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# Cloud point extraction of phenol and benzyl alcohol from aqueous stream

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## Abstract

Two-aqueous phase extraction of phenol and benzyl alcohol as a solute from their aqueous solutions was investigated using polyethoxylated alcohols (CiEj) as a biodegradable non-ionic surfactant. First, the phase diagrams of the binary systems, water–surfactant (Oxo-C<sub>10</sub>E<sub>3</sub> and Oxo-C<sub>13</sub>E<sub>9</sub>), and the pseudo-binary systems, water–surfactant with a constant concentration of solute was determined. The effect of sodium chloride and sodium sulphate on water–surfactant systems were studied. According to the given surfactants concentrations and temperatures, the extraction results were expressed by the following four parameters, percentage of extracted solute,  $E$ , which reached 95 and 90% for phenol and benzyl alcohol, respectively, residual concentrations of solute,  $X_{s,w}$ , and the surfactant,  $X_{t,w}$ , in the dilute phase and volume fraction of the coacervate at the equilibrium condition,  $\phi_c$ . The values of these parameters were determined by an analyzing central composite designs. After the first extraction process, phenol and benzyl alcohol concentrations in the effluent were reduced about ten times for the first and four times for the second, correspondingly.

*Keywords:* Cloud point; Phenol; Benzyl alcohol; Non-ionic surfactant; Extraction

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## 1. Introduction

The use of surfactants grows rapidly in the daily needs. Their consumed quantities increase with the increase of the demographic growth and with the improvement of the way of life and hygiene conditions, specially, in the third-world countries. But, the surfactants have a negative effect on surface and wastewater quality. They decrease the dissolved oxygen in water–atmosphere interface, and their toxicity are noticeably low; 10 mg/l is enough to inhibit bacterial flora, and 50 mg/l to inhibit phytoplankton [1]. The lowering of superficial tension of fish medium changes the respiratory mechanism in fish gills. The presence of surfactants also involves the death of insects living on water surface, such as hemipters [1]. As a consequence, the use of biodegradable surfactants become necessary to allow nature plays its role in the biodegradability mechanism. In 1955, Hammerton [2] proposed that the nature of surfactants hydrophobic groups is the determinant factor for their biodegrad-

ability process, while nature and position of hydrophilic groups had less effect on such process. The first work done in the chemical engineering laboratory of Toulouse [3] was focused on the use of “ethoxylated alkylphenols” non-ionic surfactants type (EAP) in phenol extraction. However, these surfactants are no more used for detergence applications in many countries, and are going to be superseded progressively because of the toxic intermediate substances generated from their biodegradation process such as alkylphenols molecules. In this work, polyethoxylated alcohols (EA) have been used as good alternatives to EAP, due to their satisfactory biodegradable activities [4,5]. The extraction method includes simultaneously cloud point and solubilization phenomenon of non-ionic surfactants medium. Thus, most of polyethoxylated non-ionic surfactants in aqueous solutions form two phases above the cloud point ( $T_c$ ): a surfactant-rich phase (coacervate), and a dilute phase, in which the concentration of the surfactant is close to its critical micelle concentration ( $\text{cmc} \approx 10^{-5} \text{ M}$ ) [6]. Therefore, due to the micellar solubilization property of the surfactants, the hydrophobic, amphiphilic or even ionic solutes can be extracted in the coacervate after increasing the temperature above  $T_c$ . This two-aqueous phase extraction process was initially applied to the separation of metals ions, in the presence of a chelating agent [6]. Later on, this process was done on the extraction of

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many other chemical species, such as various metal ions, small organic molecules and molecules of biological interest [3,7–14]. In this work, the extraction of phenol and benzyl alcohol from their aqueous solutions was investigated. The effects of temperature, surfactant concentration as well as the addition of sodium chloride and sodium sulphate on solutes extraction extent were also done. The initial phenol concentration used in water was 0.15 wt.%, which is fifteen thousand times higher than required phenols concentration in crude water. This water need physical and chemical treatment in order to get the characteristic of potable water [15] (phenol index =  $10^{-5}$  wt.%, reported by the International American Waterworks Supply Association). Benzyl alcohol concentration was also chosen on this base.

## 2. Materials and methods

The commercial surfactants used were obtained from fatty Oxo alcohol ethoxylation. The Oxo- $C_{10}E_3$  with a cloud point lower than room temperature ( $T_c = 2^\circ\text{C}$  at 1 wt.% in water) was compared with Oxo- $C_{13}E_9$  ( $T_c = 69^\circ\text{C}$  at 1 wt.% in water). About 20% of the Oxo alcohol chains are branched. These samples were kindly supplied by SEPPIC (Castres, France). The Oxo- $C_{10}E_3$  compound was free from the residual polyols by washing it with water at  $90^\circ\text{C}$ . The determinations 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 measurement cell there is a luminous source, and an optic driver which illuminates the sample. The crossed samples 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. For the extraction tests, 20 ml of solution containing the surfactant (at concentrations of 1, 4, 7, 10 or 13 wt.%) and the solute (0.15 wt.%  $C_6H_5OH$  or  $C_6H_5CH_2OH$ ) in demineralised water, were poured into graduated cylinders and heated in a precise oven or it was also cooled and kept in a thermostated bath for

