



Prediction of the cloud point of polyethoxylated surfactants and their mixtures by the thermodynamic model of Flory-Huggins-Rupert

Boumediene Haddou, Houaria Benkhedja, Katia Teixeira da Silva de La Salles, Jean-Paul Canselier, Christophe Gourdon

► To cite this version:

Boumediene Haddou, Houaria Benkhedja, Katia Teixeira da Silva de La Salles, Jean-Paul Canselier, Christophe Gourdon. Prediction of the cloud point of polyethoxylated surfactants and their mixtures by the thermodynamic model of Flory-Huggins-Rupert. *Journal of Dispersion Science and Technology*, 2018, pp.1-8. 10.1080/01932691.2018.1485577 . hal-02135611

HAL Id: hal-02135611

<https://hal.science/hal-02135611>

Submitted on 21 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte (OATAO)

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

This is an author's version published in: <http://oatao.univ-toulouse.fr/21261>

Official URL: <https://doi.org/10.1080/01932691.2018.1485577>

To cite this version:

Haddou, Boumediene and Benkhedja, Houaria and Salles, Katia Teixeira da Silva de la and Canselier, Jean-Paul and Gourdon, Christophe Prediction of the cloud point of polyethoxylated surfactants and their mixtures by the thermodynamic model of Flory-Huggins-Rupert. (2018) Journal of Dispersion Science and Technology. 1-8. ISSN 0193-2691

Any correspondence concerning this service should be sent to the repository administrator:

tech-oatao@listes-diff.inp-toulouse.fr

Prediction of the cloud point of polyethoxylated surfactants and their mixtures by the thermodynamic model of Flory-Huggins-Rupert

Boumediene Haddou^{a,b}, Houaria Benkhedja^{a,b}, Katia Teixeira Da Silva De La Salles^{b,c}, Jean Paul Canselier^b, and Christophe Gourdon^b

^aU. S. T. Oran, Faculté de Chimie, Département de Génie Chimique, Laboratoire de Physico-Chimie des Matériaux, Environnement et Catalyse, Oran, M'Nouar, Algeria; ^bLaboratoire de Génie Chimique UMR CNRS 5503, Université de Toulouse, BP84234, Toulouse, France;

^cDepartamento de Tecnologia Química, Campus Universitário do Bacanga Centro de Ciências Exatas e Tecnologia, São Luís, Brazil

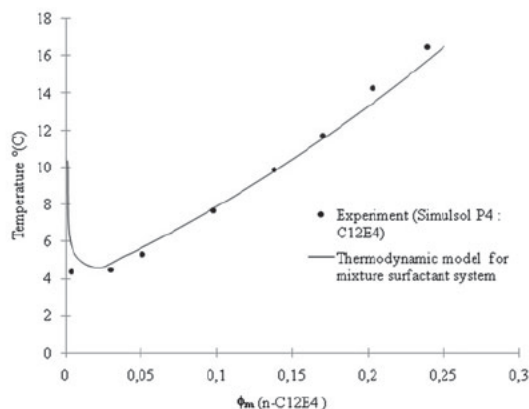
ABSTRACT

The cloud point curves of polyethoxylated surfactants are established experimentally. These experimental data are preliminary to the development of the cloud point extraction process, which appears as an interesting alternative to the usual solvent extraction unit operation. Starting from the thermodynamic model developed by Flory and Huggins for phase separation of polymer aqueous solutions, this paper aims at the prediction of cloud point curves. In this work, Rupert's approach is extended to commercial nonionic surfactants, mixtures of homologous species, namely a few alkylphenol and alcohol ethoxylates. The limit of such an approach is clearly demonstrated, provided that a fitting parameter is finally required for a successful model application to pilot-plant manufactured surfactants, like $C_8\Phi E_n$ ($n = 7.5, 10, 12$), $C_9\Phi E_n$ ($n = 8, 10, 12$), $C_{12}E_4$, $C_{12}E_6$ and commercial Tergitol 15-S-7 (linear C_{12} - C_{14} secondary alcohol with an average of 7 ethylene oxide units).

