sodium chloride lowers the cloud point [3]. This phenomenon is due to the salting-out of the surfactant, which is induced by the solvated electrolyte [5,27,23].

The result (Fig. 7) shows that 10 wt.% of NaCl (1.7 M) is able to lower the cloud point of non-ionic surfactant solutions from 38 to 5 °C. By increasing the salt concentration further (higher than 1.7 M), no change of CPT was observed. The salting-out effect favoured the weakening of surfactant head-water interaction [27]. Therefore, it is possible to reduce the heating energy cost of the large scale cloud point extraction [5], by adjusting the cloud point up to room temperature through a mere control of surfactant and salt concentrations.

The coacervate volume fraction ( $\Phi_c$ ) increases with added salt concentration ( $\Phi_c = 0.35$  at 3 wt.% of NaCl) and decrease beyond this salt concentration. These results were contrary with those obtained with polyethoxylated and alkoxyated alcohols surfactants. Nevertheless, by adding 5–20 wt.% of NaCl salt added to surfactants, the phase separation becomes very difficult [3]. However, the electrolyte does not contribute equally to the dilute phase and coacervate, and its addition increases the density of the dilute phase; this makes the separation of both phases to be easy in some non-ionic surfactant systems.

#### 3.5.2. Effect of sodium chloride on chromium extraction

The influence of ionic-strength on chromium extraction extent by NW342 non-ionic surfactant solution was studied in presence of the NaCl. It showed no significant effect, thus the yield extraction ranges from 95% to 100%. These results agree with the those pro-

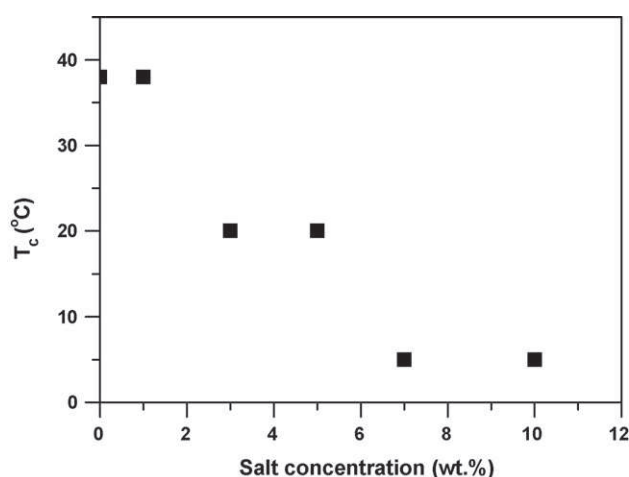


Fig. 7. Effect of NaCl electrolyte on the cloud point temperature in 6 wt.% NW342 and 0.2 wt.% SDBS surfactants mixture.

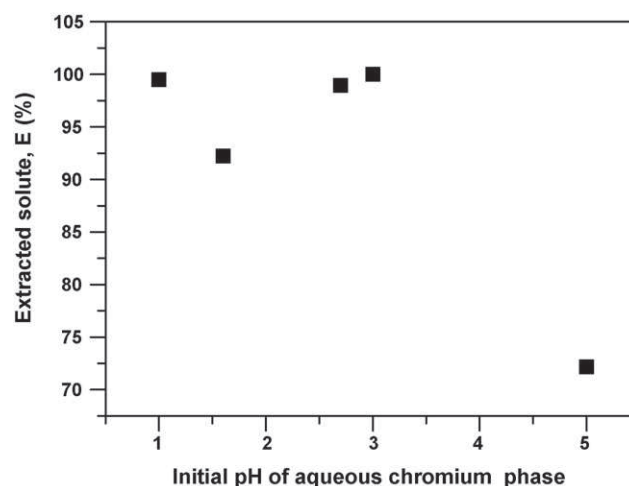


Fig. 8. Effect of initial pH on chromium extraction percentage (E) in the H<sub>2</sub>O/NW342-SDBS/chromium system at 40 °C.

vided by the literature [3,5] but no extraction takes place beyond 0.17 M (equivalent to 1 wt.%) in NaCl salt present in aqueous pollute, presumably due to the increase of the hydrocarbon solubilization capacity of non-ionic surfactant by lowering their CMC concentration. This behaviour may result from an increase in micellar number in this concentration range. The salting-out effect on both the cloud point temperature and solubilization capacity of surfactant has similar lower concentration limit, as already reported [3,23,5].