24 h to reach equilibrium. The volumes of both phases were registered. The dilute phase was analysed by HPLC: for the solute  $C_6H_5OH$  or  $C_6H_5CH_2OH$ . The chromatographic conditions were done as follows: column RP18 (ODS), pressure 95 bar, mobile phase  $H_2O/CH_3CN/CH_3OH$ , 42.5/50/7.5 (v/v), flowrate 1 ml/min;  $\lambda = 260$  nm. The conditions were slightly different for surfactant determination by HPLC: mobile phase  $H_2O/CH_3CN/CH_3OH$ , 7.5/60/32.5 (v/v), using the evaporative light scattering detector (ELSD). The ELSD enables the analysis of the chemical compounds which show no absorption in the UV range as polyethoxylated alcohols surfactants. The principle of its operation is introduction of an eluent from the HPLC column onto the top of a heated diffusion tube, followed by spraying with an aide of stream of nitrogen gas. When passing through the diffusion tube, the sprayed beads are evaporated so the mist formed in the nebulizer contains only non-volatile particles of the substance under examination, which leave the column together with the eluent used for separation. The particles are introduced onto a light beam and scatter it. Measured at a constant angle, the scattered light is proportional to the concentration of the substance under analyses [16–18]. The sensitivity of the evaporative light scattering detector (DDL 31, EUROSEP Instruments) was optimised by the control of the air flowrate in the atomizer (relative pressure: 1 bar), the evaporator temperature was  $55^\circ\text{C}$  and the photomultiplier gain was 400 mV.

## 3. Results and discussion

### 3.1. Phase diagrams of binary and pseudo-binary systems

#### 3.1.1. Phenol and benzyl alcohol effect on the cloud point

Organic solubilizes can interact with the surfactant polar head group or with its hydrophobic length after solubilization in micelles. According to their chemical nature, organic compounds can vary the surfactants cloud point [19–21]. The cloud point lowering of  $C_{13}E_9$  and  $C_{10}E_3$  surfactants by phenol and benzyl alcohol addition is shown in Fig. 1. This effect is clearer at low surfactants concentrations in the case of phenol unlike benzyl alcohol. Therefore, at low surfactant concentrations, a strong molecular interaction between phenol and surfactant occurs.

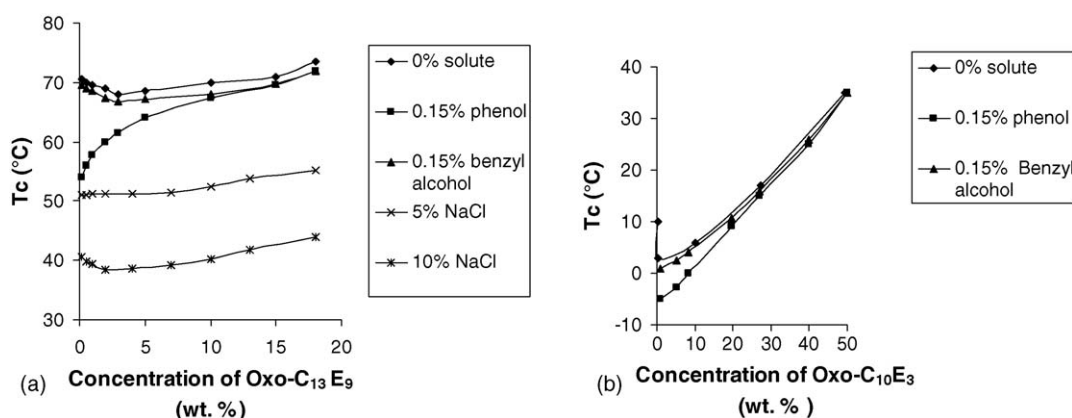


Fig. 1. (a) Effect of phenol, benzyl alcohol and NaCl on the cloud point temperature of Oxo- $C_{13}E_9$ . (b) Effect of phenol and benzyl alcohol on the cloud point temperature of Oxo- $C_{10}E_3$ .

However, the influence of benzyl alcohol is weak which does not apparently depend on the ratio of benzyl alcohol/surfactant, as in the case of phenol. This difference can be explained by the fact that the benzyl alcohol probably has less interaction with the surfactant polar head group than that of phenol. This interaction makes the surfactant less water soluble. Dondrow and Azaz [22] studied the effect of phenols, cresols and xylenols on the cloud point of the cetomacrogol [polyoxyethylene -(24)- hexadecanol], and found that all these solubilizates lower the cloud point. Moreover, the phenols effect was inversely proportional to their hydrophobicity.

