Cloud point extraction of Telon Orange anionic azo-dye from aqueous sulphate solutions using Aliquat 336 ionic liquid/Tween 40 as extracting system: factorial design optimization methodology

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ABSTRACT

An anionic azo dye Telon Orange (TO) was extracted by cloud point extraction (CPE) from aqueous sulphate solutions using two commercial non-ionic surfactants, Tween 40 and ionic liquid A336. Modeling experimental extraction results of Telon Orange were performed by a factorial design of 2^4 variables, expressed by the following four parameters: initial pH (1–9), mass of Tween 40 (Tw) (1%–10%), mass of sodium sulphate (S) (1%–10%) and concentration of TO (C) (10–100 ppm). The cloud point study indicated that the addition of Na_2SO_4 significantly decreased the cloud point of the non-ionic surfactant Tween 40. Under the optimal extraction conditions, the extraction mechanism was based on the solvation of the micelles of the mixed (IL/non-ionic) system of the TO dye. The factorial design response revealed that a high removal of the dye was achieved with a maximum extraction near 97%. The CPE technique was found to be sensitive, simple, robust and in agreement with the fundamental principles of green chemistry.

Keywords: A336 ionic liquid; CPE; Factorial design; Saline media; Telon Orange; Tween 40

1. Introduction

The extensive use of synthetic organic dyes, especially in the textile industry, is a major source of dye-rich wastewater [1]. Even at low concentrations of 1 mg L⁻¹, these organic molecules have a negative impact on biodiversity and human health, not only due to their intrinsic toxicity, but also because of their partial oxidation in nature, which produces often harmful derivatives [2]. A special interest was shown here in an anionic dye, namely Telon Orange. It is recognised as a major pollutant, whose release into the environment is greatly facilitated by its high solubility in aqueous media. The azo dye was characterized by the presence within the molecule of an azo group (–N=N–) connecting benzene rings. This category of dye is currently the most widespread in terms of application, since it represents more than 50% of the world production of coloring matter [3,4].

In the last decade, increasing interest on the use of aqueous micellar solution has been found in the field of separation science and water treatment techniques, cloud point extraction (CPE) is particularly interesting being it is recognized as an efficient extraction method for dye, metal removal [5], organic compounds, and biospecies [1,2,6–8]. The cloud point extraction of non-ionic surfactants is very sensitive to certain compounds such as hydrocarbons, alcohols, electrolytes and chelating agents [2,8–10]. It is an eco-friendly method that requires small amount of non-flammable and non-volatile surfactant, and no organic solvent [2,8]. The difficulties of the process require optimization of all the operating parameters, and also its automation [11,12].

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The application of cloud point extraction (CPE) in analytical chemistry has received much attention and has given rise to numerous researches. Work has been conducted on the nature and extent of their effects and the mechanisms involved [2,10]. The surfactant plays a very important role in the design of the cloud point extraction process. The analysis of its effect is therefore essential to determine its influence on the cloud point temperature (CPT) of the extraction system. When a surfactant is dissolved in an aqueous medium, the hydrophobic tail has a weak interaction with water molecules. In contrast, the hydrophilic head has a strong interaction with water molecules via dipole–dipole or ion–dipole forces. This strong interaction with water molecules allows surfactants to be soluble in water [13,14]. This means that the much weaker Van Der Waals forces break the much stronger hydrogen bonds between water molecules. The surfactants begin to aggregate at certain concentrations as the hydrophobic tails avoid contact with water. Thus, micelles form with the hydrophobic tails directed inwards and the hydrophilic head groups directed towards the water.

In order to obtain maximum efficiency in the separation and preconcentration of the analyte, the mixed micellar extraction system was also deployed in the CPE. Mixed ionic–nonionic surfactant systems are considerably more important in many applications [15,16]. When rigorously optimized, this technique should not only provide high performance for dye removal from wastewater, but also valuable results for considering a low-cost, large-scale technology. The CPE process requires experimental rigor, therefore optimization is more than necessary [17]. A judicious approach was adopted using a factorial design of experiment to model the extraction process of orange telon from a sulphate medium as a function of four parameters (initial pH, mass of Tween 40, mass of sodium sulphate, and concentration of TO) in order to simulate the individual effects and possible interaction of these parameters [2,7].

2. Experimental

2.1. Materials

Polyoxyethylenesorbitanmonopalmitate (Tween 40, with HLB = 15.6) a non-ionic liquid which the critical micelle concentration (CMC) was of 2.6×10^{-2} M at 25°C (Fig. 1a).

