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# Easy Removal of Methylparaben and Propylparaben from Aqueous Solution Using Nonionic Micellar System

This study aimed to investigate the simultaneous removal of methylparaben (MePB) and propylparaben (PrPB) from effluents (each one at 16 mg/L) using a nonionic micellar system containing Triton X-114. Response surface methodology (RSM) has been carried out. Extraction results using nonionic surfactant two-phase system were considered as a function of surfactant concentration and temperature variation. Four responses were investigated: MePB and PrPB extraction yield (E), solute ( $X_{s,w}$ ) and surfactant ( $X_{sf,w}$ ) concentrations in the aqueous phase and the volume fraction of micellar phase ( $\varphi_C$ ) at equilibrium. Very high extraction efficiencies (99% for PrPB and 84% for MePB) were achieved at optimal conditions. Thereby, the amounts of PrPB and MePB were reduced 80 and 5 times, respectively. The extraction improvement using sodium sulfate was also shown. Finally, the solute stripping from micellar phase by pH change was proved.

**Key words:** Methylparaben, propylparaben, non-ionic surfactant, response surface methodology, extraction

**Einfaches Entfernen von Methylparaben und Propylparaben aus wässriger Lösung mit einem nichtionischen Mizellensystem.** Ziel dieser Untersuchung war, Methylparaben (MePB) und Propylparaben (PrPB) aus Abwässern (jeweils mit 16 mg/l) unter Verwendung eines nichtionischen Mizellensystems (Triton X-114) simultan zu entfernen. Die Response-Surface-Methode (RSM) wurde durchgeführt. Die Extraktionsergebnisse unter Verwendung eines nichtionischen Tensid-Zweiphasensystems wurden als Funktion der Tensidkonzentration und der Temperaturänderung betrachtet. Es wurden vier Antworten untersucht: MePB- und PrPB-Extraktionsausbeute (E), Konzentrationen von gelöstem Stoff ( $X_{s,w}$ ) und Tensid ( $X_{sf,w}$ ) in der wässrigen Phase und der Volumenanteil der Mizellaren Phase ( $\varphi_C$ ) im Gleichgewicht. Unter optimalen Bedingungen wurde eine sehr hohe Extraktionswirkung (99% für PrPB und 84% für MePB) erreicht. Dadurch wurden die Mengen an PrPB und MePB um das 80- bzw. 5-fache reduziert. Die Extraktionsverbesserung unter Verwendung von Natriumsulfat wurde ebenfalls gezeigt. Schließlich wurde das Ablösen der gelösten Substanz aus der Mizellaren Phase durch pH-Wert-Änderung nachgewiesen.

**Stichwörter:** Methylparaben, Propylparaben, nichtionisches Tensid, Response-Surface-Methode, Extraktion

## 1 Introduction

*p*-Hydroxybenzoic acid esters, known as parabens (PBs), were widely used as preservatives in pharmaceuticals, foods and personal care products [1]. Methylparaben and propylparaben are usually used and often present together in the products [2]. The maximum concentration in cosmetics formulation is limited to 0.4% for individual paraben molecules and to 0.8% in combination [3]. However, the paraben concentration in pharmaceutical products seldom exceeds 1%. They are used as excipients to preserve the active ingredient from microbial contamination and prevent degradation [4]. In front of this craze for parabens, many papers led to a discussion about their possible carcinogenicity and estrogenic effects [5, 6]. They are suspected to change the hormone concentration in organisms and were found in breast tumors [7, 8]. Furthermore, due to their potential toxicity and estrogen-mimicking properties, parabens are resistant to biological treatment in wastewater treatment plants [9–11].

As an alternative to conventional and more recent wastewater treatments such as aerated biofilm system [12, 13], ozonation [14], electrochemical methods [15, 16], sonochemical degradation [17], photodegradation [18, 19] and photolysis [20], Cloud Point Extraction (CPE) is a relatively simple and environmentally friendly technique [21–26]. Involving a thermoseparating system, it avoids the use of an organic solvent, produces a small sludge volume and requires low energy consumption. This process is very efficient for water treatment containing hazards of different organic or metal ions [21, 27–42]. CPE could even be implemented in a continuous process [42–47].