### 3.1.2. Effect of electrolytes on the cloud point

**3.1.2.1. Sodium chloride effect.** When a small amounts of sodium chloride is added (less than 0.01 M) to non-ionic surfactant solutions, the cloud point remains constant [19]. On the contrary, at high concentrations (higher than 0.1 M), sodium chloride lowers the cloud point [23]. Fig. 1a, shows the cloud point lowering of C<sub>13</sub>E<sub>9</sub> by sodium chloride. This phenomenon is due to the salting-out of the surfactant which is induced by the solvated electrolyte. The salting-out as such favoured the weakening of surfactant head–water interaction. It seems that, the sodium chloride lowers the cloud point by a continuous medium change, more than that by direct interaction with the ethoxy groups of the surfactant [23–26]. Fig. 1a shows how 10 wt.% of NaCl (1.709 M) is able to lower the cloud point of 1 wt.% C<sub>13</sub>E<sub>9</sub> solution from 69 to 38 °C. Therefore, it is possible to adjust the cloud point to room temperature by a simple control of surfactant and salt concentrations, and reduce the heating energy cost of the large scale cloud point extraction. Salt addition can also have an application in the extraction of heat sensitive products. However, electrolyte does not contribute equally between the dilute phase and coacervate, and its addition increases the density of the dilute phase; this makes the separation of both phases easy in some non-ionic surfactant systems [6,27]. Comparing the effects of NaCl and organic solutes on the C<sub>13</sub>E<sub>9</sub> cloud point temperature as in Fig. 1a, one can notice that sodium chloride effect is largely different than that of phenol. In case of NaCl, the cloud point lowering does not change the shape of the cloud point temperature curve and it is shown to be linear for all concentrations of C<sub>13</sub>E<sub>9</sub>, while, in case of phenol, the effect depends on the surfactant concentration. On the other hand, the effect of benzyl alcohol is also independent of C<sub>13</sub>E<sub>9</sub> concentration similar to the electrolyte effect. But these two substances do not influence the cloud point in the same way (the sodium chloride by salting-out effect and benzyl alcohol by interaction with the surfactant) [23,26].

**3.1.2.2. Effect of electrolyte anions on the cloud point.** It is well known that electrolytes reduce solubility of organic compounds in water by the salting-out phenomenon [28]. This effect depends mainly on the nature of the electrolyte anion [29]. In this work, the behaviour of sodium chloride and sodium sulphate have been shown in Fig. 2. The cloud point lowering of a C<sub>13</sub>E<sub>9</sub> solution is shown to be linear for NaCl and Na<sub>2</sub>SO<sub>4</sub> concentrations [19,28–30]. From Fig. 2, one can notice that the SO<sub>4</sub><sup>2-</sup> ion is more effective than Cl<sup>-</sup>: for example, in order to have phases

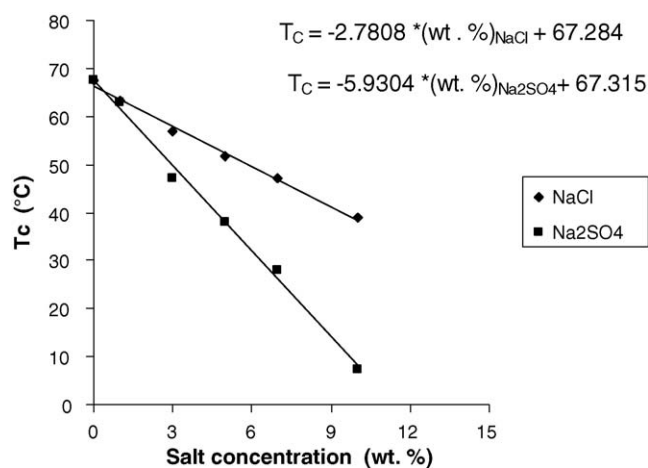


Fig. 2. Effect of electrolytes on the cloud point temperature of a C<sub>13</sub>E<sub>9</sub> solution at 3 wt.%.

separation (coacervate and dilute phase) at 38 °C, it is necessary to double the concentration of NaCl (10 wt.% = 1.709 M) relative to Na<sub>2</sub>SO<sub>4</sub> concentration (5 wt.% = 0.352 M)

## 3.2. Extraction of phenol and benzyl alcohol

### 3.2.1. Procedure

The extraction results of a 0.15 wt.% solution of solute (phenol, benzyl alcohol) by different surfactants, with two variables:  $X_t$  (wt.% surfactant) and temperature ( $T$ ), are expressed by four “responses” ( $Y$ ): percentage of extracted solute ( $E$ ), residual concentrations of solute ( $X_{s,w}$ ) and surfactant ( $X_{t,w}$ ) in the dilute phase and the coacervate volume fraction at equilibrium ( $\phi_c$ ) [3]. For each parameter determined by an analyzing central composite designs [31], these results are subjected to an empirical smoothing. In this method, the experimental values can be used to determine, the polynomial model constants which are adjusted to the studied property variations. The models were checked by plotting computed values against experimental ones. The quadratic correlation was chosen to give the slope and regression coefficient ( $R^2$ ) closest to unity.

$$Y = a_0 + a_1 X_t + a_2 T + a_{12} X_t T + a_{11} X_t^2 + a_{22} T^2 \quad (1)$$

Such correlation allows to build the response surface.

