

# Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <u>http://oatao.univ-toulouse.fr/</u> Eprints ID: 5928

> **To link to this article**: DOI:10.1080/01932690902735538 URL: <u>http://dx.doi.org/10.1080/01932690902735538</u>

**To cite this version**: Nedjhioui, Mohamed and Moulai-Mostefa, Nadji and Canselier, Jean-Paul and Bensmaili, Aicha (2009) Investigation of Combined Effects of Xanthan Gum, Sodium Dodecyl Sulphate, and Salt on Some Physicochemical Properties of Their Mixtures Using a Response Surface Method. *Journal of Dispersion Science and Technology*, vol. 30 (n° 9). pp. 1333-1341. ISSN 0193-2691

Any correspondence concerning this service should be sent to the repository administrator: <a href="mailto:staff-oatao@listes-diff.inp-toulouse.fr">staff-oatao@listes-diff.inp-toulouse.fr</a>

# Investigation of Combined Effects of Xanthan Gum, Sodium Dodecyl Sulphate, and Salt on Some Physicochemical Properties of Their Mixtures Using a Response Surface Method

Mohamed Nedjhioui,<sup>1</sup> Nadji Moulai-Mostefa,<sup>1</sup> Jean Paul Canselier,<sup>2</sup> and Aicha Bensmaili<sup>3</sup>

<sup>1</sup>LPT2R, Faculty of Science and Technology, University of Medea, Medea, Algeria <sup>2</sup>I.N.P.T-ENSIACET-5, Toulouse, France <sup>3</sup>Faculty of Process and Mechanical Engineering, USTHB, Alger, Algeria

> Aqueous solutions containing sodium dodecyl sulphate, xanthan gum, and salt were characterized by ionic conductivity, viscosity, and surface tension methods. A preliminary experimental study was performed to evaluate the effect of the mixture compositions on the surface behavior of the mixed polymer/surfactant systems under different solution conditions. An experimental design using response surface method (RSM) was then applied to assess factors interactions and empirical models regarding the physicochemical responses variables (i.e., conductivity, surface tension and viscosity). The main effects of the three independent factors: SDS concentration  $(x_1)$ , NaCI concentration  $(x_2)$  and xanthan concentration  $(x_3)$  were determined using in particular a D-optimal design. The results show an important effect of the factors on responses; they also indicate that the synergetic action of surfactant, electrolyte and biopolymer greatly influences these properties. Analysis of variance (ANOVA) showed high variance coefficient  $(R^2)$  values, thus, ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

> Keywords Interactions, physicochemical properties, polymer, surface response method, surfactant

# **INTRODUCTION**

Mixtures of polymers and surfactants are common in many industrial formulations; this is the case in food, pharmaceutical, cosmetics, and oil industries. It is known that solutions containing polymers and surfactants can give rise to molecular interactions that may affect their rheological and physicochemical properties.<sup>[1]</sup> These interactions also display features that depend on polymer and surfactant electrical charges and hydrophobicity, polymer conformation, and flexibility and the presence of additives such as salts. It is generally accepted that the hydrophobic character of both polymer and surfactant is responsible of interactions. The nature of these interactions has been investigated for several decades and is extensively documented.<sup>[2-4]</sup> They are still poorly understood, but significant variations of the physicochemical and rheological properties of these systems are observed. Most study in this

Address correspondence to Nadji Moulai-Mostefa, LPT2R, University of Medea, Ain D'Heb, 26001 Medea, Algérie. E-mail: moulai\_nadji@yahoo.fr field focus on complexes of anionic surfactants with polymers.  $^{\left[ 5-7\right] }$ 

The investigation of the polymer–surfactant interactions can be done in two ways. In the first one, the polymer is considered as being the substance influenced by the surfactant, in the second way, the surfactant is considered as being the substance influenced by the polymer. In the first case, the surfactant is adsorbed on the polymer sites that disturb the formation of the surfactant micelles. Alternatively, in the second case the association of surfactant molecules with macromolecules facilitates the phenomenon of micellization.<sup>[8,9]</sup> The examination of the evolution of the physicochemical and rheological properties of such systems, according to the chemical nature and component concentrations, makes it possible to establish relations between these factors and the system responses such as surface tension, viscosity and conductivity.