On the basis of this finding, the simultaneous CPE of methylparaben (MePB) and propylparaben (PrPB) from their aqueous solutions at 16 mg/L was studied. Triton X-114 (TX-114) which is characterized by fast separation kinetics and a low clouding temperature ( $T_c = 23^\circ\text{C}$ ), was further investigated concerning its phase behavior in water and its ability to extract the two solutes. Hence, we measured the cloud point ( $T_c$ ) of the water-surfactant, water-surfactant-solute as well as water-surfactant-sodium sulfate systems. Extraction experiments in batch mode were conducted in order to demonstrate the applicability of nonionic micellar system to the CPE of parabens. All the extraction results were modeled by an experimental design as a function of temperature and surfactant concentration. Finally, sodium sulfate addition and pH effects on extraction yield were investigated.

## 2 Materials and Methods

### 2.1 Materials

The commercial nonionic surfactant investigated in this study, Triton X-114, belongs to the polyethoxylated alkylphenol family

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(formula:  $(\text{CH}_3)_3\text{C}-(\text{CH}_2)_2\text{CH}-\text{C}_6\text{H}_4\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{-H}$ , with  $n = 7$  or  $8$ ), was supplied by Sigma Aldrich ( $T_c = 23.1^\circ\text{C}$ ). Its critical micelle concentration was  $2 \times 10^{-4}$  M. MePB (methyl 4-hydroxybenzoate), PrPB (propyl 4-hydroxybenzoate), methanol (HPLC grade), acetonitrile (HPLC grade) and sodium sulfate were provided by Sigma Aldrich. Distilled water was used for dilutions and deionized water for HPLC analyses.

## 2.2 Methods

Cloud point measurement was achieved using a Mettler FP 900 device. The cloud point temperature (CPT) was defined as the temperature at which the sample turned turbid.

The distribution of parabens (MePB and PrPB) in the two-phase system TX-114/water was studied in batch experiments. Samples (5 mL) containing 16 mg/L of each paraben and TX-114 (at concentrations of 1–5 wt.%) were prepared in distilled water. The homogenized samples were placed in a precision oven for 2 h (at temperatures between  $20^\circ\text{C}$  and  $40^\circ\text{C}$ ). Parabens and surfactant concentrations in aqueous phase were determined by using a Shimadzu RP-HPLC system, with a quaternary pump, degasser, tempered autosampler, column thermostat. Column RP18 (ODS), 1 mL/min, UV detector (wavelength 275 nm), injected volume  $20\ \mu\text{L}$ , mobile phase:  $\text{H}_2\text{O}/\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ , 7/60/33 (v/v/v).

## 3 Results and Discussion

### 3.1 Binary and pseudo-binary liquid-liquid equilibrium

*Alkylphenol polyethoxylate* (APEO) derivatives owe their solubility in water to the hydration of polar head group. However, most compounds dissolved in water decrease the solubility of a second component. Figure 1 depicts the effect of MePB and PrPB and  $\text{Na}_2\text{SO}_4$  on the cloud point curve of Triton X-114. The significant interaction between MePB, PrPB and TX-114 leads to a reduced surfactant solubility in water and thereby to a cloud point lowering [41]. One can also notice from Figure 1 that  $\text{Na}_2\text{SO}_4$  lowers the cloud point of Triton X-114. Indeed, the salt weakens the hydrogen bond between the water molecule and polyoxyethylene chain. The terminology “salting-out” effect is usually used to describe such a phenomenon [33, 48, 49]. Hence, the adjustment of

surfactant and salt concentrations allows the CPE of heat sensitive products at room temperature. Furthermore, the cloud point control contributes to the reduction of heating energy cost of large scale CPE process.