#### 3.6. The effect of initial pH on the chromium extraction extent

The pH at which NW342-SDBS surfactant at its maximum extracting capacity, 6 wt.% NW342 and 0.2 wt.% SDBS surfactants mixture, was investigated by variation of the initial pH range 1–5 for 24 h.

The solute-micelle interactions are strongly influenced by the solute ionization. Therefore, the metal chelates shared between the dilute phase and coacervate varies with the initial pH of the non-ionic surfactant solutions [28]. After the deprotonation (with KOH) or protonation (with nitric acid;  $pK_a = 0.525$ ) of chromium aqueous solution, different interactions may occur with the surfactant. From Fig. 8, the extracted chromium varies with pH and reaches 100% at pH equal to 3. Precipitation of chromium (III) appears at pH equal to 5, for this the extraction yield decreases to 72%. In these conditions, a different chromium species may solubilize and, consequently, a different amount of ionized solute can be extracted [23,29,30]. Hence, these dissociates have no more interactions with the polar head group of the surfactant and they dissolve in the coacervate water and not in the micelles [28].

In regard to the optimal extraction conditions, the pH variation between coacervate and diluted solutions was not observed. This suggested that the extraction mechanism is based on chromium species-NW342 non-ionic surfactant micelles solvation. Otherwise, the free Cr(III) is present in small quantity (6.18%) and the major species is Cr(III)<sub>4</sub>(OH)<sub>6</sub><sup>6+</sup> (93.82%). This species prevalence is estimated by a theoretical calculation using CHEAQS V. L20.1 [29].

Re-extracts chromium (III) was realized under these best conditions (6% NW342 + 0.2% SDBS), the coacervate obtained is recovered. At 1 ml of coacervate, 9 ml of water was added. Chromium (III) was re-extracted in aqueous diluted, then determined. The pH of coacervate was measured. Indeed, pH is the key-parameter for surfactant regeneration, because the extracted solute depends on its ionized form. From Table 1, the results show that, the regeneration of NW342 surfactant is possible with

**Table 1**  
Conditions of NW342 surfactant regeneration.

pH of the coacervate	wt.% of chromium release from the coacervate
2.2	0.0
2.9	7.78
3.1	1.06
3.6	0.51
4	27.8

ranging the coacervate pH from 2.2 to 4. Hence, 27.8% of chromium extracted at 40 °C can be released from the coacervate to a new dilute phase at pH equal to 4. This last pH is the maximum that can be reached using KOH (0.548 g/l) under these operating conditions.

### 3.7. Factorial design study

The study results of the extraction of chromium (III) by NW342–SDBS surfactant at optimal initial pH equal to 3, according to three variables: temperature  $T$  (°C),  $X$  (wt.% of solute concentration) and  $Y$  (wt.% of NW342 surfactant in dilute phase with fixed SDBS concentration equal to 0.2 wt.%), which are expressed in terms of the extraction yield value by the response  $Z$ . These results are subjected to an empirical smoothing. In this method, the experimental values can be used to determine the polynomial model constants (Eq. (1)) which are adjusted to the studied properties variations [31–35]. The analysis of the  $2^3$  experimental designs allow building (Table 2).

Preliminary observations show that the extraction yield of Cr(III) is significantly according to the experiment parameters, reaching values of 58.6–98.5 % under certain operating conditions (Table 2). This correlation allows building the response surface. From Table 2, it already appears that the highest yield extraction value (98.5 %) was obtained for minimal temperature value, minimal concentration of Chrome (III) and maximal concentration of surfactant in dilute phase.