Conductivity measurements were used extensively to study interactions between polymers and surfactants in aqueous solutions. They are very significant for the evaluation of electrostatic interactions in solution, especially when they involve charged substances (ionic surfactant, charged polymers and electrolyte). This method was used by Goddard<sup>[10]</sup> to investigate the effect of salt on the interaction between polymer (PEO) and SDS; by Sovilj et al.<sup>[11]</sup> to investigate the influence of hydroxypropylmethyl cellulose-SDS interactions; and by Nedjhioui et al.<sup>[12]</sup> to study the interaction between xanthan gum and SDS.

In the past, researchers used one-factor-at-a-time experimental method, which not only consumed more time and more cost but also neglected the effect of interaction between factors. Although traditional orthogonal method is capable of considering a few factors at the same time, it cannot get a function expression between the factors and response values. Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine multiple regression equations between the factors and experimental results.<sup>[13]</sup> The main advantage of this method of other statistical experimental design methods is the reduced number of experiments trials needed to evaluate multiple parameters and their interactions.<sup>[14]</sup>

In this work, sodium dodecylsulfate, sodium chloride, and xanthan gum effects on the physicochemical and rheological properties of aqueous solutions were studied using a response surface method, in particular a D-optimal design. Surface tension and conductivity measurements were used to detect the influence of the polymer on the surface activity of the surfactant. Changes in physical properties were investigated by rheological techniques. These physicochemical properties were used as responses for the model of experimental design.

# **EXPERIMENTAL**

#### **Materials**

Sodium dodecylsulfate (SDS) of analytical grade (99%) was purchased from Fluka (Buchs, Switzerland); xanthan gum (XG) was purchased from Rhodia (Paris la Défense, France). Sodium chloride (NaCl) of reagent grade (99%) was supplied by Panreac Quimica S.A.U. (Barcelona, Spain). Distilled water was used in these experiments.

# **Preparation of Polymer/Surfactant Mixtures**

Polymer dispersions were prepared by dissolution of the polymer in water under mild stirring at room temperature. After 24 hours, different amounts of surfactant and salt were added to the polymer solutions. The surfactant was dissolved under slow mixing in a helix mixer (Heidolph RZR 2020, Germany). The surfactant concentrations were chosen to be equal, higher or smaller than the critical micelle concentration (CMC) of the surfactant. However, the polymer (XG) concentrations were chosen to give variations in the solution viscosities.<sup>[15]</sup>

## **Methods**

Surface tension, critical micelle and critical aggregation concentrations of mixtures were measured with a Du Noüy tensiometer, model 70545 (CSC Scientific Co., Fairfax, VA, USA). The conductivity measurements were obtained using an Inolab conductometer (WTW, Weilheim, Germany) with (cell constant: 0.475 cm<sup>-1</sup>). Viscosimetric measurements were performed in a controlled stress rheometer (CSL2, TA Instruments, New Castle, DE, USA).

Run	SDS Concentration (% wt.)	NaCl Concentration (% wt.)	XG Concentration (% wt.)	Conductivity (mS/cm)	Surface tension (mN/m)	Viscosity (mPa.s)
01	0.050	0.020	0.100	0.653	59	
02	0.300	0.020	0.100	1.203	45	38
03	0.300	1000	0.100	17.590	43.5	37
04	0.050	0.020	0.500	1.198	54	498
05	0.300	0.020	0.500	1.715	42	527
06	0.050	1.000	0.500	15.50	52	492
07	0.300	1.000	0.500	15.070	44	495
08	0.500	1.000	0.233	17.884	55	160
09	0.500	0.673	0.100	12.210	57.5	30
10	0.133	1.000	0.100	17.580	45.5	35
11	0.300	0.510	0.300	8.110	43	237
12	0.175	0.020	0.300	1.147	46.5	240
13	0.175	0.510	0.500	7.660	45.5	522
14	0.175	0.510	0.300	7.940	45	231
15	0.175	0.510	0.300	9.260	46	227
16	0.175	0.510	0.300	6.940	45	281

 TABLE 1

 Levels of independent variables in uncoded form and responses

#### **Experimental Design**

The main effects of three independent factors: SDS concentration  $(x_1)$ , NaCl concentration  $(x_2)$  and xanthan concentration  $(x_3)$  were investigated using a D-optimal design. The D-optimal criterion was developed to select design points in a way that minimizes the variance associated with the estimates of specified model coefficients.<sup>[16]</sup> Plans with high D-value are constructed from the data by a computer algorithm. The variables were coded according to Equation (1):

$$X_i = \frac{U_i - U_i^0}{\Delta U_i}$$
[1]

where  $X_i$  is the independent variable coded value;  $U_i$  independent variable real value;  $U_i^0$ , independent variable real value on the centre point; and  $\Delta U_i$ , step change value.