### 3.2 Experimental design

Extraction results using micellar phase of TritonX-114 were considered as a function of surfactant concentration ( $X_{\text{sf}}$ ), and temperature ( $T$ ). Four responses ( $Y$ ) were investigated: MePB and PrPB extraction yield ( $E$ ), solute ( $X_{\text{s,w}}$ ) and surfactant ( $X_{\text{sf,w}}$ ) concentrations in the aqueous phase and volume fraction of micellar phase ( $\phi_c$ ) at equilibrium. A polynomial model was used to correlate the relationship among the independent variables ( $X_{\text{sf}}$  and  $T$ ) and the four responses:  $E$ ,  $X_{\text{s,w}}$ ,  $X_{\text{sf,w}}$  and  $\phi_c$  [50]. The quadratic equations examined the effects of each independent variable on the response:

$$Y = a_0 + a_1X_{\text{sf}} + a_2T + a_{12}X_{\text{sf}}T + a_{11}X_{\text{sf}}^2 + a_{22}T^2 \quad (1)$$

A central composite design was considered to determine the polynomial model constants of the predictive equation. The models were checked by plotting computed data against experimental results.

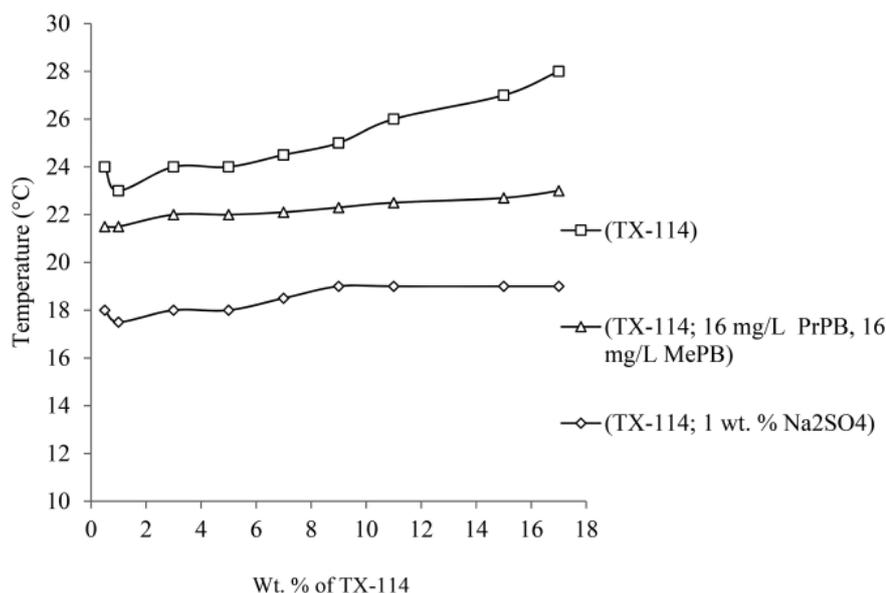
The following quadratic correlations showed a good fit with the experimental data and give the slope and the regression coefficient ( $R^2$ ) closest to unity:

$$E_{(\text{MePB})} = 63.3850 - 23.9050 X_{\text{sf}} + 1.2070 T + 1.0250 X_{\text{sf}}T - 1.5500 X_{\text{sf}}^2 - 0.0466 T^2 \quad (2)$$

$$E_{(\text{PrPB})} = 148.3263 - 21.1850 X_{\text{sf}} - 2.4525 T + 1.1065 X_{\text{sf}}T - 2.8723 X_{\text{sf}}^2 + 0.0036 T^2 \quad (3)$$

$$X_{\text{s,w}(\text{MePB})} = 7.3850 + 6.6750 X_{\text{sf}} - 0.4365 T - 0.2775 X_{\text{sf}}T + 0.4700 X_{\text{sf}}^2 + 0.0148 T^2 \quad (4)$$

$$X_{\text{s,w}(\text{PrPB})} = -6.7325 + 2.0450 X_{\text{sf}} + 0.3855 T - 0.1450 X_{\text{sf}}T + 0.4675 X_{\text{sf}}^2 - 0.0010 T^2 \quad (5)$$



