

Influence of sodium chloride on the cloud point of polyethoxylate surfactants and estimation of Flory-Huggins model parameters

Influencia de cloruro de sodio en el punto de niebla de tensioactivos polietoxilados y estimación de los parámetros del modelo de Flory-Huggins

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Abstract

In this study, the influence of NaCl on the cloud point of polyethoxylate surfactants from the family of lauryl alcohol polyethoxylates ($C_{12}EO_n$) and nonylphenol polyethoxylates (NPEO_n) was investigated. Liquid-liquid equilibrium curves of the aforementioned aqueous surfactants system with the presence of NaCl were plotted and thermodynamic parameters based on the Flory-Huggins model were obtained. The visual method was used to determine the cloud point. Solutions containing surfactant concentrations between 0.5 and 20% (by weight) and NaCl between 4.9 and 12.1% (by weight) were prepared. Salt had a *salting-out* effect, decreasing surfactant solubility in water. Furthermore, the cloud point decreased with an increase of NaCl concentration. The Flory-Huggins model satisfactorily described the experimental data for all surfactant + NaCl aqueous mixtures studied.

-----**Keywords:** Nonionic surfactant, cloud point, NaCl, Flory-Huggins model

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Resumen

Este estudio investigó la influencia de NaCl sobre el punto de niebla de los tensioactivos polietoxilados de la familia de polietoxilatos de alcohol laurílico y polietoxilatos de nonilfenol. Se representaron gráficamente las curvas de equilibrio líquido-líquido de los sistemas acuosos con tensioactivos anteriormente mencionados con presencia de NaCl, surgiendo los parámetros termodinámicos basados en el modelo de Flory-Huggins. El uso del método visual determinó el punto de niebla. Se prepararon soluciones con concentraciones de surfactante entre 0,5 y 20% (por peso) y NaCl entre 4,9 y 12,1% (por peso). La sal tenía un efecto salino, disminuyendo la solubilidad surfactante en agua. Además, el punto de niebla disminuyó al aumentar la concentración de NaCl. El modelo de Flory-Huggins describió satisfactoriamente los datos experimentales para todas las soluciones de misturas acuosas + NaCl estudiadas.

-----*Palabras clave:* surfactante no iónico, punto de niebla, NaCl, modelo de Flory-Huggins

Introduction

The cloud point is a characteristic of nonionic surfactants and represents the broken interaction between the surfactant and water at a certain temperature. This occurs due to the decrease in affinity for water of hydrophilic groups that constitutes the surfactant head. This phenomenon is important because the use of nonionic surfactants in industrial processes is limited by cloud temperature (or cloud point), since there is a small amount of surfactants at a cloud temperature of 30 °C, such as Triton X-114 surfactants. The cloud point phenomenon causes the emergence of two liquid phases in equilibrium [1]. Thus, it is important to study additive compounds that affect the cloud point of nonionic surfactants, enabling their application at controlled temperatures and their use in extraction processes [2]. Various works about the effect of salts on the cloud point have been presented in the literature. The effect of added electrolytes on the cloud point of Triton X-114 in the presence of ionic surfactants has been investigated [3]. The influence of chaotropic anions on the cloud point of surfactant octoxynol 9 (Triton X-100) has been studied [4]. The cloud-point diagram for Breox 50A-1000, an ethylene oxide-propylene oxide 50:50 (w/w) random copolymer, in water

solution and the effects of electrolytes and surfactants on the cloud-point temperature have been determined [5]. Cloud point values of the aqueous two-phase micellar system formed by the nonionic surfactant Triton X-114 have been examined in water and in McIlvaine buffer (pH 6.5), either in the presence or absence of various salts at different concentrations [6]. Electrolytes and nonelectrolytes have been investigated in order to verify their influence on the cloud point of a series of nonionic surfactants of the poly(oxyethylene) ether type $C_{12}E_n$ ($n = 6, 9$ and 10) [7]. The influence of various additives including inorganic salts, nonionic and ionic surfactants, water-soluble polymers and alcohols on the cloud points of three linear nonionic surfactants (Tergitol 15-S-7, Tergitol 15-S-9 and Neodol 25-7) has been investigated [8]. The effect of different additives such as electrolytes, urea, amphiphiles on the clouding behavior in zwitterionic surfactant/water systems has been determined [9]. Different cationic surfactants have been examined in order to determine the influence them on the cloud point of the nonionic surfactant Triton X-100 in aqueous solutions [10]. However, to the best of our knowledge, works regarding the influence of NaCl on the cloud point of polyethoxylate surfactants from the family of lauryl alcohol polyethoxylates