### 3.2.2. Results of phenol and benzyl alcohol extraction

The results of phenol extraction with C<sub>13</sub>E<sub>9</sub> and of benzyl alcohol extraction with C<sub>10</sub>E<sub>3</sub> are exposed as an example. The coefficients of checked quadratic equation (Eq. (1)) for the four properties ( $E$ ,  $X_{s,w}$ ,  $X_{t,w}$  and  $\phi_c$ ) and the correlation coefficient ( $R^2$ ) are represented in Table 1:

The Fig. 3, represents the three-dimensional isoresponse curves of the studied properties smoothed by the quadratic model (Table 1a). Fig. 3a, shows that the extent of phenol extraction,  $E$ , increases with  $X_t$ , similar to that of alkylphenol ethoxylates [3,32], or ethoxylated methyl dodecanoates [33]. In this work,  $E$  reached 95% for 10% C<sub>13</sub>E<sub>9</sub>. On the other hand,  $E$  decreases with rising temperature, which is probably due to the increase in the solubility of phenol in water [34,35]. This increase makes the

Table 1

Values of quadratic equations coefficients for  $E$ ,  $X_{s,w}$ ,  $X_{t,w}$  and  $\phi_c$  in Eq. (1) and correlation coefficient ( $R^2$ ) for: (a) phenol extraction with  $C_{13}E_9$ ; (b) benzyl alcohol extraction with  $C_{10}E_3$

Parameter	$100a_0$	$100a_1$	$100a_2$	$100a_{12}$	$100a_{11}$	$100a_{22}$	Correlation coefficient ( $R^2$ )
(a) Phenol extraction							
$E$	17682.200	1025.400	-410.600	-1.600	-32.700	2.800	0.995
$X_{s,w}$	20.000	-0.955	-0.356	0.031	0.003	0.000	0.986
$X_{t,w}$	232.300	2.500	-6.600	-0.033	0.056	0.046	0.967
$\phi_c$	-16.600	27.400	0.225	-0.350	0.015	0.000	0.961
(b) Benzyl alcohol extraction							
$E$	2485.300	1173.900	-2.500	-13.500	-34.600	-1.200	0.981
$X_{s,w}$	12.100	-1.600	-0.027	0.054	-0.0005	0.000	0.973
$X_{t,w}$	8.400	1.800	-0.071	-0.049	0.001	0.068	0.961
$\phi_c$	5.200	10.800	-0.039	-0.161	0.052	0.002	0.985

phenol extraction in the coacervate more difficult at high temperature. However, Materna and Szymanowski [33] noticed that the extent of extraction of phenol ( $E$ ) with nonaethoxylated methyl dodecanoate ( $C_{12}E_9CH_3$ ) comes to its maximum at 20 °C above the cloud point. Using alkylphenol ethoxylate, Gullickson et al.

[8] found that an increase of the 4-*t*-butylphenol concentration in the coacervate occurs between 30 and 50 °C. The partition ratio follows the same trend as above but no change was observed in the fraction of solute transferred to the coacervate phase. The behaviour of 1-hexanol [8] can be explained by minimum

