

# Effect of nonionic surfactants on the solubilization of alachlor

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## Abstract

The ability of nonionic surfactants to solubilize the pesticide alachlor was studied. Two homologue series, octylphenol ethoxylates (Triton X-114, Triton X-100 and Triton X-102) and ethoxylated decyl alcohols (Neodol 91-5E, Neodol 91-6E and Neodol 91-8E) were used at concentrations 3 critical micelle concentration (CMC) and 6 CMC. The rate of solubilization of a sufficient quantity of alachlor (for saturation) in aqueous solution containing the micelles of nonionic surfactant was recorded. The experimental data were fitted to a first-order kinetic model. The rate constant, saturation concentration and enhancement factor were estimated for each surfactant system. The effect of surfactant structure, CMC concentration, pesticide structure and its physicochemical properties on the effectiveness of solubilization was determined. In terms of solubilization capability, the nonionic surfactants of each homologue series can be ranked as follows: Neodol 91-8E > Neodol 91-6E > Neodol 91-5E and Triton X-102 > Triton X-100 > Triton X-114. The more hydrophilic Neodol series was proved more efficient in alachlor solubilization than Triton series. The enhancement factor values ranged from 1.064 to 1.995 at 3 CMC and 1.320 to 2.919 at 6 CMC. The results will be used mainly for micellar-enhanced ultrafiltration since the extent of solubilization is a critical factor.

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**Keywords:** Alachlor; Kinetics; Micelle; Solubilization; Surfactants

## 1. Introduction

Pesticides are classified among the most representative categories of organic pollutants in the environment due to their intensive use for agricultural purposes [1]. The presence of pesticides in soil and water systems can cause serious problems in both the environment and human being. Environmental regulations in developed countries have become very strict for drinking water treatment over the last few years particularly regarding pesticide compounds [2].

Surfactants at concentration above their critical micelle concentration (CMC) form aggregates called micelles. Surfactant micelles offer a relatively large microscopic nonpolar environment for solute partition (solubilization) [3]. This effect can increase the solubility of solutes in the micellar surfactant solution (so-called apparent water solubility) in comparison with water solution. The use of surfactants to decontaminate groundwater aquifers and in soil clean-up operations (surfactant-

enhanced remediation or SER) is well established. Both anionic and nonionic surfactants have been used to remediate land polluted with oils and hydrocarbons as well as other organic contaminants [4] with high contaminants removal rates in situ field tests [5]. Also, micellar-enhanced ultrafiltration (MEUF) is a recently proposed technique, which can be used to remove soluble, low molecular weight organics from water [6]. In this process, surfactant is added to the polluted aqueous stream at concentration greater than its CMC. The organic pollutant is dissolved or solubilized into the formed micelles. The stream passes then through an ultrafiltration membrane with pore sizes smaller than the size of micelles. The micelles containing the organic pollutants are rejected by the membrane [7]. In addition, it is considered that in some cases solubilization enhances biodegradation [8,9].

The recent research has focused on the solubilization of polycyclic aromatic hydrocarbons (PAHs) including experiments on the determination of the partition coefficient between micelles and water and the molar solubilization ratio (MSR, the number of moles of solute solubilized per mole of surfactant in micellar form) [10]. MSR is a dimensional equilibrium constant of solute and micelle concentration in water. The research aim was the

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estimation of surfactant effect on the solubility and partition behavior of pollutants in surface water, ground water and soil systems, as well as surfactant potential to remove contaminants [11–17]. Sandoval et al. [18] compared ramnolipids (biosurfactant) and Triton X-100 with regard to their effect on the solubilization of three pesticides (trifluralin, atrazine and coumaphos) in order to utilize the results in future biodegradation studies. Lopes et al. [19] studied the partition of pesticides of coumarin family between water and micelles of an anionic surfactant, sodium dodecyl sulfate and a nonionic surfactant, polyethylene (10) lauryl ether (C12E10) by fluorescence anisotropy method.