Table 1 presents the levels of predictor variables tested following D-optimal design of experiments.

#### RESULTS

# **Statistical Analysis**

The arrangements of D-optimal experiments are listed in Table 1, which include 16 sets of experiments. By using multiple regression analysis, the responses (conductivity, surface tension, and viscosity) were correlated with the three design factors through the second-order polynomial, as shown in Equation (2).

$$Y_{i} = b_{0} + \sum_{i=1}^{3} b_{i}X_{i} + \sum_{i=1}^{3} b_{ii}X_{i}^{2} + \sum_{i=1}^{3} \sum_{j(\neq i)=2}^{3} b_{ij}X_{i}X_{j}$$
 [2]

where  $b_o$ ,  $b_i$ ,  $b_{ii}$ , and  $b_{ij}$  are constant regression coefficients of the model, while  $X_i$ ,  $X_j$  are the independent variables. The statistical significance of the regression coefficients was determined by the Fisher, F test analysis of variance and the proportion of variance explained by the obtained model was given by the multiple coefficient of determination,  $R^2$ .

The quadratic regression model for conductivity  $(Y_1)$ , surface tension  $(Y_2)$  and viscosity  $(Y_3)$  in terms of coded factors are given by Equations (3), (4), and (5), respectively:

$$\begin{split} Y_1 &= 8.08978 - 0.09987X_1 + 7.717689 \ X_2 - 0.527107X_3 \\ &+ 0.349899X_1^2 - 0.618733X_2^2 - 0.114059X_3^2 \\ &- 0.324037X_1X_2 - 0.0738602X_1X_3 - 0.803926X_2X_3 \end{split}$$

$$\begin{split} \mathbf{Y}_2 &= 670,558 - 1051,37\mathbf{X}_1 - 8,6878\mathbf{X}_2 + 7,92458\mathbf{X}_3 \\ &+ 440,733\mathbf{X}_1^2 - 0,625047\mathbf{X}_2^2 + 0,010688\mathbf{X}_3^2 \\ &+ 7,55734\mathbf{X}_1\mathbf{X}_2 + 7,16254\mathbf{X}_1\mathbf{X}_3 + 0,824721\mathbf{X}_2\mathbf{X}_3 \end{split}$$

[4]

$$\begin{split} Y_3 &= 258.968 + 4.48771X_1 - 132119X_2 + 235.35X_3 \\ &- 30.4001X_1^2 - 28.5655X_2^2 + 14.0826X_3^2 \\ &- 1.34677X_1X_2 + 4.50195X_1X_3 - 1.6916X_2X_3. \end{split}$$

The analysis of variance (ANOVA) for the models used to estimate the conductivity K (mS/cm), surface tension  $\gamma$  (mN/m), and viscosity  $\eta$  (mPa.s), respectively, as a function of SDS, NaCl, and XG concentrations is shown in Table 2.

The statistical significance of the second order model revealed that theses regressions are statistically significant (P < 0.0001). For the conductivity, the model presented a high determination coefficient ( $R^2 = 0.995$ ) explaining 99.5% of validity in the response. However, the analysis of variance for the model used to estimate surface tension shows that the regression is less significant and presents a determination coefficient ( $R^2 = 0.982$ ) explaining 98% of the validity in the response. The analysis of variance for the model obtained for viscosity  $\eta$  (mPa.s) shows the highly significant of the model (p = 0.0001) and presents a good determination coefficient ( $R^2 = 0.990$ ) indicating that only 1% of the total variations are not explained by the model. The value of the adjusted determination coefficient  $R^{2}(adj) = 0.976$  is also very high and indicates a high significance of the model.<sup>[17]</sup>

# Influence of Mixture Composition on Conductivity

For a sample polymer surfactant system, the specific conductivity versus SDS concentrations plots in presence of xanthan shows two break points (Figure 1). In presence of pure surfactant, the behavior of the conductivity is characteristic of ionic surfactants. It quickly increases to a certain concentration called the CMC of the surfactant (first break point). In presence of polymer, the conductivity of the mixture is higher than that of the surfactant alone. This increasing is the result of the high ionic strength of the mixture due to the charged polymer and surfactant. The change of the curves slopes after the first break point, called the critical association concentration (CAC), explains the onset of the association of SDS and xanthan molecules. A second break point is observed by the decreasing of the slopes in conductivity plots versus SDS concentrations. Above this concentration, SDS molecules adsorb on the polymeric chains, and the conductivity increases only slightly with increasing surfactant concentrations until the saturation of these chains at a certain point called the polymer saturation point (PSP).