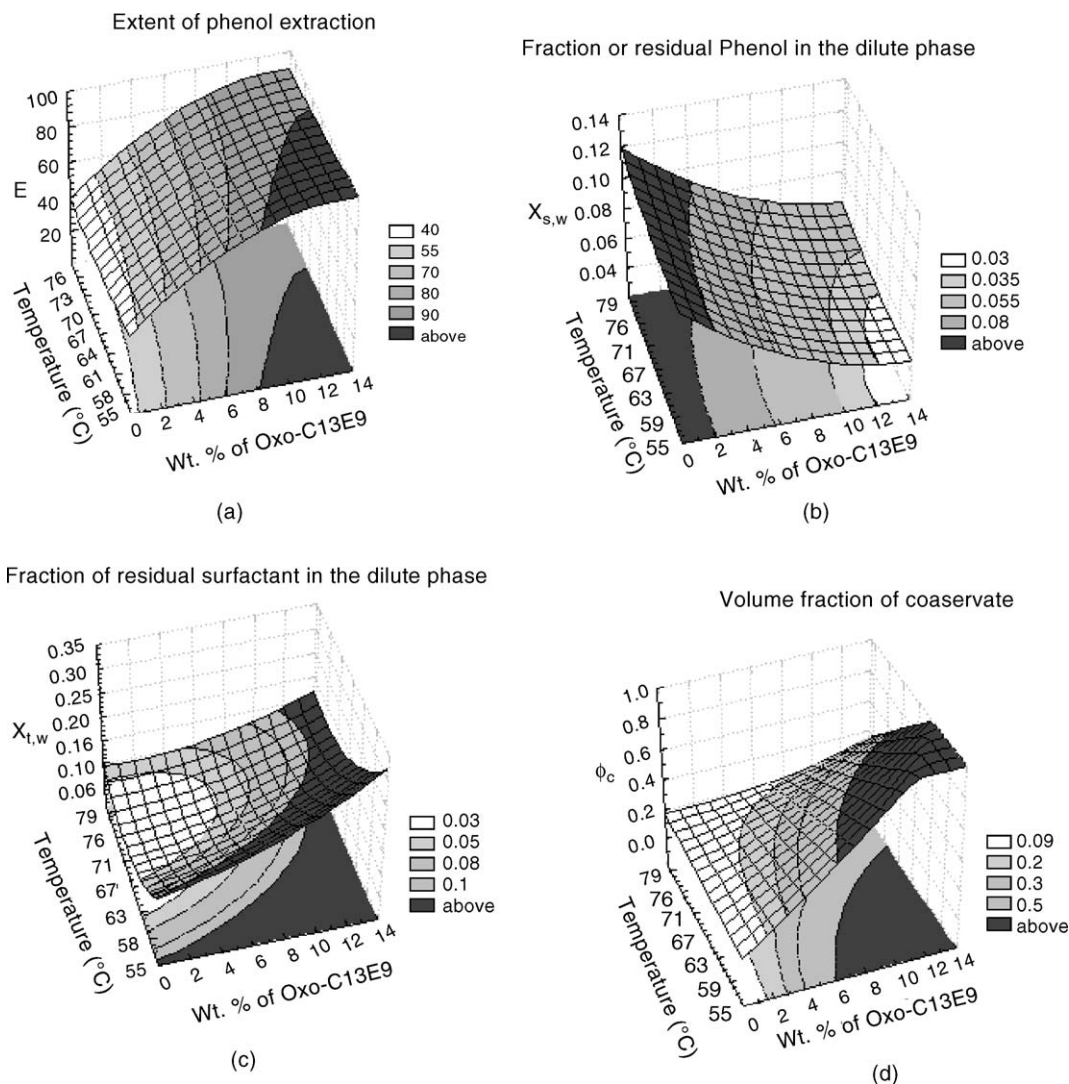


Fig. 3. Three-dimensional isoresponse curves smoothed by a quadratic model (Table 1a): (a)  $E$  (%) =  $f(X_t, T)$ ; (b)  $X_{s,w}$  (%) =  $f(X_t, T)$ ; (c)  $X_{t,w}$  (%) =  $f(X_t, T)$ ; (d)  $\phi_c$  =  $f(X_t, T)$ .

aqueous solubility around this temperature (concentration and partition ratio in the coacervate comes to its maximum around 40 °C above  $T_c$ ) [36]. In Fig. 3b, it is shown that the percentage of residual phenol in the dilute phase  $X_{s,w}$  decreases as  $X_t$  increases, but it increases slightly with  $T$ . Thus, beyond the cloud point a significant temperature rise has an opposite effect on the extraction [34]. Fig. 3c, shows that the residual concentration of surfactant is low at low surfactant concentration and goes through a minimum when plotted with  $T$ . In order to increase the concentration factor of solute, a minimal volume fraction of coacervate ( $\phi_c$ ) should be obtained when temperature increases. Hence, according to Fig. 3d, the value of  $\phi_c$  is low at high temperature and at low surfactant concentration. But, high temperature is unfavourable for efficient extraction extent (Fig. 3a), while, high surfactant concentrations induce more surfactant loss in the dilute phase (Fig. 3c). This loss is not economic even when the surfactant is biodegradable. So the optimisation of the process needs to compromise between the four studied parameters  $E$ ,  $X_{s,w}$ ,  $X_{t,w}$  and  $\phi_c$ .

In the case of benzyl alcohol extraction with  $C_{10}E_3$ , the behaviour of  $E$ ,  $X_{s,w}$ ,  $X_{t,w}$  and  $\phi_c$  as a function of  $X_t$  and  $T$ , is generally similar to that observed for phenol extraction (Figs. 3 and 4 and Table 1b). But, the values of  $X_{s,w}$  for benzyl alcohol were shown to be high. In fact, the percentage of phenol extraction,  $E$ , with  $C_{10}E_3$  is higher than that of benzyl alcohol under the same conditions [35] (Fig. 4a). Consequently, the values of  $X_{s,w}$ , are higher for benzyl alcohol than for phenol (Figs. 3b and 4b). These results are in good agreement with the partition coefficients of both solutes in octan-1-ol and water ( $\log P_{C_6H_5CH_2OH} = 1.05$ ;  $\log P_{C_6H_5OH} = 1.50$  [37]). For compounds with more effect on the cloud point, higher extraction extent can be reached [10]. In Fig. 3c, the residual concentration of the surfactant in the dilute phase ( $X_{t,w}$ ) is about 0.05 wt.%, which is higher than the critical micelle concentration, cmc, of  $C_{13}E_9$  (cmc,  $\approx 3.15 \cdot 10^{-4}$  M; 0.0128 wt.%) [35]. Comparing Figs. 3c and 4c, it is observed that  $X_{t,w}$  is high using  $C_{10}E_3$ . This surfactant is more soluble in water than  $C_{13}E_9$ . That is probably due to the shorter hydrocar-

