PHENOL ESTIMATION USING FLORY-HUGGINS PARAMETERS AND CLOUD POINT OF POLIETHOXYLATE SURFACTANTS

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ABSTRACT
This work examines the thermodynamics of phenol extraction by cloud point varying the ethoxylation degrees of nonylphenolpolyethoxylate surfactants (NPEOn) (9.5, 10, 11 and 12). The Flory-Huggins model was applied to estimate enthalpy ($\Delta H_{mix}$) and entropy ($\Delta S_{mix}$) parameters of the mixture, as well as the aggregate number ($N$). Results show that $\Delta H_{mix}$ and $\Delta S_{mix}$ values have a direct relationship with the ethoxylation degree of the surfactant used. Differently, aggregate number ($N$) values have an inverse relationship with the ethoxylation degree. The fitting to the Flory-Huggins model presented a standard deviation (SD) that ranged from 0.161 to 4.037 for each surfactant studied. It was observed that the increase of the phenol concentration in the surfactant + water system resulted in a decrease in the cloud point of the studied surfactants. These results contribute significantly to the application of this type of surfactant in phenol extraction processes.

KEYWORDS
non-ionic surfactant; cloud point; phenol; Flory-Huggins model

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1. INTRODUCTION

The application of non-ionic surfactants in the process of solute extraction from aqueous mediums has been increasing over time, implying the need for knowledge of thermodynamic properties, cloud point, or critical point of these surfactants (Inoue et al., 2008; Watanabe & Tanaka, 1978; Clark & Lipson, 2012; Stephen et al., 1992). One of the characteristics of the cloud point is the formation of a coacervate phase, which is extractant and has been used widely to replace organic solvents, usually toxins, in more efficient extraction, separation, or purification methods of various organic compounds or metallic ions (Gu & Galera-Gomez, 1992; Kulek et al. 2017; Yang et al., 2017ab).

Based on this idea, the present work studies the influence of phenol on the cloud point of polyethoxylates surfactants. Phenol is employed largely in the industry for the production of plastics, pesticides, resins, and medicines (Hou et al., 2017; Wang et al., 2017; Li et al. 2017; Delgado-Marín, 2017). Therefore, it is important to study the effects of phenol on the cloud point of non-ionic surfactants. This study will allow us to predict phase separation temperature of non-ionic surfactants in phenol extraction.

Some studies use the cloud point for extraction or purification, for example, phorbol was recovered using a cloud point extraction technique described by Phasukkarratchai et al. (2017); dyes were removed by a non-ionic surfactant using the cloud point extraction technique (Melo et al., 2014; Appusamy et al., 2014); amino acids were extracted using triton X-100 (Volodymyr & Oksana, 2017), bisphenol was extracted from water using a cationic surfactant at its cloud point (Yi-Jun et al., 2009); and Cu$^{2+}$ was extracted using a mixture of TritonX100 and dithizone (Sato et al., 2013). Mixtures of non-ionic surfactants such as Triton X114/Triton X100 have been employed in the cloud point extraction (Nazar et al., 2011). Therefore, it is important to study the temperature of the cloud point of these substances to determine the phase separation point and promote the extraction.

Several published works report the influence of additives in the cloud point, such as salts, hydroxides, or even the mixture of surfactants, aiming to estimate and control the temperature of the phase separation. Some examples found in literature are: the effect of electrolytes on Triton X-114 cloud point (Santos-Ebinuma et al., 2013); the influence of chaotropic anions on the cloud point of octoxynol 9 surfactant (Triton X-100) (Schott, 1997); as well as the presence of salts decreasing the cloud point of surfactant TX-405 (Akbas & Batigoc, 2009). Other works report thermodynamic studies, such as the determination of enthalpy, entropy, and Gibbs free energy of solutions containing surfactants in processes that involve dyes extraction by cloud point (Purkait et al., 2009; Tang et al., 2017). The influence of electrolytes on enthalpy, entropy, and Gibbs free energy in solutions containing non-ionic surfactants was also studied (Batigoc & Akbaş, 2017), and the effect of salts in mixtures containing Triton x114/Gemini 16-616 on determining the enthalpy, entropy, and Gibbs free energy of these systems (Shivaji et al., 2003).