An ionic liquid of ammonium A336 (tricaprylmethylammonium) (Fig. 1b) was also employed as the extractantagent (Molar mass = 404.16 g mol⁻¹, Density = 0.884 g cm⁻³, Boiling point = 225°C, Viscosity = 1,500 mPa·s at 30°C). The textile dye Telon Orange (TO) was supplied by Complex Textile (Soitex) in Tlemcen, Algeria. TO has the following chemical formula: monosodium salt of 6-hydroxy-5-(phenylazo)-naphthalene sulphonic acid or $C_{16}H_{11}N_2NaO_4S$ with a molecular weight MW = 350.32 g mol⁻¹ (Fig. 1c). pH values of solutions were adjusted in the range 1–9 by adding appropriate amounts of 0.1 M sulphuric acid or 0.1M sodium hydroxide. The pH measurements were performed using a HANNA Instruments HI 2210 potentiometer. Sodium sulphate (Na_2SO_4) was used to decrease the cloud point temperature. All reagents were supplied by Sigma-Aldrich (Sarl Prochima Sigma-Tlemcen, Algeria) and were of analytical purity.

Telon Orange like any anionic dyes is colored with absorption band at λ_{max} = 497 nm, and is highly soluble in water [18]. Stock dye solutions (200 mg L⁻¹) were prepared by dissolving 2 g of TO dye in 1 L of bi-distilled water. Once prepared, a stock solution of dye was kept in a dark vessel for further experiments. Experimental solutions of desired concentration were obtained by further dilution.

2.2. Cloud point temperature study

The cloud point study involves determining the CPT of the nonionic surfactant (Tween 40). The amount of the used Tween 40 varies from 1% to 10% (% w/w). The influence of adding electrolytes such as salts (Na_2SO_4, NaCl, and $Na_2S_2O_3$) alkanes and alcohols was studied using amounts of 1%–10% (w/w) in Tween 40 solutions.

The determination of the CPT was carried out on a series of samples containing 10 mL of aqueous solutions of Tween 40, placed in a thermostated bath at 98°C; then decreased from 1°C/min until trouble appears. The turbidity was measured on a TB 300 IR turbidimeter.

2.3. Extraction tests

Coacervate extraction experiments were performed in a thermo-circulating bath (Lab. Tech. Daihan, Co., LTD) is according to published literature [19]. Extraction of TO from aqueous medium was performed by CPE (Fig. 2) in
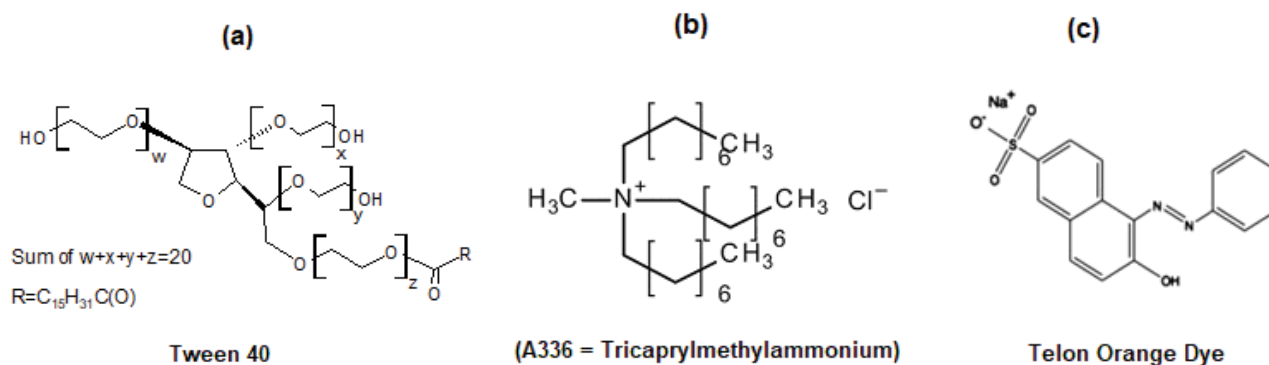

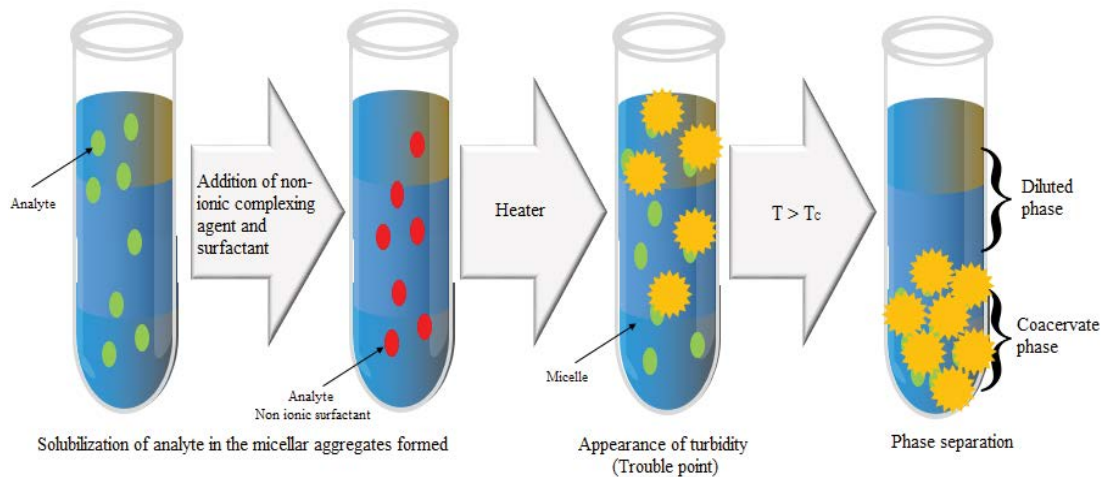Fig. 1. Chemical structure of Tween 40 (a), A336 (b) and Telon Orange dye (c).