We have already studied the ultrafiltration behavior of non-ionic surfactant solutions (flux behavior, estimations of interactions on membrane surface, fouling effect, concentration polarization phenomenon, etc.) for membrane characterization, cleaning, reuse and pretreatment in biological treatment processes [20,21]. An extension of this research includes the application of micellar-enhanced ultrafiltration for pesticides removal from aqueous streams. It is considered necessary to study as a first step the solubilization of pesticides in surfactant solution, since the extent of solubilization is an important factor [22]. Hence, the objective of this work was the evaluation of the effectiveness of selected nonionic surfactants to solubilize a typical pesticide (alachlor). The effectiveness was based on the enhancement of the aqueous plus micellar phase solubility (or apparent solubility) of alachlor. So, temporal monitoring of the aqueous plus micellar phase concentration of the pesticide in the absence or presence of surfactant was performed. Two homo-

logue series of surfactant were used. The apparent solubilities of alachlor as a function of time were then fitted to a first-order saturation equation, and nonlinear regression analysis was used to estimate the saturation concentrations  $C^*$ , aqueous phase solubility enhancement factors  $K$  and first-order rate coefficients  $k$ . Parameters obtained by optimizing the model are good approximations of the solubilization kinetics for alachlor.

## 2. Materials and methods

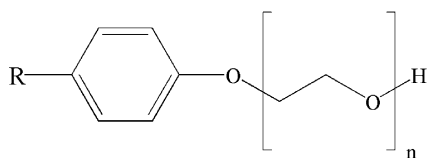
### 2.1. Materials

Two homologues series of nonionic surfactants were used: (i) the Triton series (alkylphenol ethoxylates) and (ii) the Neodol alcohol ethoxylate series purchased by Shell. Their properties are shown in Table 1 [21]. According to manufacturers' technical data sheets, Neodol surfactants series has a purity of 100% and Triton surfactants series a purity of 97%. The criteria for the selected nonionic surfactant were as follows: (a) their low CMC values and large micelles, thus permitting the use of very high molecular cut-off ultrafiltration membranes (and consequently higher flux rates) [23,24]; (b) so far the majority of these surfactants have not been used in such studies and (c) the effect of hydrophilic–lipophilic balance (HLB) on solubilization. The surfactants were used as supplied.

The pesticide chosen was alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide], kindly supplied by Benakion Phytopathologic Institute of Greece, which is still

Table 1  
Properties of surfactants

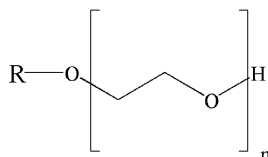
Surfactant	Number $n^a$	$\langle mm \rangle^b$ (g/mol)	HLB <sup>c</sup>	CMC $\times 10^4$ (mol/l)	Solubility
Triton series of surfactants					
X-114	8	558	12.4	2.65	s <sup>d</sup>
X-100	10	646	13.5	2.8	s
X-102	12	756	14.3	3.7	s



Formula R=C8

Neodol series of surfactants

91-5E	5	380	11.6	8	s
91-6E	6	424	12.5	9	s
91-8E	8	512	13.7	10	s



Formula

The carbon number distribution is C9, 18%; C10, 50% and C11, 32%. Thus the average carbon number of Neodol is 10.14

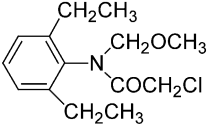
<sup>a</sup>  $n$  is the number of ethoxy groups in the above formula.

<sup>b</sup> Mean molecular mass according to the product declaration.

<sup>c</sup> HLB means hydrophile–lipophile balance.

<sup>d</sup> s means readily soluble in water.