This work determined, experimentally, the cloud points of nonylphenolpolyethoxylates non-ionic surfactants in the presence of the phenol with the goal of verifying its influence on cloud point. The Levenberg-Marquardt method was applied to estimate cloud point parameters for the surfactants using the Flory-Huggins model. This model is capable of foreseeing the cloud point of these surfactants in the presence of phenol. A minimization routine was developed in Scilab® to estimate Flory-Huggins parameters such as heat of mixing ($\Delta H_{mix}$), entropy of mixing ($\Delta S_{mix}$), and the aggregation numbers of surfactants ($N$).

2. METHODOLOGY

2.1 Materials

Type NPEOn surfactants containing different ethoxylation degrees ($n$): 9.5; 10; 11; and 12 were used in this work. These surfactants were provided by OXITENO (São Paulo, Brazil). Other reagents used had an analytical degree. Deionized purified water was used to prepare the solutions. A phenol from VETEC was used in concentrations that ranged from 0.01 to 0.25% in mass.
2.2 Experimental procedure

The cloud point was obtained through solutions containing surfactant and phenol. Surfactant concentrations varied between 0.5 and 25% (by mass), and the phenol concentrations varied from 0.01 to 0.25% (by mass). The solutions were allocated into 100 mL beakers and placed in a thermostatic bath (Water Separability Tester; Koehler Instrument Company Inc., USA) under constant stirring at 300 rpm. Bath temperature was gradually increased at a rate of 1°C/min until the solution was cloudy to the eye. In addition, a thermocouple (Salvterm 700K-SALCAS) ± 0.1 °C was inserted into the solution to determine the cloud point temperature. The cloud point was established through the average temperature during the heating process, followed by the cooling of the solution in triplicate (Wang et al., 2008). The data treatment applied to the Flory-Huggins model was carried out in a routine developed in the Scilab 5.4.1® platform.

2.3 Acquisition of cloud point parameters

2.3.1 Flory-Huggins model

The Flory-Huggins model is used commonly in polymeric solutions (Saeki, 1997), since it is based on the chemical potential of the involved phases (Eq. 1) (Inoue et al., 2003). Equations 1 to 4 estimate the enthalpy and entropy mixture parameters, as well as the aggregation number of molecules in the micelle, represented by ΔH_mix, ΔS_mix, and N, respectively.

\[ \mu^m_i - \mu^d_i = \frac{\partial \Delta G_m}{\partial n_i} \]  

(1)

Where \( \mu^m_i \) and \( \mu^d_i \) are the chemical potential of the most concentrated and diluted phase in relation to component 1, \( \Delta G_m \) is the Gibbs free energy of the mixture, and \( n_i \) is the number of moles of component 1. Eq. 2 estimated the chemical potential of the most concentrated phase.

\[ \mu^m_i = \mu^d_i + \frac{RT}{\beta} \left[ \ln(1-\phi_m) + \left(1 - \frac{1}{N}\right)\phi_m - \frac{\omega_{12}}{RT} \phi_m^2 \right] \]  

(2)

Where \( \omega_{12} \) is the interaction parameter between surfactant and water molecules represented by Eq. 3; \( \beta \) corresponds to the number of water molecules; and \( \phi_m \) is the volumetric fraction of the solute.

\[ \omega_{12} = \Delta H_{mix} - T \Delta S_{mix} \]  

(3)

Replacing Eq. 3 in Eq. 2 generates Eq. 4.

\[ \frac{\partial \Delta G_m}{\partial n_i} = \frac{RT}{\beta} \left[ \ln(1-\phi_m) + \left(1 - \frac{1}{N}\right)\phi_m - \frac{\Delta H_m \phi_m^2}{RT} + \frac{\Delta S_m \phi_m^2}{R} \right] \]  

(4)

In equilibrium, the chemical potential for component 1 in the diluted phase is equal to the chemical potential in the most concentrated phase, \( \mu^d_i = \mu^m_i \). Therefore, since the chemical potential is constant, the derivative of Gibbs free energy is zero, resulting in Eq. 5.