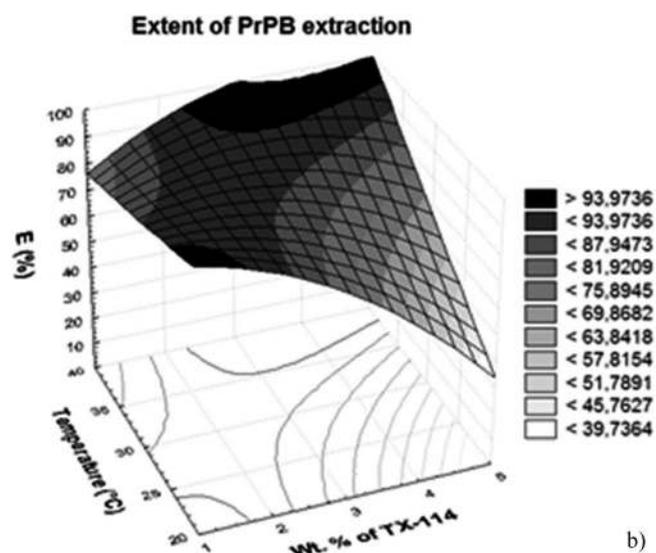
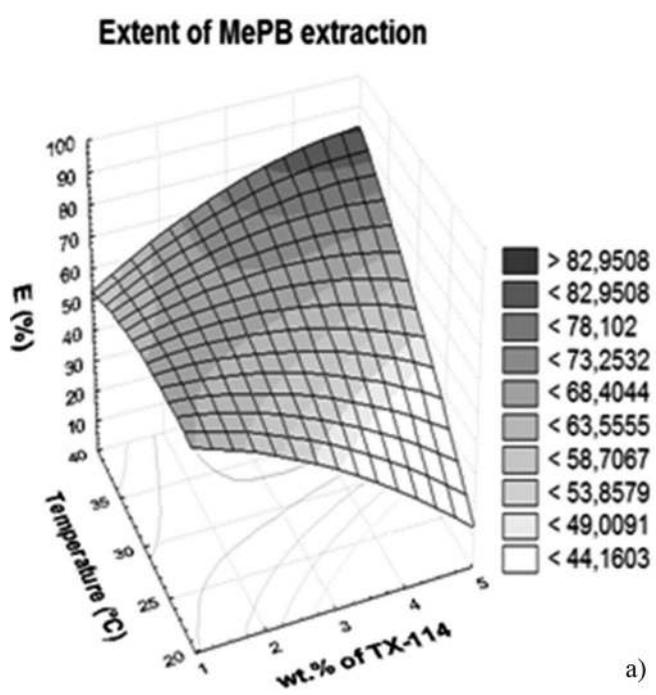
**Figure 1** Liquid-liquid equilibrium of the systems:  $\text{H}_2\text{O}/\text{MePB-PrPB}/\text{TX-114}$  and  $\text{H}_2\text{O}/\text{Na}_2\text{SO}_4/\text{TX-114}$

$$X_{s,f,w} = 0.0997 + 0.0310 X_{s,f} - 0.0039 T - 0.0003 X_{s,f} T - 0.0017 X_{s,f}^2 \quad (6)$$

$$\varphi_C = 0.1188 + 0.0900 X_{s,f} - 0.0045 T - 0.0014 X_{s,f} T + 0.0018 X_{s,f}^2 \quad (7)$$

### 3.2.1 CPE yield, E (%)

Figure 2 represents the simultaneous effect of surfactant concentration ( $X_{s,f}$ ), and temperature (T) on the extraction yield (E) smoothed by equations (2) and (3). The extraction percentage (E) of MePB and PrPB increases with  $X_{s,f}$  and reaches 99% for PrPB and 84% for MePB at 40 °C and with



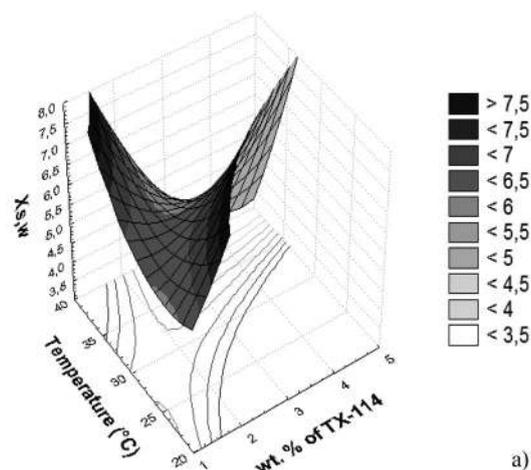
**Figure 2** Simultaneous effect of surfactant concentration ( $X_{s,f}$ ) and temperature (T) on the extraction extent:  $E(\%) = f(X_{s,f}, T)$ ; a) MePB; b) PrPB (Smoothed by Eqs. 2 and 3)

4 wt.% of TX-114. Furthermore, a temperature rise increases the extraction extent of both MePB and PrPB. Other extraction systems showed a similar behavior [27, 35, 47]. The darker area defines favorable CPE conditions for the two parabens (Figure 2). A temperature rise produces a simultaneous second effect: It increases the concentration of solute in the micellar phase induced by a decrease of the coacervate volume fraction ( $\varphi_c$ ) [33].