Fig. 2. Procedure for dye extraction by CPE.

10 mL graduated test tubes containing mixtures of Tween 40 (w/w), ionic liquid (w/w) and TO solution. After shaking the mixture and allowing it to stand for 30 min at the cloud point without agitation followed by centrifugation for 5 min with a SIGMA 2–6E device. The coacervate phase was separated from the dilute phase.

Analysis of the concentration of the TO dye in the dilute phase was performed using UV-visible spectrophotometry (Analytik Jena SPECORD 210 plus instrument) (Fig. 3). From the calibration curve; the resulting equation $Abs = f(C_{TO})$ was a straight line through the origin in the range of 1 to 100 ppm ($R^2 = 0.998$). The initial pH of the solution was varied from 1 to 9.

3. Results and discussion

3.1. Effect of additives on the CPT cloud point

3.1.1. Effect of non-ionic surfactant Tween 40

A first overview of the effect of the variation of the amount of the nonionic surfactant from 1% to 10% revealed three steps (Fig. 4). Two steps of stable cloud point temperature (CPT) at 95°C from1% to 2% of Tween 40 and at 90°C from 4% to 10% of Tween 40 separated by a temperature decrease from 95°C to 90°C for increasing Tween 40 amount from 2% to 4%.

The surfactant plays a very important role in the design of the cloud point extraction process. Increasing the concentration of Tween 40 causes an increase in viscosity which leads to a decreased in the volume of the aqueous phase [20] and increased volume of the surfactant phase in the coacervate phase. Therefore, the surfactants are forced to the interfaces of the system, where hydrophobic tails were arranged in such a way as to maintain a minimum contact with the water molecules [13,21].

3.1.2. Effect of salts on the cloud point temperature of Tween 40

To study the influence of salts on CPT, several experiments were performed with mass levels (1%–10%) of salts
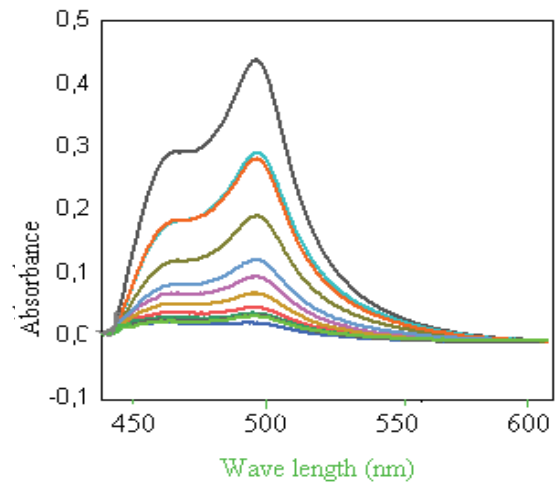

Fig. 3. Spectra of different experiments (pH_i = 5.6, TO concentrations: 5–100 ppm).

Na_2SO_4, NaCl, and $Na_2S_2O_3$, with a mass ratio of Tween 40 of 1%. According to Fig. 5, a clear decrease of the cloud point temperature "CPT" with the addition of the three salts was revealed in the following order: NaCl, $Na_2S_2O_3$, Na_2SO_4.

This is due to the dehydration of the ethylene oxide bonds by weakening the hydrogen bond between the water molecules and the polar head of the surfactant due to the salting out of the ions [2,9,10]. This reduction is called "salting out" and the phenomenon follows the arrangement of anions in the Hofmeister series [21–23]. Salinity plays an important role in phase separation but has no effect on extraction kinetics [24].