KEYWORDS

Polyethoxylated surfactants; cloud point; Flory Huggins Rupert approach; demixing curves; modeling

GRAPHICAL ABSTRACT



Miscibility curve calculated by the Flory-Huggins-Rupert model adapted for a mixture of 16 surfactants ($C_{12}E_n$, $n = 1-16$) (commercial Simulsol P4).

Introduction

Flory and Huggins formulated independently a thermodynamic theory of polymer solutions, in which thermodynamic quantities are derived from a simple concept of combinational entropy of mixing and the reduced Gibbs energy (dimensionless) χ parameter.^[1-3] This theory was initially developed for modeling the phase separation of aqueous polymer solutions. On the other hand, the phase separation of nonionic polyethoxylated surfactant solutions has been analyzed theoretically^[4-6] and the Flory-Huggins

theory has been extended to micellar systems by Goldfarb and Sepulveda,^[7] Weckström and Zulauf,^[8] Evans et al.^[6] and Rupert^[9] in order to model and predict the cloud point curves of water/nonionic surfactant systems. This approach is based on the analogy between a micelle and a polymer macromolecule: the micelle in solution, the monomer in the micelle, and the aggregation number of the micelle correspond to the polymer in solution, the segment of the polymer and the degree of polymerization, respectively. The Flory-Huggins-Rupert model still remains the most reliable. As the critical micelle concentration (cmc) of polyethoxylated

nonionic surfactants is about 10^{-2} to 10^{-3} wt. % and the cloud point is observed at a concentration higher than the cmc,^[10–13] it can be assumed that the surfactant system is only composed of micellar aggregates in water and that the monomer effect on the cloud point may be neglected. Moreover, Rupert was also able to determine a correlation for alcohol ethoxylates giving the micellar aggregation number as a function of the hydrophobic chain length and the number of ethylene oxide units of the hydrophilic head group. However, this correlation is only applicable to pure ethoxylated alcohols. An attempt to apply the Flory-Huggins-Rupert theory to surfactant mixtures has been published by Inoue et al.^[14] Now, common commercial nonionic surfactants, namely alkylphenol ethoxylates ($C_m\Phi E_n$) and alcohol ethoxylates (C_mE_n), are always mixtures of chemical species differing by their alkyl chain length (m) and their number of ethylene oxide units (n). Thus, the modeling and prediction of the demixing curves of ethoxylated surfactant/water systems represent an interest for the cloud point extraction process.^[12,15–27] In this work, we try to apply the model to commercial alkylphenol ethoxylates ($C_8\Phi E_n$ ($n = 7.5, 10, 12$), $C_9\Phi E_n$ ($n = 8, 10, 12$) and alcohol ethoxylates ($C_{12}E_4$, $C_{12}E_6$ and Tergitol 15-S-7).

Thermodynamic analysis of water/polyethoxylated surfactant systems and cloud point modeling

Let us consider a water/polyethoxylated surfactant system. Heating a solution of surfactant concentration M leads to clouding at a temperature T_c (cloud point). Above T_c , in the biphasic region, a coacervate of concentration a coexists with a dilute phase of concentration b (Figure 1).

Let μ_1^{co} and μ_1^{d} be the water chemical potentials in coacervate and dilute phase, respectively.