**Table 2**  
 $2^3$  factorial design matrixes and the responses.

Experiment no.	Factor levels			Reduced values			Reponse function
	$T$ (°C)	$X$ (wt.%)	$Y$ (wt.%)	$X_1$	$X_2$	$X_3$	Extraction yield (Z%)
1	40	0.5	1.1	-1	-1	-1	58.60
2	60	0.5	1.1	1	-1	-1	70.13
3	40	2	1.1	-1	1	-1	60.23
4	60	2	1.1	1	1	-1	88.27
5	40	0.5	2.5	-1	-1	1	98.50
6	60	0.5	2.5	1	-1	1	90.19
7	40	2	2.5	-1	1	1	75.32
8	60	2	2.5	1	1	1	60.28
(9,10,11,12) <sup>a</sup>	50	1.25	1.8	0	0	0	70.29, 70.2, 70.41, 70.5

<sup>a</sup> Four additional tests at the central point (0,0,0) for the calculation of the Student's and Fisher's tests, using the normal rule of variance [32].

**Table 3**  
Model coefficients and their corresponding effects upon yield extraction of Cr(III).

Variable	Model		Expected effect on the yield extraction
	Coefficient	Value	
	$a_0$	75.19	High average extracting capacity of the NW342
$T$	$a_1$	2.02	Favourable individual effect of $T$
$X$	$a_2$	-4.16	Detrimental individual effect of $X$
$Y$	$a_3$	5.88	Favourable individual effect of $Y$
$TX$	$a_{12}$	1.22	Favourable binary interaction of $X$ and $T$
$TY$	$a_{13}$	-7.86	Detrimental binary interaction of $T$ and $Y$
$XY$	$a_{23}$	-9.10	Detrimental binary interaction of $X$ and $Y$
$TXY$	$a_{123}$	-2.90	Ternary detrimental interaction

The chromium (III) extraction modelling was achieved on the basis of the eight measured values, using Eq. (1):

$$Z(\%) = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{123}X_1X_2X_3 \quad (1)$$

where  $X_j$  ( $j = 1-3$ ) reduced variable which takes two values: -1 (low level) and +1 (high level); low level = 2 (low value - mean)/range; high level = 2 (high value - mean)/range; mean = (high value + low value)/2; range = (high value - low value).  $X_1$ ,  $X_2$ , and  $X_3$  are the reduced variables of  $T$ ,  $X$ , and  $Y$ , respectively.

Table 3 summarizes the coefficient values of the model, supposed to describe the individual effects of parameters, along with their possible interaction.

The individual effects and interactions of the parameters were discussed on the basis of the sign and the absolute value of each coefficient. These coefficients will define the strength of the corresponding effect involved and the way it acts upon yield extraction (favourable or detrimental), respectively. The first observations from Table 3 already allow to make the following statements:

- i. High extracting capacity of the NW342 ought to be obtained within the fixed parameter ranges, justifying there by the suitable choice of the limits.
- ii. The favourable individual effect of the surfactant concentration is three times stronger than the favourable individual effect of the temperature, while the solute concentration in aqueous phase does seem to play only one weak negative role within the investigated ranges.
- iii. Except between the temperature and chromium (III) concentration, all interactions are detrimental.
- iv. No synergy must be involved by the three parameters.
- v. Pronounced maximum with respect to NW342 concentration and, to a lesser extent, to the concentration of chromium (III) solution will characterize the response surface, giving rise to precise optimal values of these parameters.

**Table 4**  
Model adequacy tests and variance analysis.

Feature	Symbol/equation	Value
Parameter number	$P$	3
Level number	$L$	2
Number of experimental attempts	$N$	12
Number of tests at (0,0,0) point	$n$	4
Model variance	$v$	3
Average yield at (0,0,0)	$Z_0 = \sum Z_{oi}/4$	70.35
Random variance	$S^2 = \sum [Z_{oi} - Z_0]^2 / v$	0.039
Square root of variance	$S$	0.197
Risk factor (chosen arbitrary)	$\alpha$	0.05 (95%) <sup>a</sup>
Student's $t$ -test factor	$t_v$	3.18 <sup>b</sup>
Average error on the coefficient value (trust range)	$\Delta a_i = \pm t_{v, 1-\alpha/2} S / N^{0.5}$	$\pm 0.181$
Number of remaining coefficients	$R$	8
Model response at (0,0,0)	$a_0 (Z_{000})$	75.19
Discrepancy on average yield	$d = Z_0 - Z(0,0,0) = Z_0 - a_0$	4.84
Error on average yield discrepancy	$\Delta d = \pm t_{v, 1-\alpha/2} S (1/N + 1/n)^{0.5}$ with $N = 8$ and $n = 4$	0.362
Average yield for the eight attempts	$Z_m = \sum Z_i / 8$	73.57
Residual variance	$S_r^2 = \sum (Z_i - Z_m)^2 / (N - R)$	435.99
Degrees of freedom	$v_1$	3
Residual degrees of freedom	$v_2$	7
Observed Fisher's test	$F_{obs} = S_r^2 / S^2$	11179.231 <sup>c</sup>
Fisher-Snedecor law	$F_{\alpha, v_1, v_2}$	$F_{0.95, 3, 7} = 8.89^c$