3.1.3. Effect of alkanes on the cloud point temperature of Tween 40

The effect of alkanes on the cloud point of Tween 40 was studied by varying the amount of the two compounds (hexane and heptane) from 1%–10% for a constant Tween 40 content of 1% (Fig. 6). Increasing the amount of the two
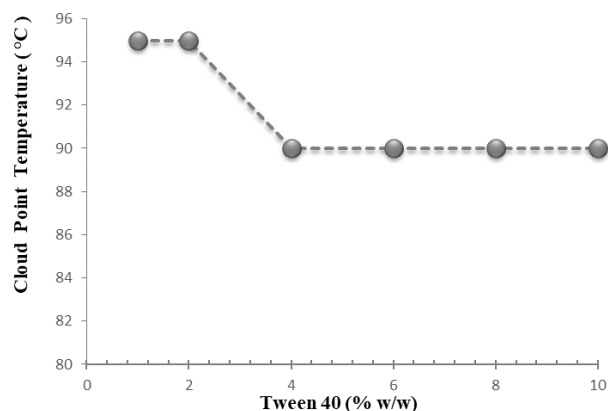
Fig. 4. Effect of the quantity of Tween 40 on the cloud point temperature Tween 40: 1%–10% (w/w).
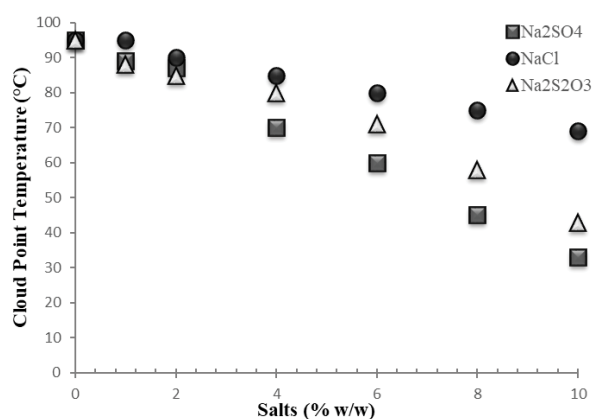

Fig. 6. CPT vs. alkane amount (Hexane and Heptane) Tween 40: 1% (w/w).

Fig. 5. Effect of salt quantity on cloud point temperature NaCl, Na$_2$SO$_3$, Na$_2$SO$_4$, Tween 40: 1% (w/w).

alkanes up to 2% (w/w) induced a marked decrease in cloud point temperature followed by a linear step beyond this threshold amount of alkane.

According to the results obtained, the cloud point temperature decreased with the addition of the two non-polar alkanes (hexane, heptane) which are comfortably solubilised in the inner core of the micelle between the ends of the hydrophilic polyoxyethylene group of the surfactant molecule, occupying the hydrocarbon port of the micelle. This solubilisation induces a change in the micelle hydration of the non-ionic surfactant Tween 40. As a result, the number and growth of micellar aggregations and the hydrophobic environment of the micelle increase with the amount of alkanes. This suggests that in the presence of non-polar alkanes, the dielectric constant of the micellar solution decreases, thus reducing the solubility of the surfactant in solution [25].

3.1.4. Effect of alcohols on the cloud point temperature of Tween 40

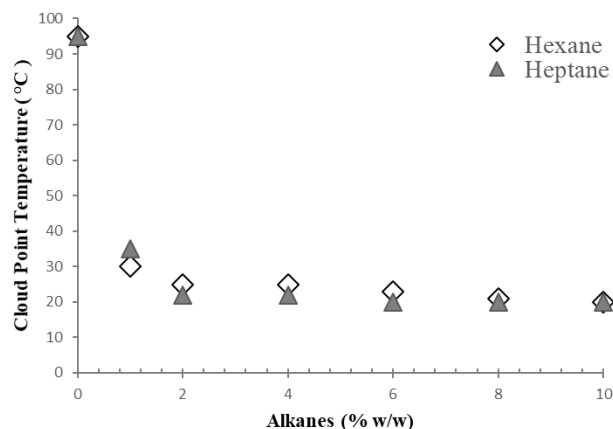The effect of alcohols (methanol, n-butanol and n-hexanol) on the cloud point of Tween 40 was examined by fixing the Tween 40 at 1% (w/w) and changing the alcohol content from 1% to 10% (w/w). The results obtained are shown in Fig. 7.

It was observed that methanol at a mass ratio varying between 1% and 10%, the cloud point temperature is constant at a temperature of 95°C; in addition this temperature decreased from 95°C to 28°C for a concentration of n-hexanol varying from 1%–10% respectively. The decrease of the cloud point temperature of the non-ionic surfactant solutions containing the same amount of alcohols follows the following order: n-hexanol > n-butanol > methanol. The presence of alcohol altered the intermicellar interactions as well as the hydration of the micelles: short chain alcohols such as methanol are fully miscible, whereas the longer carbon chain alcohols "n-hexanol" are only partially miscible in the micelles and absorb on their surface, causing the growth of micelles and the decrease of the cloud point temperature of the aqueous Tween 40 solution. The results described above are in agreement with other studies on the CPT behaviour of non-ionic surfactants with alcohols [25,26].

3.2. Effect of time on extraction

On three tubes, under the same conditions, the two phases were separated at different times: 30, 60 and 120 min. The results are presented in Table 1.

The Table 1 depicts the effect of time on the extraction efficiency of TO. It is clear from the table that the equilibrium time was obtained at 30 min. The anion of Telon Orange dye, negatively charged, reacts with the ammonium cation of the Aliquat A336, forming micelles in the coacervate phase [27].

3.3. Factorial design study

The preparation of the experiment consists first of finding all the factors that can influence the studied process, then the fields of study of each of these factors. This step is carried out using preliminary work on the cloud point. In order to quantify the effects of four variables on the dye removal, a two-level factorial design (low and high) of experiments was adopted.