The specific conductivity curves obtained from Equation (3) and given by Figures 2 through Figure 4, represent the surface response plots at varying SDS, NaCl, and XG concentrations values. The isoresponse plots show the effects of two factors while the third is kept constant at its zero level.

TABLE 2 Analysis of variance ANOVA for the model regression representing the conductivity (mS/cm) surface tension (mN/m), and the viscosity (mPa.s) using coded values

	DF	SS	MS	F	р	SD
Conductivity $(mS/cm)^a$						
Regression	9	626.326	69.6011	135.7360	0.0001	8.3427
Residual	6	3.0760	0.51266			0.7160
Lack of fit	4	0.3677	0.09193	0.0680	0.9860	0.3034
Pure error	2	2.70827	1.35413			1.16367
Total	16	1883.09	117.70			
Surface tension $(mN/m)^b$						
Regression	9	447,178	49,6864	37,0022	0,0001	7,04886
Residual	6	8,05678	1,3428			1,15879
Lack of fit	4	7,39011	1,84753	5,54257	0,159	1,35924
Pure error	2	0,666669	0,333334			0.5773
Total	16	37367,3	2335,45			
Viscosity $(mPa.s)^c$						
Regression	9	568270	63141.1	185.857	0.0001	251.278
Residual	6	2154.28	359.047			18.9485
Lack of fit	4	343.614	85.9036	0.094861	0.975	9.26842
Pure error	2	1810.67	905.333			30.088
Total	16	1.61491e + 0.06	100932			

 ${}^{a}R^{2} = 0,995, R^{2}_{adj} = 0,998.$  ${}^{b}R^{2} = 0,982, R^{2}_{adj} = 0,956.$  ${}^{c}R^{2} = 0.990, R^{2}(adj) = 0.976.$ 

Abbr.: DF, degree of freedom; SS, sum of squares; MS, mean square; F, Fisher test; p, probability; SD, standard deviation.

The specific conductivity of each species at any concentration is calculated by assuming that the total conductivity of the free ions is independent of any electrolyte present in the solution, so the sum of the conductivity of each ion in presence gives the total specific conductivity of solution. Acceptance of this assumption, the specific conductivity of solution containing the total sodium  $K_{\text{Na}}^+$  (the sum of free sodium in NaCl and in SDS  $(C_{12}H_{25}SO_4Na))$ , free dodecyl sulphate ion  $C_{12}H_{25}SO_4^-(DS^-), K_{DS}^-;\ free \ Cl^-$  containing in NaCl (K<sub>Cl</sub>-) and the conductivity of charged polymer, XG,  $(K_{XG})$  is given in Equation (6).<sup>[18]</sup>

$$K = K_{Na}^{+} + K_{DS}^{-} + K_{Cl}^{-} + K_{XG}$$
[6]

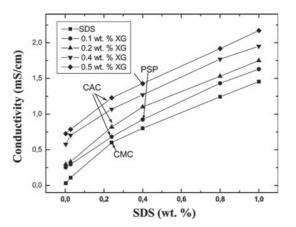


FIG. 1. Effect of SDS on conductivity in the presence and absence of xanthan.

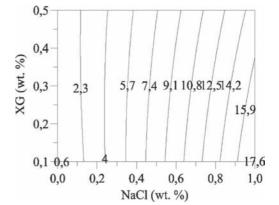


FIG. 2. Effect of NaCl and XG concentrations on conductivity (mS/cm): isoresponse plot (0.175 wt.%, SDS).

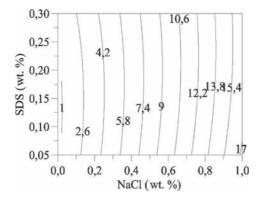


FIG. 3. Effect of NaCl and SDS concentrations on conductivity (mS/cm): isoresponse plot (0.3 wt.%, XG).

In the present context, only the total conductivity of solution, K, is obtained from the conductivity measurements.

Figure 2 shows the effects of NaCl and XG concentrations on the conductivity when the SDS concentration is kept constant at its zero level. The presence of xanthan gum (charged polymer) increases slightly the conductivity values with increasing NaCl at SDS constant concentration (0.175 wt.%). By adding xanthan to the NaCl solutions at constant SDS concentration, the total conductivity of solution depends strongly of NaCl concentration as shown in the model of Equation (6). In this case, we assume that complete dissociation of all species in solution because the SDS, at this constant concentration, is below the CAC. The effect of the addition of salt to aqueous solution of the electrolyte shows that the behavior of the CMC of the surfactant is not governed by the principle of ionic strength or the Debye-Hûckel relationships; this fact has not been clearly recognized previously.