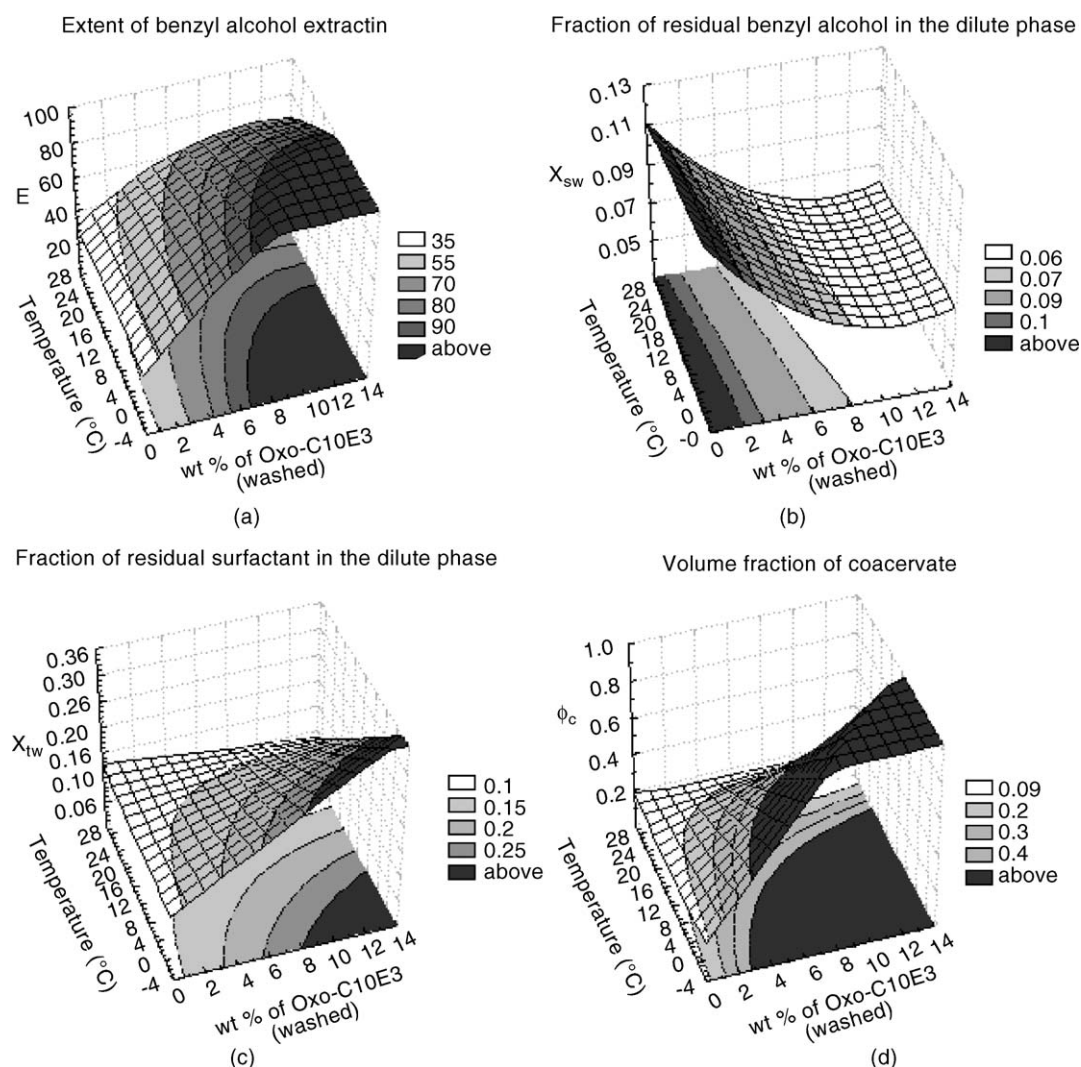


Fig. 4. Three-dimensional isoresponse curves smoothed by a quadratic model (Table 1b): (a)  $E$  (%) =  $f(X_t, T)$ ; (b)  $X_{s,w}$  (%) =  $f(X_t, T)$ ; (c)  $X_{t,w}$  (%) =  $f(X_t, T)$ ; (d)  $\phi_c$  =  $f(X_t, T)$ .

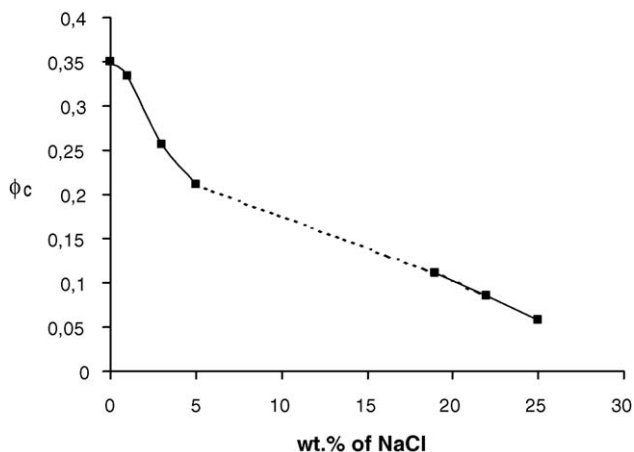


Fig. 5. Effect of sodium chloride on the coacervate volume fraction ( $\phi_c$ ) in the  $H_2O/Oxo-C_{13}E_9$ /phenol system ( $T=50^\circ C$ ; 0.15 wt.% of phenol; 4 wt.% of  $Oxo-C_{13}E_9$ ); for the intermittent line part phases separation is very slow.

bon chain length of  $C_{10}E_3$ . At room temperature the solution of  $C_{10}E_3$  was cloudy, which cannot give cmc value for that surfactant.

### 3.3. Effect of sodium chloride on $\phi_c$ , $E$ , and $X_{w,s}$

The coacervate volume fraction evolution as a function of NaCl concentration of  $H_2O/C_{13}E_9/C_6H_5OH$  solution is shown in Fig. 5. The sodium chloride addition induced coacervate volume fraction reduction due to the cloud point lowering of the surfactant solution. At constant surfactant and phenol concentrations at a given temperature ( $T$ ), the presence of NaCl decreases the cloud point temperature (Fig. 1a) and the values of  $\phi_c$ , and increases the values of  $(T - T_c)$ . Therefore, in the presence of NaCl, small coacervate volumes with a high surfactant concentrations were obtained. The dotted part of the curve in Fig. 5 represents a slow phases separation rate which is due to the similarity in densities of both coacervate and dilute phase.