3.3.1. Experimental design

The study of the effects at two levels based on the factorial design of 2^4 experiments of the four factors: initial pH (pH), amount of Tween 40 (Tw), amount of sodium sulfate (S) and TO concentration (C). The A336 concentration was 100 ppm. Moreover, each of them was studied in an identical domain of influence as shown in Table 2. On the other hand, it is essential to note that all the experiments in this factorial design (2^4) were performed at $T = 30°C$.

Thus, 16 experiments with all possible combinations of variables were performed, and a matrix was established according to their high (+1) and low (–1) levels, to which three central points (0) were added to estimate the experimental error. The results of the TO dye extraction were expressed in terms of extraction yield (Table 3).

3.3.2. Design modeling

The extraction yield (Y, %) was calculated according to Eq. (1):

$$Y(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final aqueous phase concentrations, respectively. The coded model used for 2^4 factorial designs was as follows:
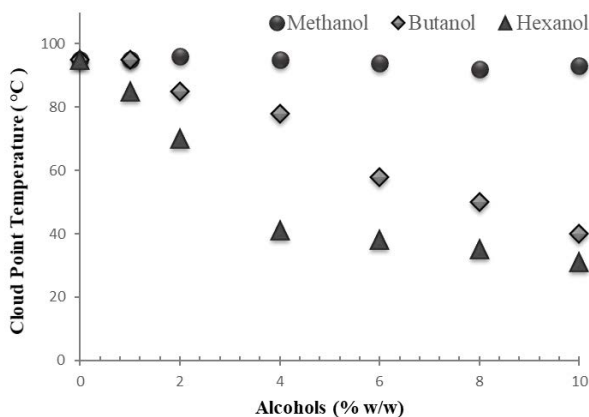

Fig. 7. CPT vs. alcohol amount (Methanol, n-Butanol and n-Hexanol) Tween 40: 1% (w/w).

$$Y(\%) = a_0 + \sum_1^4 a_i X_i + \sum_{i=1,j=2}^{i=3,j=4} a_{ij} X_i X_j + \sum_{i=1,j=2,k=3}^{i=2,j=3,k=4} a_{ijk} X_i X_j X_k + a_{1234} X_1 X_2 X_3 X_4 \tag{2}$$

where a_0 represents the overall mean and a_m ($m = i, ij, ijk, ijkl$) represents the regression coefficient corresponding to the main interactions and effects of the factors.

The empirical relationship between experimental parameters and extraction yield was found as it is shown in Eq. (3).

$$Y(\%) = 69.931 + 2.987\ X_1 + 4.387\ X_2 + 9.201\ X_3 + 0.522\ X_4 \\ + 1.308\ X_1 X_2 + 2.134\ X_1 X_3 - 1.464\ X_1 X_4 - 2.127\ X_2 X_3 \\ + 1.843\ X_2 X_4 + 0.972\ X_3 X_4 - 0.518\ X_1 X_2 X_3 - 0.747\ X_1 X_2 X_4 \\ + 0.065\ X_1 X_3 X_4 + 0.478\ X_2 X_3 X_4 - 1.668\ X_1 X_2 X_3 X_4 \tag{3}$$

For reasons of reproducibility, it is necessary to verify that this model accurately describes the process studied by determining which coefficients may be neglected, using Student's *t*-test and Fisher's test. To this end, three additional attempts at center points (0,0,0) are required to estimate the average error in the value of each coefficient as a function of random variance. The calculations are summarized in Table 4.

Thus, with 95% confidence ($\alpha = 0.05$), and for two variances (three attempts at the central point), the value of t_v, $1 - \alpha/2$ was calculated as 4.3. Therefore, and at $(1 - \alpha)$, the confidence interval for all the estimated coefficients, using 19 tests ($N = 19$), were $\ddot{A}a_i = \pm 1.06$.

From the Student's *t*-tests, it results that $|a_i| < |\Delta a_i|$ for the effect of the factors a_4, a_{34}, a_{123}, a_{134} and a_{234} from which they must be removed from the model because they do not display significant effect upon the response function. The final form of the polynomial model that describes the extraction of TO dye was as follows:

$$Y(\%) = 69.931 + 2.987\ X_1 + 4.387\ X_2 + 9.201\ X_3 + 1.308\ X_1 X_2 \\ + 2.134\ X_1 X_3 - 1.464\ X_1 X_4 - 2.127\ X_2 X_3 + 1.843\ X_2 X_4 \\ - 1.668\ X_1 X_2 X_3 X_4 \tag{4}$$

Table 1
Time effect on the extraction efficiency ($pH_i = 4.5$, Mass % Tween 40 = 5, Mass % of Na_2SO_4 = 5, TO concentration = 50 ppm)