The effect of salts upon the CMC has been investigated; it was shown that the addition of salt to surfactant

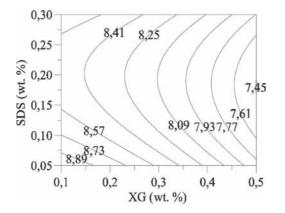


FIG. 4. Effects of XG and SDS concentrations on conductivity (mS/cm): isoresponse plot (0.51 wt.%, NaCl).

solutions is known to decreases the CMC and it has been reported that the addition of electrolyte increases the binding ratio of surfactant to polymer.<sup>[19]</sup> Figure 3 shows the conductivity plots at different SDS and NaCl concentrations when XG is kept constant at its zero level (0.3 wt.%). At this concentration, the CAC points are obtained and they are taken from plots of conductivity versus SDS concentrations (Figure 1). The specific conductivity increases only slightly with increasing SDS concentrations at high salt concentrations as expected in Equation (6). However, the increase in conductivity is due to the increase in NaCl concentration; this is evident because NaCl is a strong electrolyte in comparison with SDS ions.

The effect of XG and SDS concentrations when NaCl concentration is kept constant at its zero level (0.51 wt.%) is shown in Figure 4. The conductivity decreases with increasing XG at any SDS concentrations in the range of study. This behavior can be explained by the saturation of solution with polymer at low concentration; then we assume that the PSP is lower than the CMC of pure SDS because the saturation occurs before the surfactant monomer activity and it is equivalent to that at CMC. In this case, then, at constant concentration of salt (0.51 wt.%), for the salt effect on the conductivity plots, the CAC is driven by SDS micellization; also, the contributions of XG-SDS complexes and the SDS micelles to the total ionic content and consequently to the ionic mobility are different. On the other hand, SDS aggregates on XG begin to form at lower SDS concentrations than in normal SDS micelles and the surfactant monomer activity for aggregation is lower.

# Effect of Mixture Composition on the Surface Properties

The interaction of water-soluble polymers with anionic surfactants has been conventionally monitored by surface tension and specific or equivalent conductivity measurements plotted against the surfactant concentration.<sup>[20,21]</sup> The surface tension method is also used to explain the micellization process of surfactant solutions as well as the distribution of molecules in presence of an additive, the surface activity and the micelle formation of ionic surfactants in combination with charged polymer and salt.

The surface tension behavior of multicomponents system can be obtained from the classical thermodynamic relationships for interfacial properties. The formulation adopted is that due to Gibbs and represented by:<sup>[22]</sup>

$$d\gamma = -\sum \Gamma_i d\mu_i$$
 [7]

where  $\gamma$ ,  $\Gamma_i$ , and  $\mu_i$  are the surface or interfacial tension, surface excess component, and chemical potential of the component ( $\mu_i = \mu_i^0 + RT \ln a_i; \mu_i^0$  is the standard chemical potential and  $a_i$  is the activity of i).

Using the expression of the chemical potential in Equation (7), we obtain, for dilute solution:

$$d\gamma = -RT \sum \Gamma_i d\ln C_i$$
[8]

In a mixed multicomponents system of constant composition, we have:

$$C_1 = KC_2 = KC_3 = \dots$$
 [9]

Taking the log and differentiating, we have:

$$d \ln C_1 = d \ln C_2 = d \ln C_3 \dots$$
 [10]

Using this identity in Equation (7), the Gibbs adsorption equation for a system containing three components (SDS, NaCl, and XG) becomes:

$$d\gamma = -RT(\Gamma_{SDS} + \Gamma_{NaCl} + \Gamma_{XG})d\ln C_1 \qquad [11]$$

As shown above, we assumed complete dissociation of NaCl, XG, and the dissociation of SDS produces  $DS^-$  and Na<sup>+</sup> of equal strength, below the CMC, hence:

$$\Gamma_{\rm SDS} = \Gamma_{\rm DS}^- + \Gamma_{\rm Na}^+, \qquad [12]$$

This assumption is to consider positive adsorption, so, only the solute occupies the surface (the surface excess of pure solvent (here water)  $\Gamma_{\text{Solvent}} = 0$ )). Thus, the change in  $\Gamma$ , due to the change in concentration of any component can leads to the evaluation of the total excess:

$$\Gamma_{\rm tot} = \Gamma_{\rm SDS} + \Gamma_{\rm NaCl} + \Gamma_{\rm XG}$$
[13]

In the present work, only the total surface tension  $\gamma$  was obtained from the surface tension measurements.