Table 2  
Alachlor properties

Pesticide	Alachlor
Chemical structure	
Appearance	Yellow white to wine red, odorless solid (technical grade 90%)
Solubility (water)	0.14 g/l of water at 23 °C, slightly soluble in water
Density	1.1125 g/cm <sup>3</sup> , 25 °C
K <sub>OW</sub>	log P = 3.09
Molecular weight	269.8 g/mol
Melting point	40.5–41.5 °C

one of the most widely used pesticides. It persists in soil for 6–10 weeks and in surface water 55% degrades in 28 days [25]. Alachlor is a restricted use pesticide (RUP). In accordance with the US Environmental Protection Agency (EPA) proposed guidelines for carcinogen risk assessment, alachlor was characterized as probable carcinogen for humans (group B2). The commission of the European Union has classified this compound among the high priority pesticides, including those products used in amounts over 50 tonnes per year and with some potential to leach [26,27]. Alachlor properties are shown in Table 2.

## 2.2. Experimental procedure

Aqueous solutions for each surfactant were prepared using ultra pure water at two concentrations 3 CMC and 6 CMC. A 15 ml volume of each solution was placed in 20 ml volume Erlenmeyer flasks, and 30 mg of pesticide were added as solid to ensure solution saturation once equilibrium was established. So, preliminary experiments were performed for each pesticide–surfactant system or water in order to define the initial required amount of pesticide for saturation. The flasks were placed in a wrist-moving shaker equipped with a thermostatic bath at 25 °C, 30 rpm. Triplicates of each surfactant–alachlor system were prepared. In addition, the same procedure was applied for alachlor–water system (three repetitions). Aliquots of 300 µl from the supernatant liquid were taken temporarily and analyzed for the determination of herbicide concentration with high pressure liquid chromatography (HPLC chromatography).

## 2.3. Analysis

Analysis of alachlor was performed with a GBC Scientific Equipment Pty Ltd. High Pressure Liquid Chromatography apparatus (GBC LC 1120 pump and GB 1200 UV–vis detector and a 250 mm × 4.6 mm Hypersil C18 BDS reverse phase column (particle size 5 µm)). The HPLC was operated under the following conditions: mobile phase acetonitrile/H<sub>2</sub>O = 60/40, flow rate 1 ml/min, injection volume 10 µl, UV-detector, λ 220 nm. The retention time of alachlor was 8.3 min approximately. The samples before being analyzed were filtered with millipore HV

syringe filters (0.45 µm). The analysis was performed in duplicates. Analyses of all six surfactants solutions at both concentrations were obtained to verify that there was no interference with alachlor measurement at 220 nm.

## 2.4. Theory and calculations

A simple first-order saturation equation was used to model the solubilization phenomenon of alachlor. The rate frequently used is an empirically based saturation kinetic model and states that the dissolution is controlled by the rate of diffusion of dissolved substances from the solid phase [16,28]. According to the rate law:

$$\frac{dC}{dt} = k(C^* - C) \quad (1.1)$$

where  $C^*$  is the saturation concentration of the target analyte (mg/l),  $C$  the time variable concentration of the target analyte (mg/l) and  $k$  is the first-order rate constant ( $\text{h}^{-1}$ ). The rate and extent of dissolution is altered in the presence of surfactants micelles (because of solubilization) and Eq. (1.1) takes the form of:

$$\frac{dC}{dt} = k(KC^* - C) \quad (1.2)$$

where  $K$  is the aqueous solubility enhancement factor due to the presence of surfactants. It is defined as the ratio of the analyte concentration in surfactant solutions to that in aqueous solutions. The analytical solutions of these equations are:

Eq. (1.1):

$$C = C^*(1 - e^{-kt}) \quad (1.3)$$

Eq. (1.2):

$$C = KC^*(1 - e^{-kt}) \quad (1.4)$$

Parameter estimation of each model provided the saturation concentration ( $C^*$ ), rate coefficients ( $k$ ) and solubility enhancement factors ( $K$ ) for each pesticide–surfactant system. The parameters were estimated by nonlinear regression analysis using MATLAB<sup>®</sup> software. The procedure of nonlinear regression was based on the Levenberg–Marquardt algorithm which has been used for many years and was proved to work most of the time for a wide range of nonlinear models and starting values. The adequacy of the kinetic model was proved by the goodness of fit statistics for parametric models:  $R$ -square ( $R^2$ ), adjusted  $R$ -square (adjusted  $R^2$ ) and root mean squared error (RMSE) obtained from the aforementioned software:

$$R^2 = 1 - \frac{\text{SSE}}{\text{SST}} \quad (1.5)$$

$$\text{SST} = \sum_{i=1}^n (C_i - \bar{C})^2$$

$$\text{SSE} = \sum_{i=1}^n (C_i - \hat{C}_i)^2 \quad (1.6)$$

where  $C_i$  is the observed response value,  $\hat{C}_i$  the fitted response value and  $n$  is the number of the response values (experimental points).  $R^2$  can take on any value between 0 and 1, with a value closer to 1 indicating a better fit.

$$\text{Adjusted } R^2 = 1 - \frac{\text{SSE}(n-1)}{\text{SST}(\nu-1)} \quad (1.7)$$

where  $\nu$ , the residual degrees of freedom, is defined as the number of response values  $n$  minus the number of fitted coefficients  $m$  estimated from the response values:

$$\nu = n - m \quad (1.8)$$

### 3. Results and discussion

#### 3.1. Solubilization kinetics experiments

The solubilization process of alachlor as a function of time in aqueous solution containing the nonionic Triton surfactants at 3 CMC and 6 CMC is given in Figs. 1 and 2.

It is evident that the micelles capability of the more hydrophilic Triton surfactant (Triton X-102) to solubilize the

herbicide was higher in comparison to that of the more hydrophobic Triton X-114 and Triton X-100 at 3 CMC (Fig. 1). Similar behavior was observed at 6 CMC (Fig. 2). The solubilization curve of alachlor in Triton X-100 solution at both concentrations is higher than that of Triton X-114 and lower but close to the curve of Triton X-102. Although alachlor is a hydrophobic organic molecule (14 carbon atoms), it is observed that it is solubilized in a higher degree in the more hydrophilic Triton micelles. This behavior can be explained considering the polar character of alachlor molecule (carbonyl group and ether group) and its moderate solubility in water (see Table 2). According to solubilization theory, the extent and location of solubilization is determined mainly by a variety of hydrophilic and hydrophobic interactions developed between the polar and hydrophobic sites of the solute and the external (mantle) and inner part (core) of the micelle [3]. In addition, the orientation of the solubilizate and the exact location in the micelle is affected by the balance between the above two basic mechanisms. Since Triton surfactants possess the same hydrocarbon chain and differ in the number of ethyleneoxides (hydrophilic part), in the case of alachlor the hydrophilic interactions (hydrogen bonding, dipole–dipole, dipole-induced attraction forces, etc.) between alachlor–surfactant micelle should dominate the ever-present van der Waals forces (hydrophobic). Therefore, the polar molecule of alachlor is likely to be solubilized in the outer layer of the micelles with its polar groups oriented toward the polar ethyleneoxide chains and its hydrocarbon portion toward the interior of the micelle [29]. Consequently, since the polar interaction should be stronger between alachlor and the more hydrophilic mantle of surfactant micelle, the solubilization effectiveness of Tritons should be proportional to ethyleneoxide number of surfactant ( $n$ ): Triton X-102 ( $n=12$ ) > Triton X-100 ( $n=10$ ) > Triton X-114 ( $n=8$ ). The small difference in solubilization between Triton X-102 and Triton X-100 could be attributed to the higher hydrophobicity of Triton X-100 micelle (due to its higher aggregation number) giving rise to stronger hydrophobic forces between alachlor–hydrophobic part of the micelle in combination with the less steric hindrance (shorter polyethyleneoxide chains in the mantle of the micelle). It should be noticed that a decrease in the hydrophilicity, e.g. a shorter polyoxyethylene chain, causes an increase of the aggregation number of monomer surfactant molecules in the micelle [29,30]. It is probable that alachlor molecule penetrates more deeply in Triton X-100 micelle in comparison with Triton X-102 micelle.