Frankewich and Hinze [38] studied the effect of NaCl ionic strength on the extraction extent of phenol and 4-chlorophenol using the  $C_8E_9$  surfactant in presence and absence of 0.1 M (equivalent to 0.55 wt.%). They showed that NaCl has no effect on the extraction extent (15.2% against 16.8% for phenol and 79.9% against 79.0% for 4-chlorophenol). These results are in good agreement with the results given in the literature [39,40]. But according to Saito and Shinoda [24], the addition of 0.17 M of NaCl (equivalent to 1 wt.%) to non-ionic surfactant solutions increases their hydrocarbon solubilization capacity, by lowering cmc concentration. This behaviour may be the result of an increase in micellar number in this concentration region. The salting-out effect on both the cloud point temperature and the solubilization capacity of surfactant has similar lower concentration limit [19,23,24,39,40]. It is shown here (Fig. 6) the influence of NaCl on coacervate extraction extent of phenol with concentrations higher than 0.17 M. Fig. 6 gives the increase in the extraction percentage of phenol with sodium chloride concen-

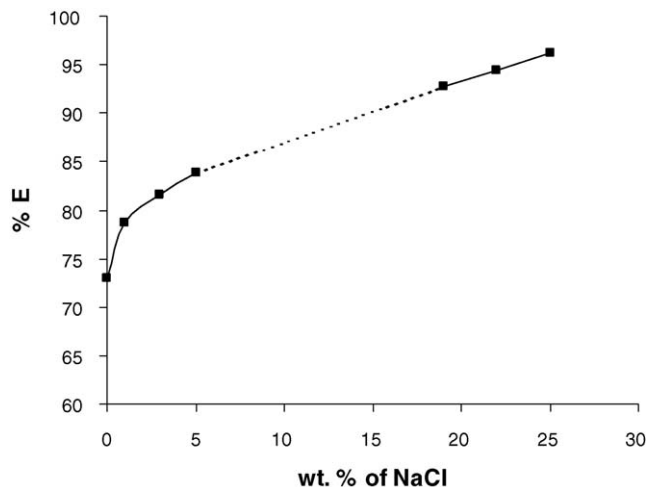


Fig. 6. Effect of sodium chloride on the extraction extent in  $H_2O/Oxo-C_{13}E_9$ /phenol system ( $T=50^\circ C$ ; 0.15 wt.% of phenol; 4 wt.% of  $Oxo-C_{13}E_9$ ); for the intermittent line part phases separation is very slow.

tration (up to 96% of extraction at 25% of NaCl), the dotted part of Fig. 6 is explained in Fig. 5.

As mentioned above, the salting-out effect resulted from the solvated electrolyte depends on the hydrogen bonding between water molecules and the surfactant polar head group as well as with the phenol hydrophilic part. In the presence of electrolyte, phenol and surfactant molecules are less soluble in water.

Therefore, in the presence of 25 wt.% of NaCl solution, the surfactant and phenol solubilized in micelles are pushed out to the coacervate phase. Hence, the dilute phase became less concentrated in phenol (0.0051 wt.%) as shown in Fig. 7. This concentration is almost 30 times less than that of the initial effluent concentration (0.15 wt.%). The only disadvantage of high concentration of NaCl is the excessive salinities of the dilute phase which prevents the analyses of the dilute phase by light diffusion detector (DDL31). The encasement of NaCl can damage the detector evaporator.

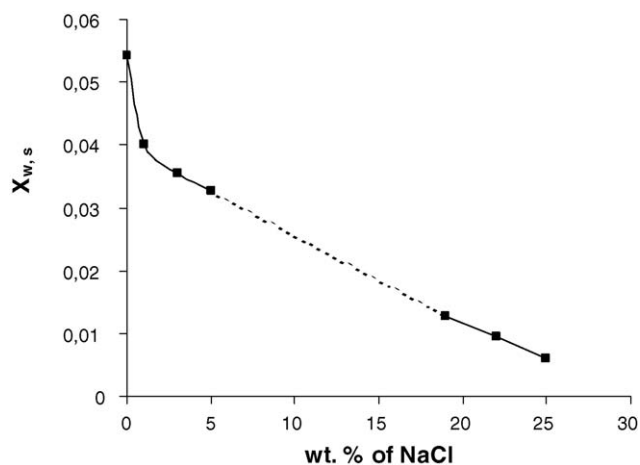


Fig. 7. Sodium chloride effect on the remaining of phenol in the dilute phase of the  $H_2O/C_{13}E_9$ /phenol system ( $T=50^\circ C$ ; 0.15% of phenol; 4 wt.% of  $Oxo-C_{13}E_9$ ); for the intermittent line part phases separation is very slow.