Time (min)	30	60	90	120
Y (%)	69.2	70.4	70.9	71.2

Table 2
Factors and their levels used in the 2^4 factorial design experiment

Settings	Reduced variable	Value of the actual variable	
		Minimum	Maximum
pH_i	X_1	1	9
Mass % Tween 40 (Tw)	X_2	1	10
Mass % of sodium sulfate Na_2SO_4 (S)	X_3	1	10
TO concentration (C) (ppm)	X_4	10	100

Table 3
Experimental matrix data

Tests	Reduced variables				Yield, %
	X_1	X_2	X_3	X_4	
1	−1	−1	−1	−1	51.76
2	+1	−1	−1	−1	55.18
3	−1	+1	−1	−1	61.75
4	+1	+1	−1	−1	69.56
5	−1	−1	+1	−1	75.22
6	+1	−1	+1	−1	83.09
7	−1	+1	+1	−1	67.46
8	+1	+1	+1	−1	90.56
9	−1	−1	−1	+1	53.18
10	+1	−1	−1	+1	45.05
11	−1	+1	−1	+1	65.37
12	+1	+1	−1	+1	70.29
13	−1	−1	+1	+1	70.84
14	+1	−1	+1	+1	83.54
15	−1	+1	+1	+1	85.58
16	+1	+1	+1	+1	96.41
17, 18, 19*	0	0	0	0	69.10, 68.15, 68.95

*Three additional tests at the central point (0, 0, 0) for the calculation of the Student's *t*-test and Fisher's tests, using the normal rule of variance.

Table 4
Model adequacy tests and analysis of variance

Characteristics	Symbols	Values
Average yield at (0,0,0)	Y_0	68.07
Random variance	S^2	1.16
Square root of the variance	S	1.08
Risk factor	α	0.05 (95%)[a]
Student's test factor	$t\nu$	4.3[b]
Average error on the coefficient value	Δa_i	±1.06
Number of remaining coefficients	R	10[c]
Model response to (0,0,0)	$a_0\ (y_{000})$	69.931
Discrepancy on average yield	D	1.86
Average performance of the 19 attempts	Y_m	69.64
Residual variance	Sr^2	337.87
Fisher's test	F	291.06[d]

[a]α = 0.05 was arbitrary chosen. In this case, one regarded that a 95% confidence may be satisfactory.
[b]Student law of freedom at a 95% confidence.
[c]After removing the less significant coefficients.
[d]See Fisher–Snedecor tables.

Fig. 8 presents the values of the coefficients of the model, to describe the individual effects of the parameters, and their eventual interactions. On the basis of the sign and the absolute value of each coefficient, the individual effects and the interactions of the parameters were discussed. These characteristic coefficients will define the strength of
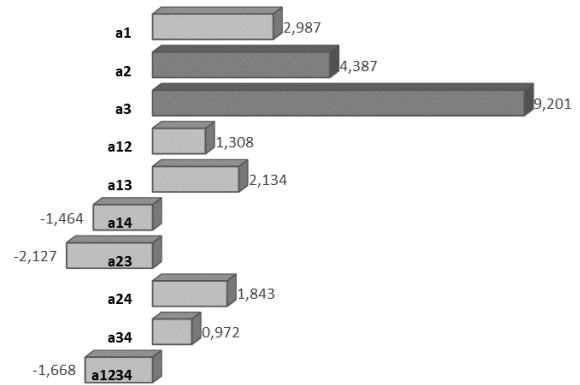

Fig. 8. Model coefficients and their corresponding effects upon extraction yield of TO dye.

the corresponding effect involved and how it acts on the extraction yield (favorable or unfavorable), respectively.

The preliminary observations in Fig. 8 already allow the following statements to be made:

- The principal effect of the four factors was favorable: initial pH (pH_i), amount of Tween 40 (Tw), amount of sodium sulfate (S) and TO concentration (C).
- The effect of the amount of Na_2SO_4 salt is three times stronger than that of the pH effect and almost more than twice the effect of the amount of surfactant "Tween 40". While the initial pH of the aqueous phase seems to play only a weak positive role in the studied range.
- For the second degree interactions, except between pH and TO dye concentration and between the amount of Na_2SO_4 and Tween 40, all interactions are favorable.
- No synergy should occur simultaneously between the three parameters.

The adequacy of the model strongly depends on the accuracy of the experiment. Before proceeding with the interpretations, it is necessary to verify the smoothing of the results. It is therefore necessary to ensure that the selected mathematical model approximately represents the measured responses (extraction yield).

The plot of the observed data against that obtained from Eq. (4) presented in Fig. 9 shows that the predicted response from the empirical model is in good agreement with the observed data. According to the values of the correlation coefficient ($R^2 = 0.998$) and the slope of the line to 0.962, the smoothing of the results was confirmed.

As results, Fig. 10 shows the three-dimensional isometric response curves of TO dye extraction and the effects of the different factors on its extraction yield.