Figure 5 shows the surface tension plots as a function of SDS concentrations in absence and presence of xanthan. In the absence of polymer, it quickly decreases to the surfactant CMC and thereafter remains constant. In the presence

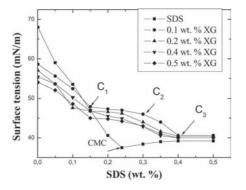


FIG. 5. Effect of SDS on surface tension in the presence and absence of xanthan.

of polymer, it was noticed that for weak concentrations of SDS, the surface tension of the mixture is lower than that of the pure surfactant. This decrease in surface tension is probably due to the adsorption of the polymer at the interface (below  $C_1$ ). In this region, the surface tension depends inversely on the polymer concentration. A second region is observed in the surface tension plot versus surfactant concentrations, where the surface tension of the mixture is higher than for pure surfactant. At this concentration, the SDS molecules adsorb on the polymeric chains, and the surface tension of the polymer-surfactant system decreases with increasing surfactant concentrations. Above C<sub>3</sub>, the surface tension slightly decreases towards a lower value to become constant. This is due to the increase of free SDS monomers in the bulk solution after the saturation of the polymeric chains.

Figure 6 shows the isoresponse plots for surface tension at varying NaCl and XG concentrations, the other factor (SDS) is held at its zero level (0.175 wt.%). As anticipated, the surface tension values decrease with increasing NaCl and XG concentrations. The minimum value (43.82 mN/m)is obtained near the concentration of NaCl (1 wt.%) and for XG concentration near (0.5 wt.%). In the presence of NaCl, the CMC of SDS is lowered and the aggregation number of individual micelles increases with salt concentrations; similarly, adding NaCl to XG/SDS solutions lowers the CAC and increases the size number of the micellar aggregates that attach to the polymer coil. This is an indication that stronger effect of surfactant presence is to be expected in solutions with NaCl. On the other hand, an excess of sodium ions in solution should screen the electrostatic repulsions between micellar aggregates attached to the polymer chain, thus, reducing the degree of coil expansion. In spite of the electrolytic affinity of the dissolved XG molecule, the presence of NaCl does not affect the extension thickening behavior of pure XG solutions.

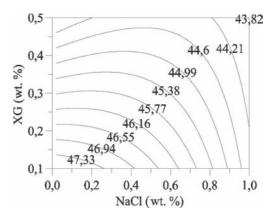


FIG.~6.~ Effect of NaCl and XG concentrations on surface tension (mN/m): isoresponse plot (0.175 wt.%, SDS).

Figure 7 represents the isoresponse plots for surface tension at varying NaCl and SDS concentrations, the XG is held at its zero level (0.3 wt.%). The surface tension values decrease with increasing SDS concentrations. The minimum of surface tension (42.6 mN/m) is obtained for NaCl (1 wt.%) and for SDS concentration near 0.25 wt.%. In presence of electrolyte, here NaCl, the decreasing of surface tension can be explained as for Figure 6, but at constant SDS concentration. Here, the addition of NaCl normally increases the surface tension. The reason is that the electrolyte is depleted from the surface; and consequently, the ions absorb at the liquid air surface.

Figure 8 represents the isoresponse plots for surface tension at varying XG and SDS concentrations, the other factor (NaCl) is held at its zero level (0.51 wt.%). As anticipated, the surface tension values depend strongly on SDS and XG concentrations. In the range study of SDS, the increasing in xanthan concentration contributes to a decreasing in surface tension. This phenomenon explained as for Figure 5 by the onset of the association of the SDS molecules with those of xanthan at the concentration known as the CAC. At this concentration, the SDS molecules adsorb on the polymeric chains, and the surface tension of the polymer-surfactant system decreases with increasing polymer concentrations until the saturation of these chains at the polymer saturation point.

The minimum of surface tension (42.6 mN/m) is obtained near the CMC of pure SDS at a concentration of 0.24 wt.% and a concentration of salt of 1.0 wt.%.