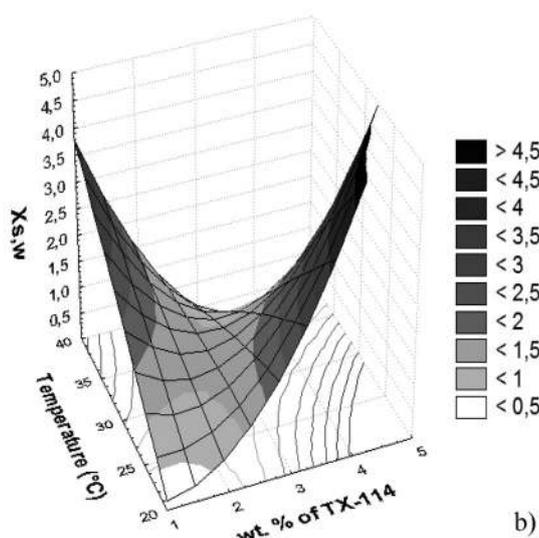
### 3.2.2 Residual concentration ( $X_{s,w}$ ) of MePB and PrPB,

Figures 3a and 3b show the simultaneous effect of the parameters ( $X_{s,f}$ ), and (T) on the studied response ( $X_{s,w}$ ) of MePB and PrPB, respectively, smoothed by equations (4) and (5). The figures show that the remaining concentrations of parabens in the dilute phase  $X_{s,w}$  go through a minimum according to  $X_{s,f}$  and T. Indeed, PrPB concentration was reduced to 0.18 mg/L and that of MePB to 3.23 mg/L. Hence, under propitious conditions of  $X_{s,f}$  and T (light colored zones), solute concentrations are almost 80 and 5 times low-

### Residual concentration of MePB in the dilute phase (mg/L)



### Residual concentration of PrPB in the dilute phase (mg/L)



**Figure 3** Simultaneous effect of surfactant concentration ( $X_{s,f}$ ) and temperature (T) on the remaining concentration of solute:  $X_{s,w} = f(X_{s,f}, T)$  a) MePB; b) PrPB, (Smoothed by Eqs. 4 and 5)

er than the initial concentrations for PrPB and MePB, respectively. Indeed, the extraction yield,  $E$ , of MePB is lower than that of PrPB (Figures 2a and 2b). However, residual concentrations of MePB are higher than those obtained for PrPB (Figures 3a and 3b). These results are in good agreement with the partition coefficients of both solutes in octan-1-ol and water. Moreover, MePB is more soluble in water than PrPB (Table 1), which makes the extraction of the latter easier.

### 3.2.3 Residual concentration of surfactant, $X_{sf,w}$

Although TX-114 is biodegradable, high residual concentration of surfactant in aqueous phase ( $X_{t,w}$ ) will compromise the CPE process [38, 52–54]. Indeed, it is more economical to minimize this response. Figure 4 illustrates the effect of surfactant concentration ( $X_{sf}$ ), and temperature ( $T$ ) on the response,  $X_{sf,w}$  smoothed by equation (6). This figure shows that the remaining concentration of TX-114 is high at high values of  $X_{sf}$  and decreases slightly when the temperature rises, which, however, corresponds to favorable conditions for high extraction efficiency [54].