From these results obtained through the factorial design of experiments, it appears that:

- The effect of the Na_2SO_4 salt is the most important factor in this study. In this context, Na_2SO_4 was investigated as an electrolyte in the range of 1%–10%. From the iso-response plot it can be noticed that the extraction yield of the TO dye increases from 60% to 85% by adding
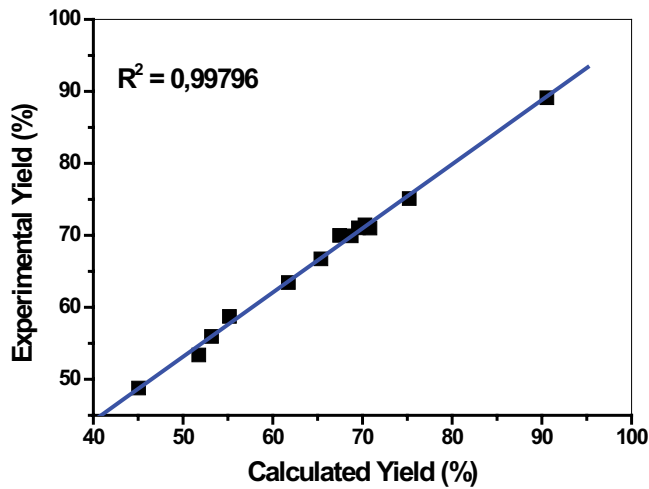
Fig. 9. Experimental and predicted yield values of TO dye extraction by CPE.

more quantity of Na_2SO_4. The dehydration of the ethoxy groups on the outer surface of the micelles is favored in the presence of the salts, leading to the increase of the aggregates and consequently of the quantity of dyes solubilized [28,29].

- The variation of extraction yield as a function of mass percentages of Tween 40 was followed in the range of 1% to 10%, increasing from 75% to 91%, respectively as shown in Fig. 10. For low percentages of the nonionic surfactant, extraction recovery of the complex was likely incomplete due to the inability of the aggregates to trap quantitatively the hydrophobic TO dye [13,19,30]. The chelating agent A336 in the surfactant-rich phase caused an increase in viscosity, facilitating the separation between the two phases [31]. The concentration of the micelles in the solution varies proportionally to the concentration of the surfactant: a higher concentration of surfactant results in a higher solubilisation of the TO dye in the coacervate phase. Consequently, the extraction efficiency increases.

- The pH is an important factor for CPE as it regulates the partitioning of the target micellar phase for organic molecules [32]. Note that the percentage extraction of the TO dye is lower in acidic media and increases with pH, it is equal to 75% at pH = 1 and 90% at pH = 9. At acidic pH, the efficiency is not quantitative, due to the increase of the ionic character of the oxy group of the nonionic surfactant, resulting in the decrease of the solubility of TO dye in micelles [33]. On the other hand, at a basic pH the CMC is lowered because of the cracking hydrophobicity of the oxy groups which increases the size of the micelles as well as the number of aggregations. Consequently, their solubilization increases leading to an increase in extraction yield [34].

- As shown in the presentation of the factors (Fig. 10), extraction yields increase slightly with increasing TO dye concentration. As the TO dye becomes more solubilized, the inter-micellar repulsion decreases thus increasing the micelle size and thus the volume of the coacervated
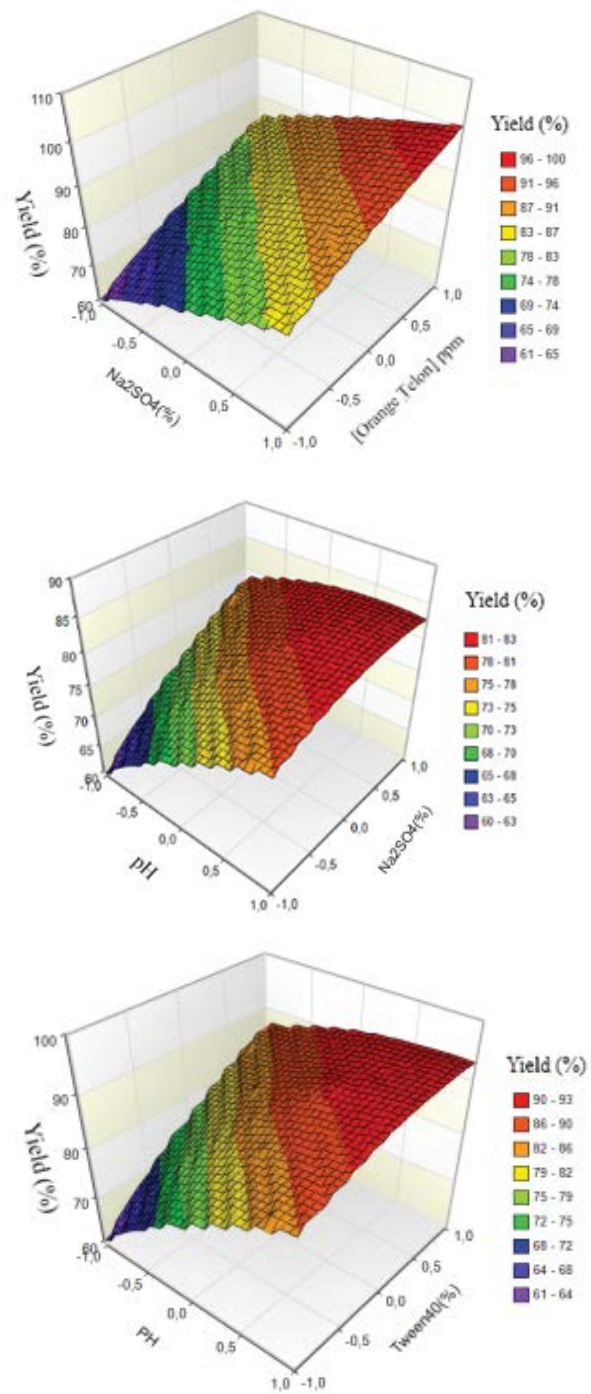
Fig. 10. Three-dimensional isometric response curves of TO dye extraction.