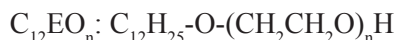
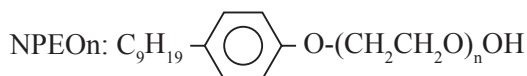
(C₁₂EO_n) (with degree of ethoxylation (n) of 8 and 9) and nonylphenol polyethoxylates (NPEO_n) (with degree of ethoxylation (n) of 10 to 13) have not been yet investigated.

In this context, the influence of NaCl on the cloud point of polyethoxylate surfactants from the family of lauryl alcohol polyethoxylates (C₁₂EO_n) and nonylphenol polyethoxylates (NPEO_n) was investigated. Liquid-liquid equilibrium curves of the aforementioned surfactants with the presence of NaCl were plotted and thermodynamic parameters based on the Flory-Huggins model, which described the binodal cloud point curve of the respective surfactants, were then determined.

Experimental

Materials and procedures

The nonionic surfactants used in this study were nonylphenol polyethoxylate (NPEOn), with ethoxylations 10, 11, 12 and 13 and lauryl alcohol polyethoxylate (C₁₂EOn), with ethoxylations 8 and 9. NPEOn and C₁₂EOn are represented by the following chemical structures:



A visual method was employed for determining the cloud point [6, 11-14]. In experimental methodology, solutions of 0.5% to 20% by weight of surfactant were prepared. Subsequently, these solutions were homogenized in magnetic stirrers. Then, they were placed in a jacketed cell under refrigeration and then using a magnetic bar to keep the homogenized solution, they were stirred. This experimental display was connected to a thermostatic bath. During the experiments the bath temperature was gradually increased and the cloud temperature of the solution was measured with a thermocouple (Salvterm 700K- SALCAS, ± 0.1 °C). For the purpose of confirming the cloud point, the solutions were cooled until they

became clear and heated again to the temperature of the cloud, for the purpose of the measure confirmation. This procedure was repeated three times and only the mean values were reported. The maximum deviation observed was about 3.5 %. The NaCl solutions were prepared at concentrations of 4.9 and 12.1% by weight.

Flory-Huggins Model

Thermodynamic equilibrium is characterized by the difference in chemical potential in each phase, as Eq. (1):

$$\mu_1^m - \mu_1^d = \frac{\partial \Delta G_m}{\partial n_1} \quad (1)$$

Where $\frac{\partial \Delta G_m}{\partial n_1}$ is a derivative from mixing Gibbs energy in relation to the number of moles of component 1, μ_1^m and μ_1^d represent the chemical potential of the most concentrated and diluted phases in relation to component 1, respectively.

The chemical potential of the most concentrated phase is estimated by Eq. (2).

$$\mu_1^m = \mu_1^d + \frac{RT}{\beta} \left[\ln(1 - \phi_m) + \left(1 - \frac{1}{N}\right) \phi_m - \frac{\omega_{123}}{RT} \phi_m^2 \right] \quad (2)$$

where ω_{123} is the parameter of the interaction between surfactant molecules (1), water (2) and NaCl (3) (represented by Eq. (3)), N corresponds to the number of surfactant aggregations, T is the temperature, R is the Universal Ideal Gas Constant, β is the number of water molecules and ϕ_m is the weight fraction of surfactant.

$$\omega_{123} = H_{123} - TS_{123} \quad (3)$$

Substituting Eq. (3) in Eq. (2), results in Eq. (4).

$$\frac{\partial \Delta G_m}{\partial n_1} = \frac{RT}{\beta} \left[\ln(1 - \phi_m) + \left(1 - \frac{1}{N}\right) \phi_m - \frac{H_{123} \phi_m^2 + S_{123} \phi_m^2}{RT + R} \right] \quad (4)$$

In equilibrium, the chemical potential for component “1” in the diluted phase is equal to the chemical potential in the most concentrated

phase, $\mu_1^d = \mu_1^m$. Since the chemical potential is constant, the derivative from Gibbs free energy is equal to zero. Therefore, it results in Eq. (5).

$$T_{Calc} = \frac{H_{123}\phi_m^2}{R \left[\ln(1-\phi_m) + \left(1 - \frac{1}{N}\right)\phi_m \right] + S_{123}\phi_m^2} \quad (5)$$

where T_{calc} is the temperature calculated by Flory-Huggins model, H_{123} is the enthalpy of the interaction between the surfactant, water and NaCl, S_{123} is the entropy of the interaction between the surfactant, water and NaCl, N is the number of surfactant aggregations and ϕ_m is the weight fraction of the solute.