# Effect of Mixture Composition on Viscosity

The viscosity behavior is due essentially to the presence of polymer; hence, viscosity measurement is a convenient way to study the hydrodynamic volume in the solution. The viscosity measurement ( $\eta$ ) values of the solutions, below, and above the critical aggregation concentration, were determined and presented as apparent viscosity  $\eta_{app}$ 

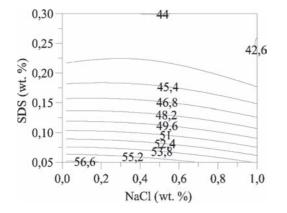


FIG. 7. Effect of NaCl and SDS concentrations on surface tension (mN/m): isoresponse plot (0.3 wt.%, XG).

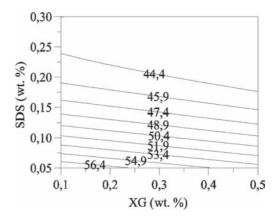


FIG. 8. Effect of XG and SDS concentrations on surface tension (mN/m): isoresponse plot (0.51 wt.% NaCl).

(mPa.s) values. As shown in Figure 9 and as expected, the polymer has a strong effect on the viscosity. Thus, apparent viscosity values increase with increasing XG concentrations. The maximum of viscosity ( $\sim$ 490 mPa.s) is obtained at XG concentration near 0.5 wt.%. Figure 9 shows, also, that the effect of NaCl on viscosity is negligible at any XG concentrations and at constant SDS concentration (0.175 wt.%).

Figure 10, shows the slight effects of SDS and NaCl concentrations on viscosity values. In fact, the range of obtained viscosities values is insignificant, the minimum of the viscosity (228.5 mPa.s) is obtained for 0.9 wt.% NaCl concentration and the maximum of viscosity (245.5 mPa.s) is obtained at NaCl concentration (0.15 wt.%) and for SDS concentration near the CAC (0.24 wt.%) at constant XG concentration (0.3 wt. %). At this point, the figure presents a symmetric behavior of the curve at 0.20 wt.% NaCl and 0.225 wt.% SDS concentrations. In the first region, (SDS below 0.225 wt.% and NaCl under 0.20 wt.%), the viscosity increases with increasing SDS concentrations at any NaCl

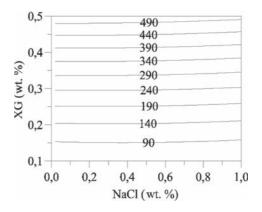


FIG. 9. Effect of NaCl and XG concentrations on viscosity (mPa.s): isoresponse plot (0.175 wt.%, SDS).

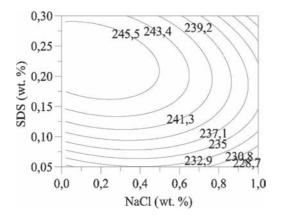


FIG. 10. Effect of NaCl and SDS concentrations on viscosity (mPa.s): isoresponse plot (0.3 wt.%, XG).

concentration. Here, the increasing of SDS leads to increasing viscosity. In this case, the phenomena can be explained as follow: An added surfactant will interact strongly with hydrophobic group of the polymer, leading to a strengthened association between polymer chains and, thus, to an increase in viscosity. In the second region, for NaCl concentrations up to 0.2 wt.% and SDS below 0.22 wt.%, the viscosity increases with increasing SDS concentrations at any NaCl concentrations and increases only slightly with increasing NaCl. Such behavior has been attributed to the interactions of the surfactant micelles with polymer chains.<sup>[23,24]</sup>

Figure 11 shows the strong effect of XG on the viscosity. As explained in Figure 9, the increasing of the apparent viscosity values is due essentially to the polymer concentrations. As expected, the viscosity increases with increasing XG concentrations in the studied range. Here, also, the dispersions of molecules of XG in presence of SDS exhibit significant changes in the rheological parameters with increasing surfactant concentrations. This figure shows,

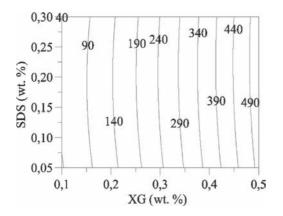


FIG. 11. Effect of XG and SDS concentrations on viscosity (mPa.s): Isoresponse plot (0.51 wt.%, NaCl).

also, the slight effect of SDS on the viscosity at any XG concentrations. The maximum of viscosity ( $\sim$ 490 mPa.s) is obtained for XG concentration of 0.5 wt.%.

# CONCLUSION

In the present study, the combined effects of SDS, NaCL, and XG concentrations on the physicochemical properties (conductivity, surface tension, and viscosity) of their aqueous mixture were investigated, with the aim to determine whether any interaction could occur using a response surface method (RSM). Previous study on the conductivity profiles of SDS/XG systems revealed the existence of interactions between polymer and surfactant and, the curves presented linearity as expected. The plots representing the effects of these factors on the surface tension and the viscosity have shown that these effects are much larger comparing with the conductometric plots, so, the effect of the three factors on the surface tension and viscosity is well demonstrated using this statistical method and the isoresponse plots.