The apparent solubility of alachlor against time in aqueous solution containing the nonionic Neodol surfactants at 3 CMC and 6 CMC is given in Figs. 3 and 4, respectively.

A similar solubilization behavior of alachlor in Neodol micelles as that in Triton micelles was observed. So, the most hydrophilic Neodol 91-8E was proved more effective in comparison to the less hydrophilic Neodol 91-6E and certainly to the most hydrophobic Neodol 91-5E. Since Neodol surfactants are nonionic as Triton having the same hydrophobic chain and different number of ethyleneoxides, a similar explanation of their solubilization effectiveness could be given as that for Triton, mentioned in the previous paragraph. As far as

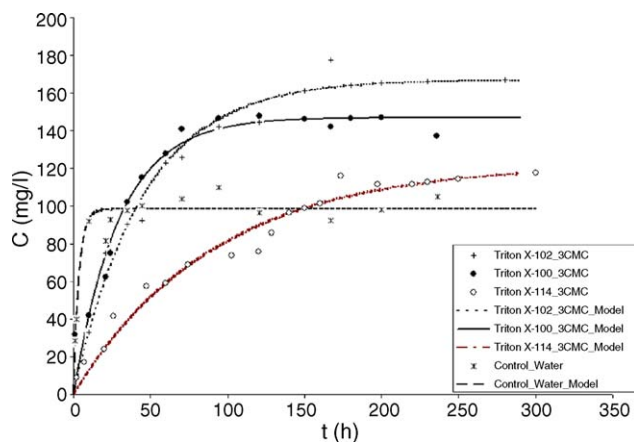


Fig. 1. Aqueous plus micellar phase concentration of alachlor over time in the absence and presence of Triton surfactants at 3 CMC and 25 °C (S.D. of experimental points: 5%).

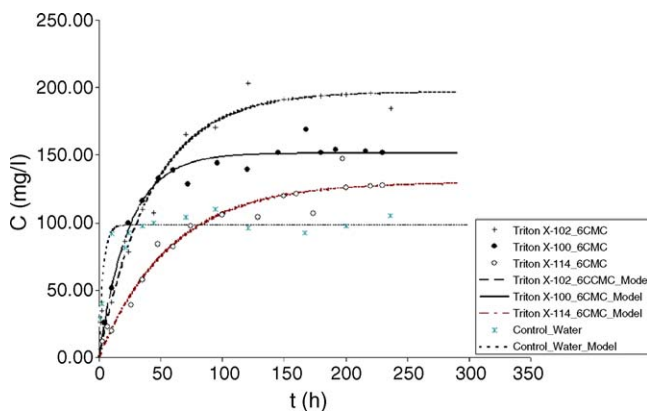


Fig. 2. Aqueous plus micellar phase concentration of alachlor over time in the absence and presence of Triton surfactants at 6 CMC and 25 °C (S.D. of experimental points: 5%).

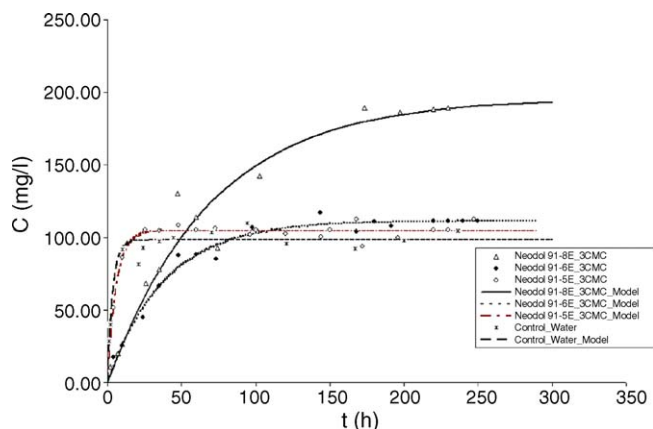


Fig. 3. Aqueous plus micellar phase concentration of alachlor over time in the absence and presence of Neodol surfactants at 3 CMC and 25 °C (S.D. of experimental points: 5%).