\[ T_{i}^{calc} = \frac{\Delta H_m \phi_m^2}{R} \left[ \ln(1-\phi_m) + \left(1 - \frac{1}{N}\right)\phi_m \right] + \Delta S_m \phi_m^2 \]  

(5)

Where \( T_{i}^{calc} \) corresponds to the temperature of the estimated cloud point, according to the Flory-Huggins model; and \( \Delta H_{mix} \Delta S_{mix} \) and \( N \) are the thermodynamic parameters, respectively. These parameters were estimated for each system using a minimization routine of the Levenberg-Marquardt numerical method. Thus, Eq. 5 represents the model used for the estimation of cloud point parameters. Eq. 6 displays the representation of the objective function used for calculating the minimization.

\[ F.O = \sum_{i=1}^{n} \left( T_{i}^{exp} - T_{i}^{calc} \right)^2 \]  

(6)

Where \( T_{i}^{exp} \) represents the temperatures obtained from the experiments, and \( n \) is the data number.

3. RESULTS AND DISCUSSION

Phenol extraction by cloud point, including the thermodynamic study, has been the object of previous works (Neves Silva et al., 2015; Sayem & Mandal, 2015). Results show that ethoxylation degree, surfactant concentration, and phenol concentration affect significantly the process. Figure 1 shows the construction of the Flory-Huggins model curves by predicting the turbidity point curves, along with the experimental data.
Figure 1 shows the cloud point, also called critical point of phase separation. It is calculated according to the surfactant concentration. The temperature of the cloud point increases with the increase of the ethoxylation degree for both surfactants (Inoue & Yasutaka, 2010). This can be associated to the greater affinity of the surfactant of the highest ethoxylation degree with water. Therefore, more energy is needed to break these bonds and, consequently, the cloud temperature increases (Zana & Weill, 1985).

Figure 1. Experimental cloud point data for NPEO 9.5, NPEO10, NPEO11, and NPEO12; and adjustment by Flory-Huggins model.
Figure 1 also shows the effect of phenol concentration ($X_j$) on the decrease of surfactant’s cloud point (Duarte & Canselier, 2005). There was a significant interaction between phenol and surfactant. This interaction suggests that the phenol interacts mainly with the surfactant’s head, obtaining a less hydrophilic character (Naqvi et al., 2010).

Table 1 shows the values of the obtained parameters.

Positive $\Delta H_{\text{mix}}$ values indicate that the surfactant solubilization in water is endothermic (Darshak et al., 2015; Badruzzaman et al., 2015). One can observe that there is a decrease in $\Delta H_{\text{mix}}$ value and a corresponding increase in the phenol concentration for a fixed concentration of surfactant. This change is related to the decrease of the phenol solubility in the surfactant. Results also show an increase in $\Delta S_{\text{mix}}$ value, related to an increase of the free surfactant chain in the diluted phase. On the other hand, the micellar concentration of the surfactant decreased with the increase in phenol concentration. This result leads to a reduction in the number of surfactant molecules in the diluted phase, causing a decrease in $\Delta S_{\text{mix}}$ value. Positive values of enthalpy and entropy were also reported in literature (Batıgocet al., 2011; Molina-Bolívar et al., 2013).

For the NPEO surfactant, one can observe that $\Delta H_{\text{mix}}$ and $\Delta S_{\text{mix}}$ increase with the increase in ethoxylation degree. Surfactants with a higher ethoxylation degree need greater energy (enthalpy) to break bonds formed with water. Molecules are more agitated when the amount of heat is increased during enthalpy, resulting in an increase of entropy. Surfactants with a higher ethoxylation degree have a larger polar region, and because of this increase in diameter of the polar part, fewer surfactant molecules will come together to form micellar aggregates (Boruah et al., 2010). The presence of the phenol causes a decrease in system enthalpy, a fact that is related directly to the interaction of the phenol with the surfactant’s head group. In this case, the phenol will decrease the effect of the surfactant molecules solvation, causing the decrease of enthalpy and entropy.

Table 1. Parameters of Flory-Huggins model with phenol.