<sup>a</sup>  $\alpha = 5\%$  was arbitrary chosen. In this case, one regarded that a 95% confidence may be satisfactory.

<sup>b</sup> Student tables with three degrees of freedom at a 95% confidence,  $t_{crit}(3; 0.05)$ .

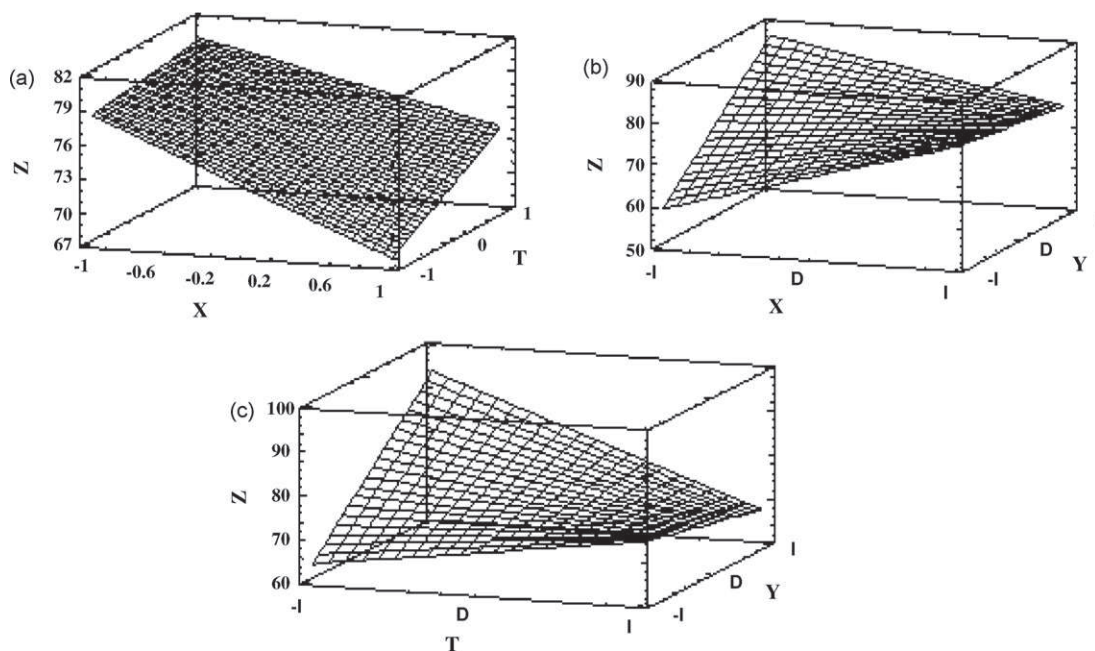
<sup>c</sup> See Fisher-Snedecor tables,  $F_{crit} = 8.89$ .

The optimum is supposed to be included in the vicinity around these central values, but accurate determination should take into account all the possible effects and interactions.

For the sake of reproducibility, one must check whether this model accurately describes the process investigated by determining which coefficients could be neglected, through Student's and Fisher's tests [31–33,35]. The model adequacy strongly depends on the accuracy of the experiment. In the current experiment, the main errors arise from the volume and weight measurements. For this purpose, four additional attempts at the central point (0,0,0) are required for estimating the average error in the value of each coef-

ficient, on the basis of the random variance. The calculations made are summarized in Table 4.