Parameters H_{123} , S_{123} and N from the Flory-Huggins model for each system was determined using a programming routine developed on the *Scilab*® platform, based on the modified Levenberg-Marquardt least squares numerical method. The routine used the objective function (O.F.) represented by Eq. (6):

$$O.F. = \sum_{i=1}^n (T_i^{exp} - T_i^{calc})^2 \quad (6)$$

The Figure 1 shows the calculation procedure for estimating the parameters of the Flory-Huggins model.

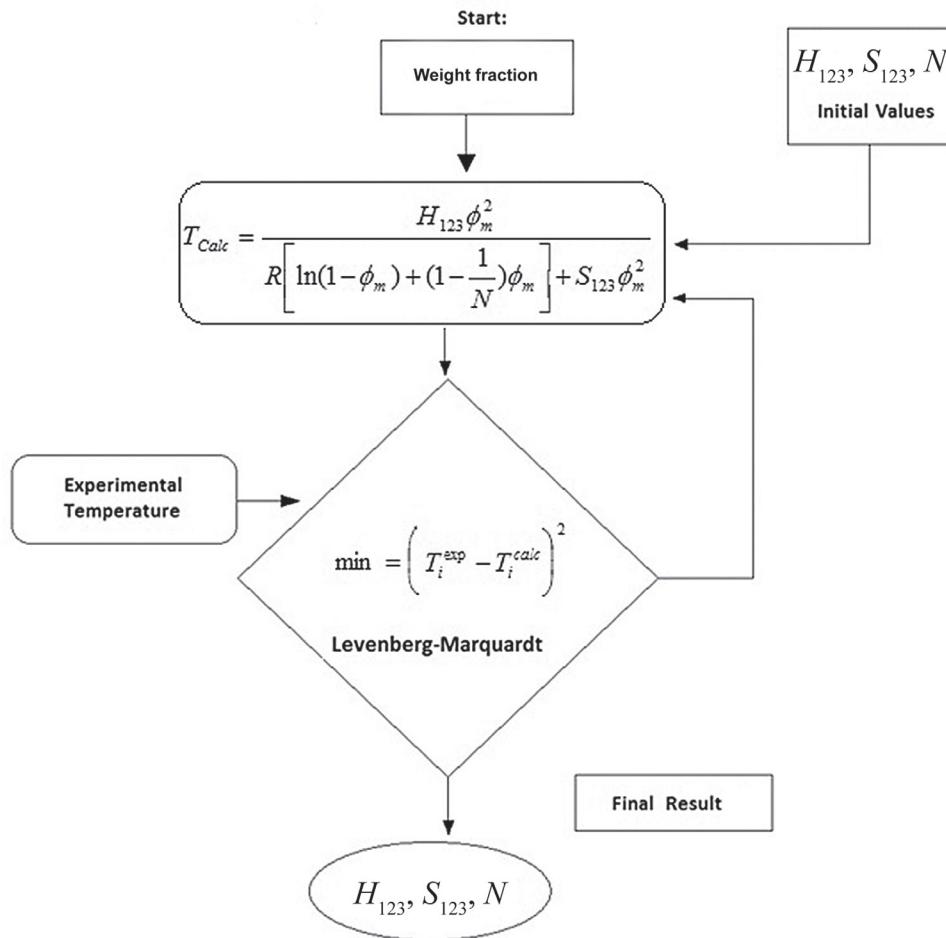


Figure 1 Flow chart of the calculation method for determining the parameters of the Flory-Huggins model in *Scilab*®.