The water chemical potential in the dilute phase is considered being equal to the chemical potential of pure water (μ_1^0), because this phase is extremely diluted. At equilibrium, these chemical potentials are equal:

$$\mu_1^{\text{d}} = \mu_1^0 \quad [1]$$

Now, temperature, T , and pressure being constant, the chemical potential variation of the solvent is obtained by deriving ΔG_M , the free energy of mixing (here corresponding to the free energy change due to micellar solution formation from pure water and pure surfactant^[14]) with respect to n_1 , the number of moles of solvent:

$$\mu_1^{\text{co}} - \mu_1^0 = \left(\frac{\partial \Delta G_M}{\partial n_1} \right) \quad [2]$$

ΔG_M is related to the enthalpy and entropy of mixing, ΔH_M and ΔS_M , respectively, by:

$$\Delta G_M = \Delta H_M - T \Delta S_M \quad (3)$$

with, according to the Flory-Huggins theory^[2] adapted by Rupert^[9] and Inoue et al.^[14] to water/surfactant systems:

$$\Delta S_M = -k(n'_1 \ln \phi_1 + n_m \ln \phi_m) \quad (4)$$

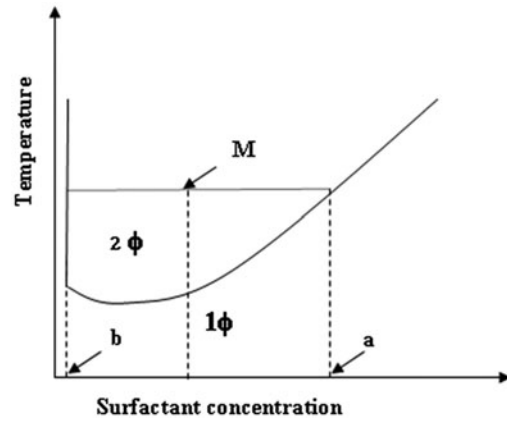


Figure 1. Schematic representation of the cloud point curve of a non ionic surfactant.

$$\Delta H_M = -n'_1 \phi_m w_{12} \quad (5)$$

where n_m and ϕ_m are the number and volume fraction of micelles, respectively, n'_1 the number of lattice points which contain β water molecules ($n'_1 = n_1/\beta$), solvent volume fraction (ϕ_1) and w_{12} an interaction energy parameter. β is thus the ratio of the volume of a segment (here a surfactant monomer) to that of a water molecule. Now:

$$\phi_1 = \frac{n'_1}{n'_1 + N n_m} = \frac{n_1}{n_1 + \beta n_2} \quad (6)$$

$$\phi_m = \frac{N n_m}{n'_1 + N n_m} = \frac{\beta n_2}{n_1 + \beta n_2} \quad (7)$$

where N is the aggregation number and n_2 the number of surfactant molecules ($n_2 = N n_m$).

Combining Equations (2) to (7) yields (on the molar scale)^[9]:

$$\mu_1^{\text{co}} - \mu_1^0 = \frac{RT}{\beta} \left[\ln(1 - \phi_m) + \phi_m \left(1 - \frac{1}{N} \right) - \phi_m^2 \frac{w_{12}}{RT} \right] \quad (8)$$

The third term ($\phi_m^2 \frac{w_{12}}{RT}$) in Equation (8) describes the deviation from ideal mixing behavior, which occurs as a result of the interaction of a segment with the solvent.

In fact, w_{12} , which describes the segment transfer from hydrous micelle to system containing pure water and pure surfactant, is a free energy term, composed of enthalpic (H_{12}) and entropic (S_{12}) contributions, according to the following equation:

$$w_{12} = H_{12} - T S_{12} \quad (9)$$

By introducing Equation (9) into Equation (8) and taking equilibrium conditions into account ($\mu_1^{\text{co}} = \mu_1^{\text{d}} \cong \mu_1^0$ at $T = T_c$), we can then derive the expression of the cloud point temperature, T_c , as a function of ϕ_m ^[9]:

$$T_c = \frac{H_{12} \phi_m^2}{R \left[\ln(1 - \phi_m) + \phi_m \left(1 - \frac{1}{N} \right) + S_{12} \phi_m^2 \right]} \quad (10)$$

Therefore, T_c also depends on the surfactant/water interaction parameters and the micellar aggregation number.