### 3.2.4 Volume fraction of coacervate, $\phi_c$

In order to increase the concentration factor and the volume of the treated effluent,  $\phi_c$  needs to be as low as possible. Figure 5 represents the iso-response surfaces of  $\phi_c$  vs.  $X_{sf}$  and  $T$  smoothed by equation (7). When  $X_{sf}$  increases,  $\phi_c$  increases almost linearly. The coacervate owes this behavior to the progressive enrichment of the micellar phase following reten-

Characteristic	MePB	PrPB
Molecular weight (g/mol)	152.16	180.21
$pK_a$	8.17	8.35
Log octanol–water partition coefficient (log P)	1.66	2.71
Solubility in water at 25 °C (g/100 mL)	2.00	0.30

Table 1 Physical and chemical characteristics of MePB and PrPB [7]

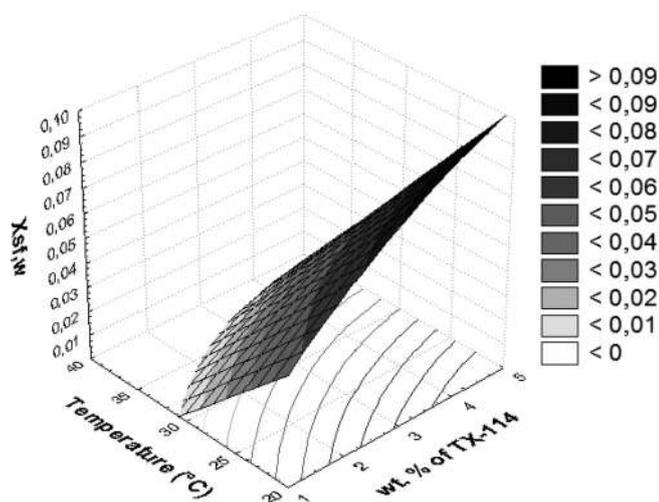


Figure 4 Simultaneous effect of surfactant concentration ( $X_{sf}$ ) and temperature ( $T$ ) on the remaining concentration of TX-114:  $X_{sf,w} = f(X_{sf}, T)$ . (Smoothed by Eq. 6)

tion of water molecules by the polyoxyethylene chain of TX-114. However, high values of initial concentrations of surfactant ( $X_{sf}$ ) are favorable for the CPE extraction of parabens (Fig. 2). Such antagonist behavior was obtained with several micellar systems investigated in our previous studies [31, 35]. Figure 5 also shows that low values of  $\phi_c$  were obtained as the temperature increased. Indeed, the heat induced a dehydration of the polar head group of surfactant in the micellar phase; thereby a more concentrated and smaller coacervate was obtained at high temperatures.

### 3.4 Electrolyte ( $Na_2SO_4$ ) effect on the CPE parameters

Figure 6a shows that the  $Na_2SO_4$  concentration increases the MePB and PrPB extraction yields ( $E$  %). The salting-out effect of electrolyte reduces the solubility of solutes and surfactant in water. Hence, residual concentration of MePB and TX-114 decreased as the salt concentration was increased (Figs. 6b and 6c). According to Saito and Shinoda [56], the addition of salting-out electrolytes to nonionic micellar solution lowers cmc, which induces a micellar number increase. Consequently, the hydrocarbon solubilization capacity of such system is improved. Furthermore, one can see from Figure 6c that the electrolyte addition to the TX-114-parabens-water system minimizes the coacervate volume fraction ( $\phi_c$ ) and improves the concentration factor.

### 3.5 Stripping of solutes from the micellar phase

Ionic and neutral molecules are distributed differently between aqueous and micellar phases in a CPE [35]. In fact, ionic species have more affinity to water molecules. Slight interactions may occur with the surfactant and such species. For acidic or basic solutes, the influence of the pH can be used for extraction and back-extraction processes. Figure 7 shows that the distribution of MePB and PrPB between aqueous and micellar phases is highly affected by pH. The extraction yield ( $E$  %) decreases significantly at pH above  $pK_a$  values of MePB ( $pK_a = 8.17$ ) and PrPB ( $pK_a = 8.35$ ) (Table 1). Parabens are mainly in neutral form ( $R-OH$ ) at pH below their  $pK_a$  and in ionic form ( $R-O^-$ ) above their  $pK_a$ . The ionic form is more soluble in water than the neutral form. Hence, as in our previous works [34, 35, 37, 38], the solute was stripped from micellar phase by a pH shift above  $pK_a$  of MePB and PrPB.