Results and discussion

Figure 2 (a-f) shows a representation of the Flory-Huggins model and the experimental data for the cloud of surfactants NPEO₁₀, NPEO₁₁, NPEO₁₂, NPEO₁₃, C₁₂EO₈ and C₁₂EO₉, respectively, in the presence of NaCl. The curves depicted in Figure 2 (a-f) show that the Flory-Huggins model is a satisfactory representation of experimental data with the presence of sodium chloride. For all the surfactants, the presence of NaCl reduces the cloud point curve symmetrically, that is, the temperature variation is the same, regardless the salt concentration. This indicates that salt acts directly on water, where once surfactant affinity for the polar medium is reduced, any amount promotes formation of the surfactant-rich phase (coacervate). It can also be observed that for all the surfactants studied, the systems exhibit a lower critical solution temperature, which represents the region of liquid-liquid immiscibility; one phase is water-rich and the other is surfactant-rich. [15-17]. These results corroborate the evidence given by other researchers [18, 19]. The diminishing cloud point phenomenon is caused by the salting-out effect, which produces a decrease in surfactant solubilization in water. At concentrations of 4.9 % NaCl, the cloud point

falls by about 12 °C, and for concentrations of 12.1% NaCl, it decreases by 23.4°C, compared to the experimental condition without salt, for all surfactant concentrations studied. These results show that salt influences the cloud point of the surfactant. Thus, NaCl can be used in extraction processes to reduce the cloud point in order to save energy in this process.

Table 1 shows the Flory-Huggins parameters obtained for surfactants NPEO₁₀, NPEO₁₁, NPEO₁₂, NPEO₁₃, C₁₂EO₈ and C₁₂EO₉ in the presence of NaCl. Table 1 also demonstrates that, except for the surfactant C₁₂EO₉, both enthalpy (H_{123}) and entropy (S_{123}) increase proportionally with NaCl concentration, indicating that the addition of NaCl to the system increases the internal energy and, consequently, phase separation becomes easier; that is, interactions between the surfactant and water become increasingly smaller. Therefore, enthalpy and entropy increase by the increasing the salt concentration, and it is explained by the effect of the dissociation of the salt where the sodium chlorine ions unite with the water molecules forming strong bonds, thus increasing the enthalpy and entropy. These results confirm that the presence of NaCl promotes a *salting-out* effect on the surfactants.

Table 1 Parameters of the Flory-Huggins model with NaCl

<i>Parameters</i>	<i>NPEO</i> ₁₀	<i>NPEO</i> ₁₁	<i>NPEO</i> ₁₂	<i>NPEO</i> ₁₃	<i>C</i> ₁₂ <i>EO</i> ₈	<i>C</i> ₁₂ <i>EO</i> ₉
H_{123} (0 % NaCl) (J/mol)	8,600	11,000	12,000	16,800	7,549	410.37
S_{123} (0 % NaCl) (J/mol.K)	30	36	38	51	26.50	9.81
N (0 % NaCl)	1,000	1,500	1,000	800	2,388	2,065
Standard Deviation	0.217	0.272	0.403	0.285	0.880	0.766
H_{123} (4.9 % NaCl) (J/mol)	13,055	21,237	52,926	54,061	12,406	26,000
S_{123} (4.9 % NaCl) (J/mol.K)	45	69	160.62	163	43	81
N (4.9 % NaCl)	2,191	25,894	779	709	1,698	1,272
Standard Deviation	0.172	0.074	0.146	0.088	0.116	0.094
H_{123} (12.1 % NaCl) (J/mol)	25,820	23,471	57,818	66,042	20,734	20,133
S_{123} (12.1%NaCl) (J/mol.K)	88	79	183	208	71	65.66
N (12.1 % NaCl)	1,743	1,168	462	628	1,925	1,898
Standard Deviation	0.078	0.198	0.179	0.152	0.107	0.039