According to Flory's approach,^[2] the solute volume fraction, ϕ_m^c , at the minimum clouding temperature is related to the number of segments (here: N):

$$N = \left[\frac{(1 - \phi_m^c)}{\phi_m^c} \right]^2 \quad (11)$$

So:

$$\phi_m^c = \left[\frac{1}{1 + \sqrt{N}} \right] \quad (12)$$

Application to pure alcohol ethoxylate/ water systems

It has been shown by Barry and Russel^[28] that the logarithm of the aggregation number of alkyltrimethylammonium salts is linearly related to the carbon atom number in the hydrocarbon chain. On the basis of this finding, Rupert^[9] established the following logarithmic relation for N as a function of the carbon number of the hydrophobic chain, m, and the number of ethylene oxide units, n:

$$\log N = 0.444m - 0.458n + 0.662 \quad (13)$$

He calculated w_{12} at 50 °C (as a reference case), H_{12} and S_{12} :

$$w_{12} \text{ (50)} = -23m + 120n - 750 \text{ (cal mol}^{-1}\text{)} \quad (14)$$

$$H_{12} = -440m + 710n + 3200 \quad (15)$$

$$S_{12} = -1.28m + 1.83n + 12.2 \quad (16)$$

$$T_c = \frac{(710n - 440m + 3200) \phi_m^2}{R \left[\ln(1 - \phi_m) + \left(1 - \frac{1}{N}\right) \phi_m \right] + \phi_m^2 (1.83n - 1.28m + 12.2)} \quad (17)$$

Application to a multicomponent system

Equation (8), adapted by Inoue et al.^[14] to mixture of water (1), surfactant A (2) and surfactant B (3), becomes:

$$\mu_1^{co} - \mu_1^0 = \frac{RT}{\beta} \left[\ln(1 - \phi_m) + \phi_m \left(1 - \frac{1}{N}\right) - \phi_m^2 \frac{x_2 w_{12}}{RT} - \phi_m^2 \frac{x_3 w_{13}}{RT} + \phi_m^2 \frac{x_2 x_3 w_{23}}{RT} \right] \quad (18)$$

x_2 and x_3 are the mole fractions of surfactants A and B in the mixed micelle and w_{23} the free energy of interaction between the two surfactants in the micelles,

At equilibrium, the demixing temperature of the mixture, T_c , is given by the following equation:

$$T_c = \frac{[x_2 H_{12} + x_3 H_{13} - x_2 x_3 w_{23}] \phi_m^2}{R \left[\ln(1 - \phi_m) + \left(1 - \frac{1}{(x_2 N_2 + x_3 N_3)}\right) \phi_m \right] + [x_2 S_{12} + x_3 S_{13}] \phi_m^2} \quad (19)$$

Generalizing to a mixture of water and n surfactants, the equation becomes:

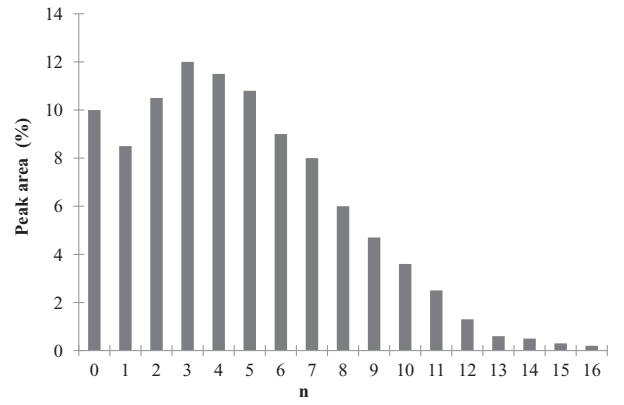


Figure 2. Distribution of the number of ethylene oxide units, n, in C₁₂E₄ (SEPPIC data).

$$T_c = \frac{\phi_m^2 \sum_{i=1}^n x_{i+1} H_{1(i+1)} - \phi_m^2 \sum_{i,j=2,j>i}^n x_i x_j w_{ij}}{R \left[\ln(1 - \phi_m) + \left(1 - \frac{1}{\sum x_i N_i}\right) \phi_m \right] + \phi_m^2 \sum_{i=1}^n x_{i+1} S_{1(i+1)}} \quad (20)$$

where w_{ij} is the free energy of interaction between the surfactants in the micelles.