<table>
<thead>
<tr>
<th>Phenol (m/m%)</th>
<th>0.01%</th>
<th>0.05%</th>
<th>0.10%</th>
<th>0.15%</th>
<th>0.20%</th>
<th>0.25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{mix}}$ (kJ/mol)</td>
<td>9.094</td>
<td>6.201</td>
<td>4.555</td>
<td>3.693</td>
<td>3.223</td>
<td>4.460</td>
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<tr>
<td>$\Delta S_{\text{mix}}$ (J/mol.K)</td>
<td>31.994</td>
<td>23.375</td>
<td>18.459</td>
<td>15.923</td>
<td>14.537</td>
<td>18.430</td>
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<tr>
<td>$N$</td>
<td>3900</td>
<td>3900</td>
<td>3900</td>
<td>3900</td>
<td>3900</td>
<td>3900</td>
</tr>
<tr>
<td>$SD$</td>
<td>0.959</td>
<td>1.082</td>
<td>1.332</td>
<td>1.637</td>
<td>4.037</td>
<td>3.311</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9591</td>
<td>0.8050</td>
<td>0.9404</td>
<td>0.9113</td>
<td>0.7361</td>
<td>0.6638</td>
</tr>
<tr>
<td>$\Delta S_{\text{mix}}$ (J/mol.K)</td>
<td>35.082</td>
<td>25.084</td>
<td>21.608</td>
<td>16.946</td>
<td>17.028</td>
<td>17.064</td>
</tr>
<tr>
<td>$N$</td>
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<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>$SD$</td>
<td>1.136</td>
<td>1.532</td>
<td>2.434</td>
<td>3.962</td>
<td>1.775</td>
<td>1.835</td>
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<tr>
<td>$R^2$</td>
<td>0.8306</td>
<td>0.8206</td>
<td>0.7998</td>
<td>0.7893</td>
<td>0.8999</td>
<td>0.9029</td>
</tr>
<tr>
<td>$\Delta H_{\text{mix}}$ (kJ/mol)</td>
<td>16.135</td>
<td>10.736</td>
<td>8.289</td>
<td>8.289</td>
<td>4.202</td>
<td>5.764</td>
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<tr>
<td>$SD$</td>
<td>0.773</td>
<td>0.586</td>
<td>1.219</td>
<td>2.591</td>
<td>3.015</td>
<td>2.158</td>
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<tr>
<td>$R^2$</td>
<td>0.9612</td>
<td>0.9541</td>
<td>0.8688</td>
<td>0.9515</td>
<td>0.8805</td>
<td>0.7903</td>
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<tr>
<td>$\Delta H_{\text{mix}}$ (kJ/mol)</td>
<td>24.796</td>
<td>12.011</td>
<td>11.211</td>
<td>9.394</td>
<td>6.670</td>
<td>6.356</td>
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<tr>
<td>$\Delta S_{\text{mix}}$ (J/mol.K)</td>
<td>73.827</td>
<td>38.326</td>
<td>38.326</td>
<td>31.049</td>
<td>23.438</td>
<td>22.637</td>
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<tr>
<td>$N$</td>
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<td>5000</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>$SD$</td>
<td>0.161</td>
<td>1.962</td>
<td>0.949</td>
<td>1.457</td>
<td>2.497</td>
<td>3.337</td>
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<tr>
<td>$R^2$</td>
<td>0.9507</td>
<td>0.9847</td>
<td>0.9028</td>
<td>0.8710</td>
<td>0.8083</td>
<td>0.7597</td>
</tr>
</tbody>
</table>

$SD$ (standard deviation), $\Delta H_{\text{mix}}$ (enthalpy of mixing), $\Delta S_{\text{mix}}$ (entropy of mixing), $R^2$ (correlation coefficient)
4. CONCLUSIONS

Results presented in this work show that phenol influences negatively the cloud point. This effect was triggered by interaction between phenol and the polar region of the surfactant. In addition, ethoxylation degree interferes positively in the temperature of the cloud point. The Flory-Huggins model adjusted satisfactorily to experimental data, showing positive enthalpy and entropy. Therefore, the presence of phenol caused a decrease in cloud point, while the ethoxylation degree of the surfactant caused an increase in the cloud point.

5. REFERENCES