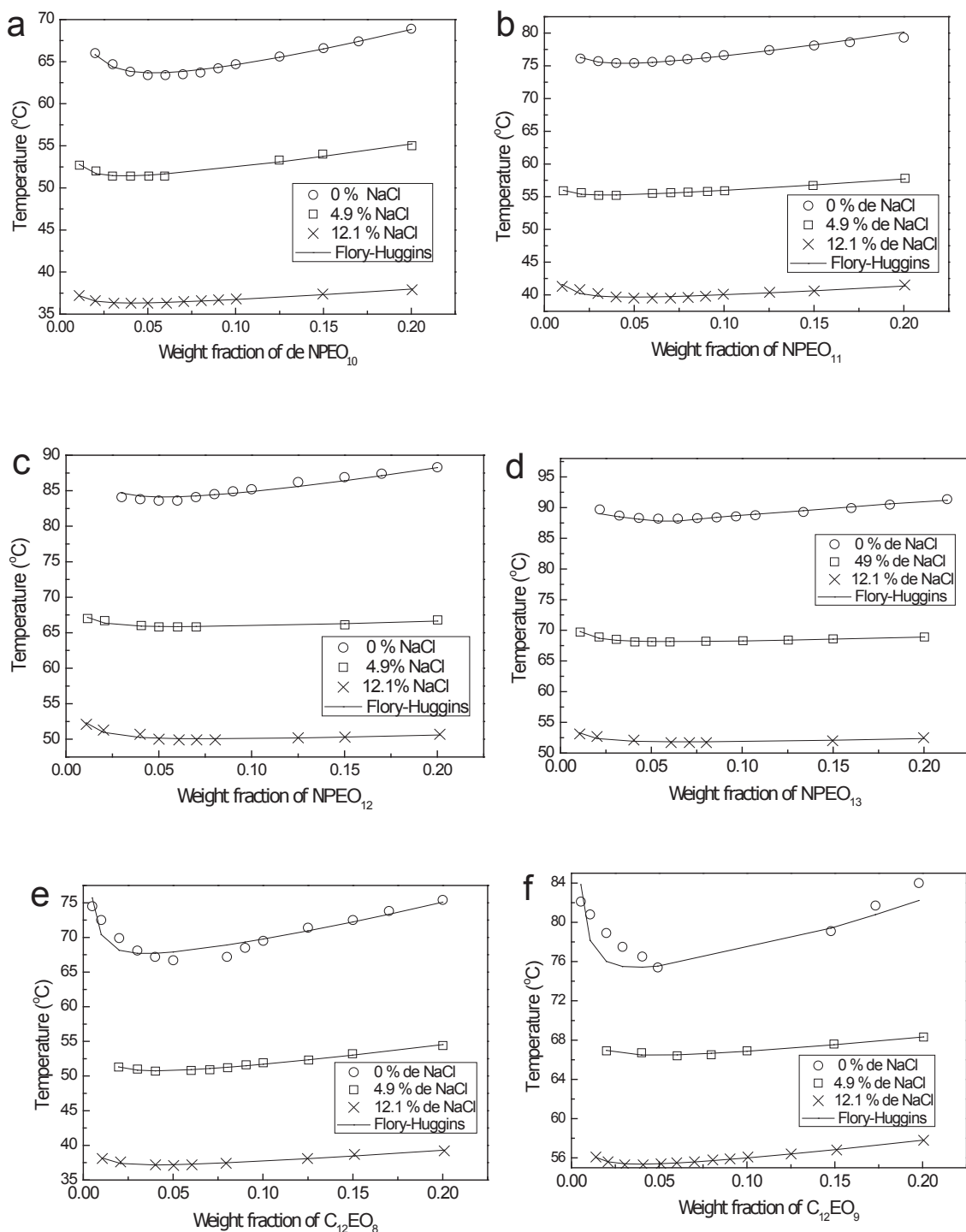


Figure 2 Cloud point curves calculated by the Flory-Huggins model and experimental data as a function of NaCl concentration, for surfactants (a) NPEO₁₀, (b) NPEO₁₁, (c) NPEO₁₂, (d) NPEO₁₃, (e) C₁₂EO₈ and (f) C₁₂EO₉

Conclusions

The effect of sodium chloride (NaCl) on the cloud point of different polyethoxylate surfactants (NPEO_n and C₁₂E_n) was investigated. Binodal cloud point curves of the respective surfactants were determined by the Flory-Huggins model. In addition, thermodynamic parameters involved on the interactions between surfactant, water and NaCl (enthalpy and entropy) were obtained from the Flory-Huggins model. The cloud point curves of surfactants NPEO_n and C₁₂E_n in the presence of NaCl were satisfactorily described by the Flory-Huggins model. The presence of salt in the surfactant solution caused a drop in cloud temperature, and an increase in its concentration influence on the decrease of this cloud point.

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