In this work, Equation (20) was used to predict the cloud point of commercial surfactants.

Experimental

Chemical species

Alcohol ethoxylates, C_mE_n, are mixtures of polyethoxylated dodecanols containing residual alcohol. In the same way, alkylphenol ethoxylates are designated as C_mΦE_n. TERGITOL 15-S-7 is a mixture of secondary alcohol ethoxylates with the average formula C₁₂₋₁₄H₂₅₋₂₉O(CH₂CH₂O)₇H ('7' stands for the average number of ethylene oxide, EO, units, but actual EO numbers range between 3 and 40). Except TERGITOL 15-S-7, purchased from the Dow Chemical Company, the non-ionic surfactants used in this work were kindly provided by SEPPIC (Castres, France). C₁₂E₄ (SIMULSOL P4) was a commercial sample; C₁₂E₆ and alkylphenol ethoxylates (C₈ΦE_{7,5}, C₈ΦE₁₀, C₈ΦE₁₂, C₉ΦE₈, C₉ΦE₁₀ and C₉ΦE₁₂) were pilot-plant manufactured. The composition of SIMULSOL P4 and C₁₂E₆ are illustrated in Figures 2 and 3, respectively.

Cloud point measurements

The determination of the cloud point was carried out using a Mettler FP 900 apparatus, consisting of an oven, a control unit and several measuring cells. The temperature of the sample, placed inside a cell, was measured using a highly accurate Pt100 sensor (probe) placed in a small oven. In the lower part of the cloud point measuring cell, FP81C, an optical fiber can illuminate three samples. The residual transmitted light is converted into a proportional electric signal. The light transmission is measured

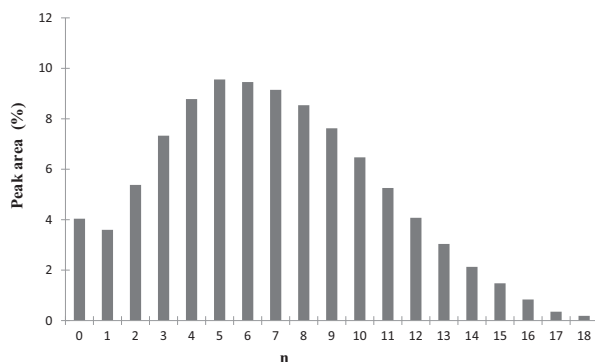


Figure 3. Distribution of the number of ethylene oxide units, n , in $C_{12}E_6$ (SEPPIC data).

Table 1. Volume fractions of surfactant, ϕ_m^c , at critical point and aggregation numbers, N , in water/alkylphenol ethoxylate systems.

Surfactant	ϕ_m^c (%)	N
$C_8\Phi E_{7.5}$	0.87	12980
$C_8\Phi E_{10}$	5.02	358
$C_8\Phi E_{12}$	7.46	154
$C_9\Phi E_8$	0.62	25693
$C_9\Phi E_{10}$	1.09	8234
$C_9\Phi E_{12}$	6.82	187

continuously while the cell temperature increases linearly at the heating rate chosen. The cloud point is the temperature at which the solution becomes cloudy, as a result of the appearance of a second phase, inducing a transmission decrease.

Application of the thermodynamic model to multicomponent systems

Polyethoxylated alkylphenols

Aggregation number

The thermodynamic model can be applied to alkylphenol polyethoxylate/water systems. However, we need to first calculate the aggregation number, N from the minimum (ϕ_m^c) of the experimental miscibility curve using Equation (11). Experimental ϕ_m^c and calculated N values are given in Table 1. N values range from 154 to 25693. This result seems to be not realistic because of the large variation of the aggregation number. However, Rupert^[9] also obtained similar variation in “ N ” values, between 5.7 and 24100, for C_4E_1 and $C_{16}E_6$ respectively. Therefore, the hypothesis of similarity between the segment number and aggregation number with regard to the cloud point phenomenon was assessed.