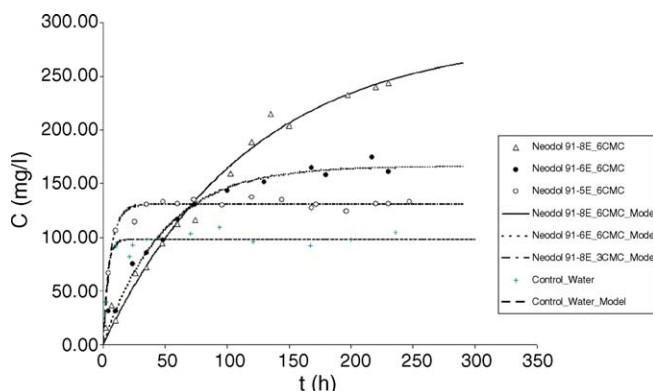


Fig. 4. Aqueous plus micellar phase concentration of alachlor over time in the absence and presence of Neodol surfactants at 6 CMC and 25 °C (S.D. of experimental points: 5%).

the slight changes in solubilization efficiency between Neodol 91-5E and Neodol 91-6E, these can be due to the increase of hydrophobic interactions (higher aggregation number) and less steric hindrance permitting the deeper penetration of alachlor

Table 3  
Model parameters for alachlor–surfactant system and alachlor–water

Surfactant	Concentration (CMC)	$K$ , 95% confidence bounds	$k$ ( $\text{h}^{-1}$ ), 95% confidence bounds
Triton X-114	3 CMC	1.243 (1.133, 1.353)	0.011 (0.008, 0.013)
Triton X-100	3 CMC	1.492 (1.396, 1.589)	0.034 (0.016, 0.051)
Triton X-102	3 CMC	1.7 (1.593, 1.806)	0.022 (0.017, 0.027)
Neodol 91-5E	3 CMC	1.064 (1.041, 1.088)	0.173 (0.139, 0.207)
Neodol 91-6E	3 CMC	1.132 (1.078, 1.186)	0.026 (0.021, 0.031)
Neodol 91-8E	3 CMC	1.995 (1.736, 2.255)	0.014 (0.009, 0.019)
Triton X-114	6 CMC	1.32 (1.218, 1.421)	0.017 (0.013, 0.022)
Triton X-100	6 CMC	1.539 (1.481, 1.597)	0.041 (0.034, 0.049)
Triton X-102	6 CMC	2.002 (1.868, 2.136)	0.0232 (0.018, 0.029)
Neodol 91-5E	6 CMC	1.329 (1.299, 1.359)	0.169 (0.138, 0.200)
Neodol 91-6E	6 CMC	1.691 (1.596, 1.786)	0.021 (0.017, 0.024)
Neodol 91-8E	6 CMC	2.919 (2.558, 3.28)	0.008 (0.006, 0.011)
Water (without surfactant)	0	$C^*$ (mg/l) (with 95% confidence bounds) 98.24 (94.84, 101.6)	$k$ ( $\text{h}^{-1}$ ) (with 95% confidence bounds) 0.281 (0.194, 0.368)

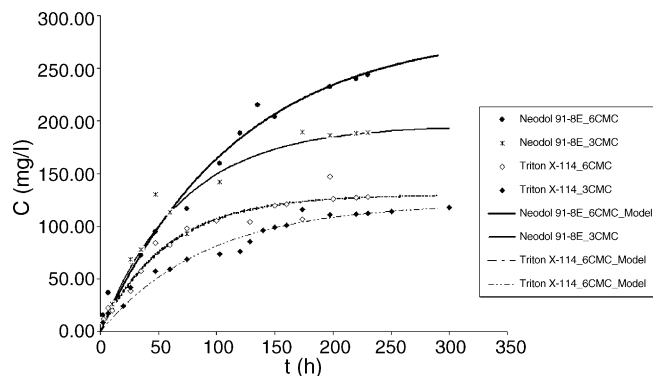


Fig. 5. Comparison of the solubilization of alachlor at 25 °C in aqueous solution of surfactants containing the same number of ethyleneoxides (S.D. of experimental points: 5%).

molecule in Neodol 91-5E micelle compared to Neodol 91-6E micelle.