Table 2  
Conditions of coacervate regeneration

[Ca(OH) <sub>2</sub> ] (mg/l) in the coacervate	pH of the coacervate	wt.% of phenol release from the cocervate	[CaC <sub>2</sub> O <sub>4</sub> ] (ppm) in the dilute phase
0	6.56	10.52	6.5
0.12	9.85	24.97	6.6
0.24	10.07	29.34	6.7
0.36	11.03	38.37	6.7
0.65	11.52	42.49	6.4
0.75	12.02	45.48	6.8
1.25	12.30	45.8	6.8
1.53	12.4	46.22	6.7

### 3.4. The effect of pH on the extraction extent of phenol and benzyl alcohol

The solute-micelle interactions are strongly influenced by solute ionisation [40]. Therefore, the metallic chelates sharing between the dilute phase and coacervate vary with the pH of the non-ionic surfactant solutions [41]. After the deprotonation of a weak acid or the protonation of a weak base, slight interactions may occur with the surfactant. In these conditions, a small amount of those species may be solubilize, unlike neutral molecules. Consequently, a small amount of ionised solute can be extracted.

Indeed, pH is the key-parameter for surfactant regeneration. After a first extraction process of phenol (as weak acid) at 10 °C, the coacervate pH was increase beyond its pK<sub>a</sub> (pK<sub>a</sub> = 9.82) [42] using Ca(OH)<sub>2</sub> to give a complete dissociation of the solute (Table 2). 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 (Fig. 8). Moreover, the previous coacervate was separated into two new phases at 25 °C, a small quantity of an aqueous phase where concentrated the solute, and a new coacervate phase containing most of the surfactant [3]. In order to use the surfactant again, it is necessary to decrease its pH and to precipitate the base (Ca(OH)<sub>2</sub>). Therefore, it is better to choose an acid forming an insoluble salt with the base cation, such as H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (Table 2).

Hence, 46% of phenol extracted at 10 °C can be released from the coacervate to a new dilute phase (at 25 °C and pH 12.4), this pH is the maximum which can be reached by using Ca(OH)<sub>2</sub> with a solubility limit of 1.53 g/l [43]. The last pH is the double value of the phenol's pK<sub>a</sub>. Under these conditions, the dissociated phenol was predominant. After filtration, the soluble salt concentration of CaC<sub>2</sub>O<sub>4</sub> was calculated from the initial mass of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and from the mass balance of the acid–base reaction. The concentration of CaC<sub>2</sub>O<sub>4</sub> is shown in Table 2, this concentration is closed to its solubility limit in water at 25 °C (6.8 ppm) [43]. In the case of a neutral solute such as, benzyl alcohol (pK<sub>a</sub> = 15.4) [44], the change of pH does not affect the dissociation of benzyl alcohol. Unlike phenol extraction, benzyl alcohol extraction extent remains constant in all pH values (Fig. 8). In this case, surfactant regeneration is not possible by changing pH. Benzyl alcohol processing should be done carefully due to the presence of a similar functional group (CH<sub>2</sub>OH) to that of the surfactant.

## 4. Conclusions

The presence of both phenol and benzyl alcohol lowers the non-ionic surfactants cloud point. The influence of phenol was found to be high at low surfactant concentrations. The first contact between surfactant and effluent solutions gave extraction percentages, *E*, around 95% for phenol and 90% for benzyl alcohol, provided that the surfactant concentration should be higher than 7 wt.%. Hence, the solute concentration in the effluent was reduced to about 7–10 in the first extraction process. The biodegradable surfactant concentration in the dilute phase was higher than its cmc. On the other hand, a significant temperature rise beyond the cloud point decreases the extraction percentage, *E*. Although, the solubility of benzyl alcohol in water is half of that for phenol (40 g/l against 82.8 g/l at 25 °C) [45], it is more difficult to be extracted than phenol. This is probably due to the low effect of benzyl alcohol on the surfactant cloud point temperature, and consequently, it has small interactions with the surfactant. The sodium chloride reduced the coacervate volume fraction because of the cloud point lowering of the surfactant solution, and also increased the solute extracted percentage. The surfactant recycling in a cloud point extraction process depends mainly on the extracted species. In the case of weak acid such as phenol, the coacervate regeneration is possible by changing pH, but in the case of a neutral substance, as benzyl alcohol, surfactant recycling becomes difficult.

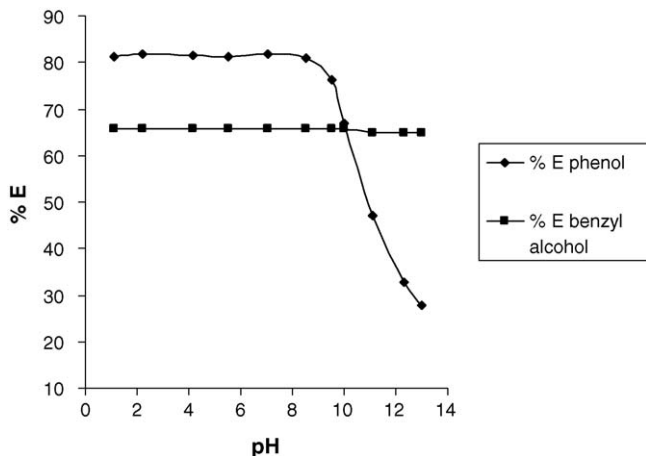


Fig. 8. Effect of pH on phenol and benzyl alcohol extraction percentage, *E*, in the H<sub>2</sub>O/C<sub>10</sub>E<sub>3</sub>/solute system (5 wt.% of Oxo-C<sub>10</sub>E<sub>3</sub>/solute:0.15 wt.%) at 10 °C.



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