It was shown from the contor plots, the relative effects of the three independent variables on surface tension and viscosity. It was been noted that the surface tension decreases with increasing of xanthan and SDS concentrations. The effect of salt is also important; it is responsible of reduction of surface tension because the electrostatic repulsion between the charged molecules at the interface. In industrial applications, essentially in oil enhanced oil recovery, the required properties for such systems are often in contrast. They must confer a high viscosity to the formulation and preserve the surface properties during their use. Thus, the conductivity, surface tension, and viscosity results demonstrated the existence of an optimum composition of the system formed by SDS, XG, and NaCl for each case. Then the optimal values obtained from the isoresponse curves are: 0.5 wt.%. of salt, 0.175 wt.% of SDS, and 0.5 wt.% of XG. Under these conditions the surface tension is minimum (42.60 mN/m) and the viscosity is maximum (490 mPa.s). However, these results illustrate the experimental conditions under which the present work was made.

#### REFERENCES

- Smitter, L.M., Guédez, J., and Müller, A.J. (2001) J. Colloid Int. Sci., 236: 343–353.
- [2] Avarnas, A. and Panagiotis, I. (2003) J. Colloid Int. Sci., 258: 102–109.
- [3] Gilanyl, T. and Wolfram, E. (1981) Colloids Surf. A, 3: 181–198.
- [4] Barreiro-Iglesias, R., Alvarez-Lorenzo, C., and Concheiro, A. (2003) Int. J. Pharm., 258: 165–177.
- [5] Minatti, E. and Zanette, D. (1996) Colloids Surf. A, 113: 237–346.

- [6] Casgrove, T., Mears, S.J., Obey, T., Thompson, L., and Welsey, R.D. (1999) Colloids Surf. A, 149: 329–338.
- [7] Guo, W., Sun, Y.W., Luo, G.S., and Wang, W.J. (2005) Colloids Surf. A, 252: 71–77.
- [8] Puvvada, S. and Blankschtein, D. (1990) J. Chem. Phys., 92: 3710–3712.
- [9] Jönsson, B., Lindman, B., Holmberg, K., and Kronberg, B. (1998) Surfactants and Polymers in Aqueous Solution; New York: John Wiley.
- [10] Goddard, E.D. (1986) Colloids Surf. A, 19: 255-300.
- [11] Sovilj, V.J. and Petrovic, L.B. (2006) *Carbohydrate Polym.*, 64: 41–49.
- [12] Nedjhioui, M., Moulai-Mostefa, N., Bensmaili, A., and Morsli, A. (2005) *Desalination*, 185: 543–550.
- [13] Meyers, R.H. and Montgomery, D.C. Response Surface Methodology, Process and Product Optimisation Using Design Experiments; New York: John Wiley, 2nd ed.
- [14] Khuri, A.I. and Cornell, J.A. *Response Surface, Design and Analysis*; New York: Marcel Dekker, 2nd ed.

- [15] Hemar, Y., Tamehana, M., Munro, P.A. and Singh, H. (2001) Food Hydrocolloids, 15: 513–519.
- [16] Cochran, W.G. and Cox, G.M. *Experimental Designs*; New York: John Wiley, 2nd ed.
- [17] Montgomery, D.C. *Design and Analysis of Experiments*; New York: John Wiley, 3rd ed.
- [18] Fishman, M.L. and Eirich, F.R. (1975) J. Phys. Chem., 79: 2740–2744.
- [19] Corrin, M.L. and Harkins, W.D. (1947) J. Chem. Abst., 69: 683-688.
- [20] Moulai-Mostefa, N., Khalladi, R., and Nedjhioui, M. (2007) Ann. Chim. Sci. Mat. 32: 421–429.
- [21] Dal Bo, A., Schweitzer, B., Felippe, A.C., Zanette, D., and Lindman, B. (2005) *Colloids Surf. A*, 256: 171–180.
- [22] Ghosh, S. and Moulik, S.P. (1998) J. Colloid Int. Sci., 208: 357–366.
- [23] Petit, F., Audeberg, R., and Iliopoulos, I. (1995) Colloid Polym. Sci., 273: 777–781.
- [24] Koetz, J., Beitz, T., and Tiersch, B. (1999) J. Dispersion Sci. Technol., 20: 139–163.