A comparison of the effectiveness between Triton X-114 and Neodol 91-8E in alachlor solubilization can be made (Fig. 5) because these surfactants have the same number of ethyleneoxide units ( $n=8$ , same hydrophilicity), and differ in hydrocarbon chain structure and length. The linear hydrocarbon chain of Neodol 91-8E has an average carbon atoms number equal to 10.15 (see Table 1), while the hydrophobic part of Triton X-114 consists of 8 carbon atoms plus an aromatic ring equivalent to 3.5 linear carbon atoms [3], namely an average carbon atoms number equal to 11.5. The increase in solubilization effectiveness of Neodol 91-8E compared to that of Triton X-114 (at 3 CMC and 6 CMC) should be due to the difference in hydrophobicity between the two surfactants.

### 3.2. Model parameters estimation

The estimated parameters of the model employed are presented in Table 3. The increase of the enhancement factor  $K$  from 3 CMC to 6 CMC for the Triton surfactant series was 6.2% (Triton X-114), 3.2% (Triton X-100) and 17.8% (Triton X-102), and for the Neodol surfactant series was 24.9% (Neodol 91-5E),



Table 4  
Values of goodness of fit statistics in dissolution of alachlor in aqueous surfactant solutions

6 CMC	$R^2$	Adjusted $R^2$	RMSE
Surfactant			
Triton X-114	0.9592	0.9564	8.909
Triton X-100	0.9674	0.9649	7.487
Triton X-102	0.9641	0.9614	12.950
Neodol 91-5E	0.9210	0.9154	5.072
Neodol 91-6E	0.9774	0.9753	7.742
Neodol 91-8E	0.9848	0.9836	10.520
3 CMC			
Surfactant			
Triton X-114	0.9664	0.9645	6.686
Triton X-100	0.9293	0.9246	11.910
Triton X-102	0.9598	0.9571	10.880
Neodol 91-5E	0.9028	0.8967	4.367
Neodol 91-6E	0.9743	0.9722	5.557
Neodol 91-8E	0.9512	0.9468	15.470
	$R^2$	Adjusted $R^2$	RMSE
Water	0.9383	0.9339	5.786

49.4% (Neodol 91-6E) and 46.3% (Neodol 91-8E). It is obvious that the values of enhancement factor reflect the effectiveness of surfactants in alachlor solubilization and it is in accordance with the conclusion that the more hydrophilic surfactant can solubilize more extensively the polar pesticide. The rate constants  $k$  do not appear to follow a consistent trend with variations in surfactant structure and surfactant concentration, which reveals the complicated micelle system including a variety of interactions, and alteration of micelle structure and shape (different aggregation number and ethylene oxide units). Similar remarks are reported in the literature [31].

The dissolution rate constant  $k$  of alachlor in water is higher comparing to those calculated in the presence of surfactant micelles. This event could be explained considering that in pure water there are more water molecules available to dissolve the pesticide. In contrary, a number of water molecules are attracted towards the hydrophilic layer of the micelle, delaying the rate of solubilization.

The values of the goodness of fit statistics are given in Table 4. In all cases the value of  $R^2$  was greater than 0.90 indicating a good fit. Also, the values of adjusted  $R^2$  were close to 1 and the values of RMSE were low, supporting that the model can describe successfully the dissolution of alachlor in the presence and absence of surfactants [32]. Consequently, the adequacy of kinetic model was confirmed.

#### 4. Conclusions

The dissolution of alachlor was significantly enhanced in aqueous solutions containing nonionic surfactant micelles. By increasing the hydrophilicity of surfactant, the solubilization of alachlor was increased. The rate of solubilization of alachlor was smaller with regard to that of dissolution in pure water and it should be affected by the nature of the surfac-

tants micelles and the interactions developed in the surfactant micelle–alachlor–water system.

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