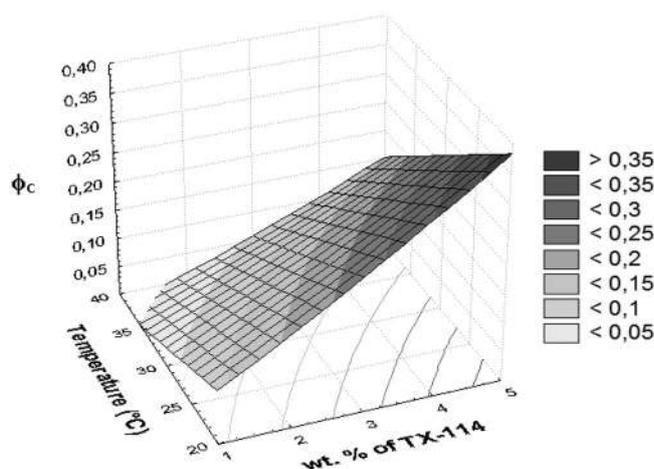


Figure 5 Simultaneous effect of surfactant concentration ( $X_{sf}$ ) and temperature ( $T$ ) on the micellar volume fraction:  $\phi_c = f(X_{sf}, T)$ . (Smoothed by Eq. 7)

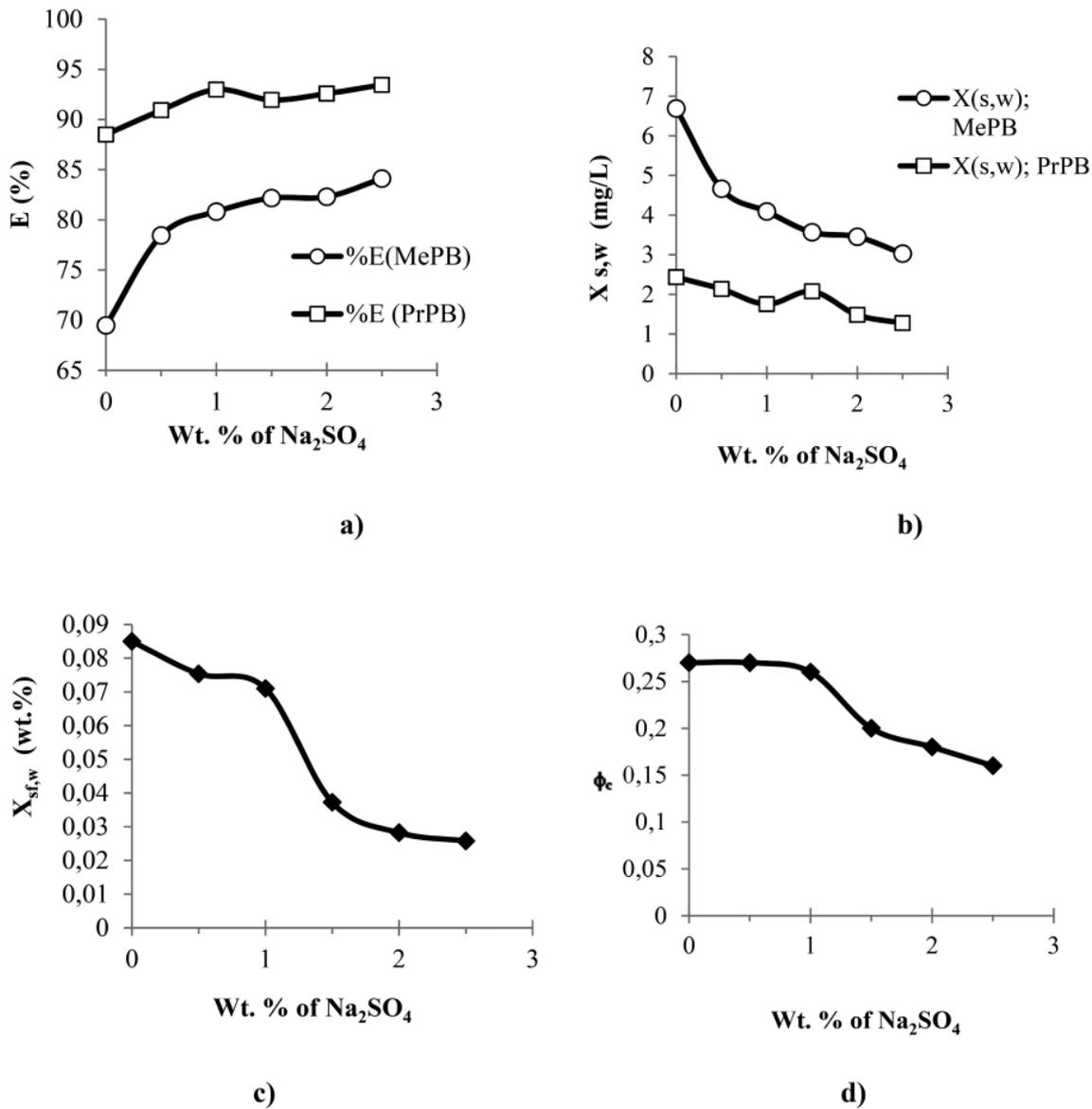


Figure 6 Effect of  $\text{Na}_2\text{SO}_4$  at 2 wt.% of TX-114 and 20 °C on: a) MePB and PrPB extraction extent (E %); b) remaining concentration of MePB and PrPB ( $X_{s,w}$ ); c) remaining concentration of TX-114 ( $X_{sf,w}$ ); d) micellar volume fraction: ( $\phi_c$ )

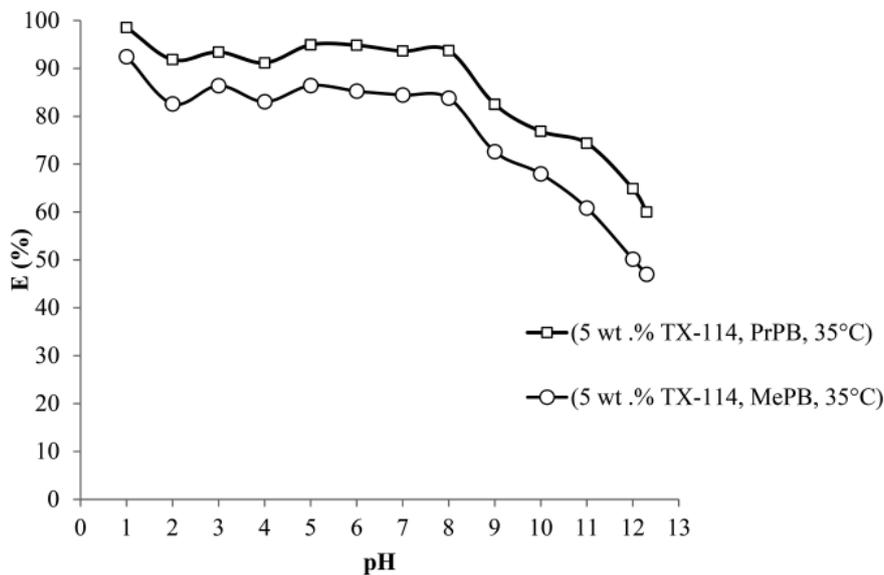


Figure 7 pH effect of on MePB and PrPB extraction extent (E %)

## 4 Conclusion

The aim of this work is to move towards “green”, *i.e.* non-polluting, energy-saving chemical processes. Cloud Point Extraction (CPE) was used to efficiently remove parabens (MePB and PrPB) from wastewater. The effects of surfactant concentration and temperature on extraction extent, solute and surfactant residual concentrations and coacervate volume fraction were studied. The best compromise between the parameters governing extraction effectiveness was found using the response surface methodology. A temperature ranging between 20 °C and 30 °C and a surfactant concentration lower than 5 wt.% (to minimize coacervate volume fraction) are suitable for CPE of the two parabens. These yielded extraction rates of 99% and 84% for PrPB and MePB, respectively. After CPE, the remaining concentrations of PrPB and MePB were 80 and 5 times lower than initial concentration (16 mg/L), respectively. Na<sub>2</sub>SO<sub>4</sub> improved the extraction yield of MePB and PrPB. The extraction of the solutes was high in the acidic pH range (below pK<sub>a</sub> values of MePB and PrPB). Thus, it was shown that pH can be used for solute stripping from micellar phase and surfactant recycling in the CPE process.

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