phase. This yield improvement could also be due to the increase in the number of moles of dye solubilized per mole of surfactant [2,8].

3.4. Mechanism of interaction extraction

The mixture of ionic liquid-ILs/surfactant induces a synergistic effect on the cloud point extraction, which may
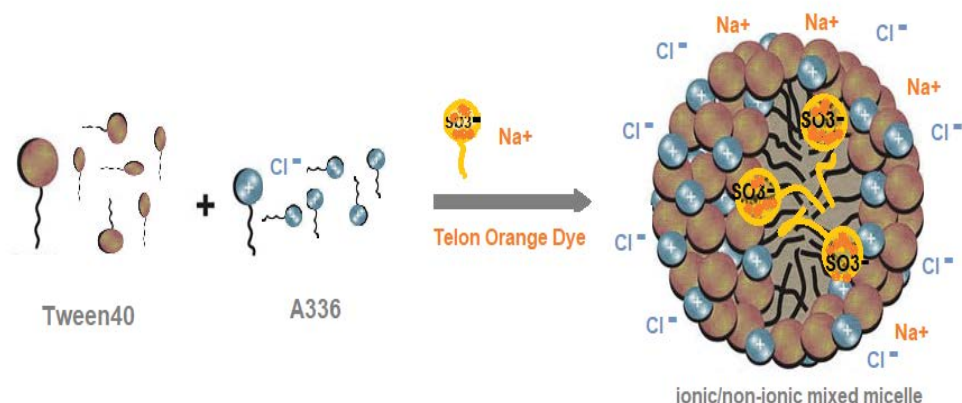
Fig. 11. Extraction mechanism of the TO dye by mixed Aliquat 336/Tween 40 micelles

depend on the type of surfactants used and the nature of the dye (anionic, cationic.) as well as the types of interactions between compounds in this system which has an advantageous solubilisation for different organic compounds [2,8,14,35]. Various studies have shown that Aliquat 336 forms mixed micelles in the presence of a non-ionic surfactant, which allows the solvation of various pollutants [27].

In this study, it was attempted to extract an anionic azo dye Telon Orange with a mixed system (ionic/non-ionic) using Tween 40 as surfactant and A336 as ionic liquid, as shown in Fig. 11.

In the present study, micelles will begin to form only above the critical temperature. The TO dye molecules can migrate to the center of the micelle, associate with the hydrophobic chains, or associate with the polar head groups of the surfactant through electrostatic, π-ion, or hydrogen bonding interactions [21,36,37]. Sun et al. reported that the micellar system (imidazolium based ILs/TX-114) can form mixed micelles in aqueous solutions by H-bonding and hydrophobic interactions; interactions between IL cation/anion and surfactants are very complicated, including electrostatic, H-bonding, induced dipole and hydrophobic interactions [36].

4. Conclusion

The results of this research clearly show the potential and versatility of this method for the extraction of TO dye from aqueous media.

The study showed that the CPT decreases with the addition of quantities (1%–10%) of salts in the following order (NaCl, $Na_2S_2O_3$ and Na_2SO_4), alkanes (Hexane, Heptane) and alcohols (Methanol, n-Butanol and n-Hexanol).

Following the results obtained, modelling of the cloud point extraction of the anionic TO azo dye using the non-ionic surfactant Tween 40 and an ionic liquid Aliquat 336 allowed the estimation of influential factors and possible interactions between the factors studied.

A significant influence with salt concentration, pH and amount of Tween 40 surfactant, but a minimal effect with dye concentration. The extraction efficiency is clearly influenced by the use of a mixture of cationic/non-ionic

surfactants (Aliquat 336/Tween 40) in the form of mixed micelles (the extraction efficiency reaches 97%).

The use of CPE as an alternative to conventional extraction techniques to separate compounds in a complex matrix and presented many advantages, such as excellent concentration factors, lower costs, greater safety and simplicity, and does not require the handling of a large volume of organic solvent, which is usually toxic. The difficulties of the process require optimization of all the operating parameters, and also its automation.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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