Thus, with a 95% confidence (i.e.,  $\alpha = 0.05$ ), and for a three variance (i.e., for four attempts at the central point), one assessed the value of  $t_{v, 1-\alpha/2}$  as being equal to (3.18;  $t$ -critical). Therefore, at this  $(1 - \alpha)$  level, the confidence range for all the coefficients estimated using eight runs ( $N = 8$ ), will be  $\Delta a_i = \pm 0.181$  at 95% confidence (see Table 4). From the Student's tests, it results that  $|\Delta a_i| < |a_i|$  for all coefficients (Eq. (1)) [36]. Consequently no coefficient will be removed from the mathematical model because they display significant effect upon the response function, being shaded by their average error. Consequently, the final form of the polynomial model



**Fig. 9.** Three-dimensional isoresponse curves of the yield extraction of chromium (III) by NW342-SDBS at fixed: (a) [NW342-SDBS] = 1.8 wt.%, (b)  $T = 50^\circ\text{C}$ , and (c)  $[\text{Cr}^{3+}] = 1.25 \text{ wt.}\%$ .

that describes the chromium (III) extraction by NW342–SDBS is the following, Eq. (2):

$$Z(\%) = 75.19 + 2.02X_1 - 4.16X_2 + 5.88X_3 + 1.22X_1X_2 - 7.89X_1X_3 - 9.10X_2X_3 - 2.90X_1X_2X_3 \quad (2)$$

This model is supposed to accurately fit to the extraction process of chromium (III) investigated herein. Thus in the vicinity of the expected optimal parameters values, it appears that only NW342 concentration and interactions between concentration of solute in aqueous phase and temperature are important effects on the chromium (III) extraction.

Furthermore, adequacy tests were applied to check whether the model calculated is valid within the parameter ranges investigated. For this purpose, a first method of adequacy calculations [37] showed that the observed Fisher's test (18,460) higher than critical Fisher's test (8.89), indicating that the model can be applied within the whole range investigated.

3D representations of the surfaces response function were plotted three times (Fig. 9a–c) by fixing successively the three parameters at the central values, and by using Eq. (2).

#### 4. Conclusion

Two-aqueous phase extraction experiments were carried out on H<sub>2</sub>O/CiEj/solute systems by merely contacting dilute aqueous solutions of chromium (III) with pure polyethoxylated alcohols (C<sub>10</sub>E<sub>3</sub>, NW342). The presence of SDBS modifies the cloud point temperatures of NW342 or C<sub>10</sub>E<sub>3</sub> non-ionic surfactants. This effect is marked in the case of NW342. In addition, the increase of chromium (III) quantity in aqueous solution increase partially the CPT. The contact between surfactant and effluent solutions (0.15 wt.% in Cr<sup>3+</sup>, pH 3) gave extraction yield at 98.5% for NW342 and 60% for C<sub>10</sub>E<sub>3</sub>, provided that the surfactant concentration is NW342–SDBS equal to 12.5 where SDBS was to 0.2 wt.%.

With higher salts concentrations (between 0.17 and 1.7 M), the cloud point of non-ionic surfactant weakens, making possible the adjustment of the cloud point to room temperature, reducing, hereby, the heating energy cost of the large scale CPE. In the meantime, the coacervate volume fraction increases ( $\Phi_c = 0.35$  at 3 wt.% of NaCl). In terms of chromium extraction, weak effect was observed, since the yield extraction ranges from 95% to 100%. The chromium extraction yield varies with pH and reaches 98.5% at pH equal to 3. Under these optimal extraction conditions, the suggested extraction mechanism is based on the solvation of chromium Cr(III)<sub>4</sub>(OH)<sub>6</sub><sup>6+</sup> species–NW342 non-ionic surfactant micelles. The prevalence of the latter (93.82%) is given by a theoretical calculation using CHEAQS V. L20.1. The first regeneration of the surfactant NW342 is of 27.82% to pH equal to 4. This study showed that the optimum initial conditions were: (i) minimal temperature (40 °C), (ii) minimal concentration of Cr<sup>3+</sup> (0.5 wt.%) and (iii) maximal concentration of surfactant in dilute phase (2.5 wt.% with fixed SDBS concentration equal to 0.2 wt.%).

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