One can notice that the aggregation number (and thus micellar size) decreases as the ethylene oxide number (n) increases (Table 1). However, at fixed n , micellar size increases with the carbon number in the hydrophobic chain (m). This is in agreement with the findings from the literature.^[9,28,29] Hence, the aggregation number depends on surfactant structure. Thus, from data in Table 1, a relation between N and the structural parameters, m and n , was determined:

$$\log N = 0.514m - 0.413n + 3.099 \quad (21)$$

Table 2. Thermodynamic parameters of interaction.

Surfactants	H_{12} (kJ mol ⁻¹)	S_{12} (J mol ⁻¹ K ⁻¹)
$C_8\Phi E_{7.5}$	3.47	15.95
$C_8\Phi E_{10}$	10.35	35.25
$C_8\Phi E_{12}$	19.56	59.14
$C_9\Phi E_8$	4.47	18.81
$C_9\Phi E_{10}$	10.10	34.23
$C_9\Phi E_{12}$	13.24	42.07

Thermodynamic quantities

The thermodynamic parameters, H_{12} and S_{12} were obtained experimentally in the concentrated surfactant part of the cloud point curve (Figure 1). Using the experimental values of T_c and ϕ_m and applying Equation (10), we can obtain H_{12} and S_{12} (Table 2). From the data in Table 2, it can be seen that the interaction quantities, H_{12} and S_{12} , increase with n and decrease as m increases. Therefore, the influence of the carbon number, m , and the number of ethylene oxide units, n , on H_{12} and S_{12} was evaluated and correlations between enthalpy and entropy as a function of the surfactant structure are established as follows:

$$H_{12} = -2.348 m + 2.948 n + 0.925 \text{ (kJ mol}^{-1}\text{)} \quad (22)$$

$$S_{12} = -6.392 m + 7.891 n + 10.335 \text{ (J mol}^{-1}\text{K}^{-1}\text{)} \quad (23)$$

During the phase separation of a micellar solution, water molecules surrounding surfactant polar heads must be released, which leads to an increase in enthalpy and entropy. According to Inoue,^[14] the positive coefficient of n in Equations (22) and (23) corresponds to this situation. It is likely that the hydrophobic chains contribute to decreasing the enthalpy as well as the entropy when the surfactant molecules are transferred from the micelles to the pure surfactant phase; this can be the reason of the negative coefficients for m . H_{12} and S_{12} are bound by an affine function. The correlation coefficients of the plotted straight lines of $(H_{12})_{\text{calc}}$ and $(S_{12})_{\text{calc}}$ vs. $(H_{12})_{\text{exp}}$ and $(S_{12})_{\text{exp}}$ are 0.9275 and 0.9280, respectively. Such a relationship between the enthalpy and entropy of interaction has been observed in some aqueous systems, e.g. protein denaturation^[30] and micelle formation.^[31]

Miscibility curve

The polyethoxylated alkylphenols being considered as pure species, the substitution of Equations (22) and (23) in Equation (10) leads to the relation between the cloud point, T_c , and the structural parameters m and n :

$$T_c = \frac{\phi_m^2 (2.948 n - 2.348 m + 0.925)}{R [\ln(1 - \phi_m) + (1 - 1/N)\phi_m] + \phi_m^2 (7.891 n - 6.392 m + 10.335)} \quad (25)$$

Figures 4a and 4b compare the calculated miscibility curves and the experimental values for the $C_m\Phi E_n$ surfactants. Although the presence of starting reagent and impurities can change the cloud point of commercial surfactants compared with pure species, the agreement between calculated and experimental values is satisfactory for surfactant

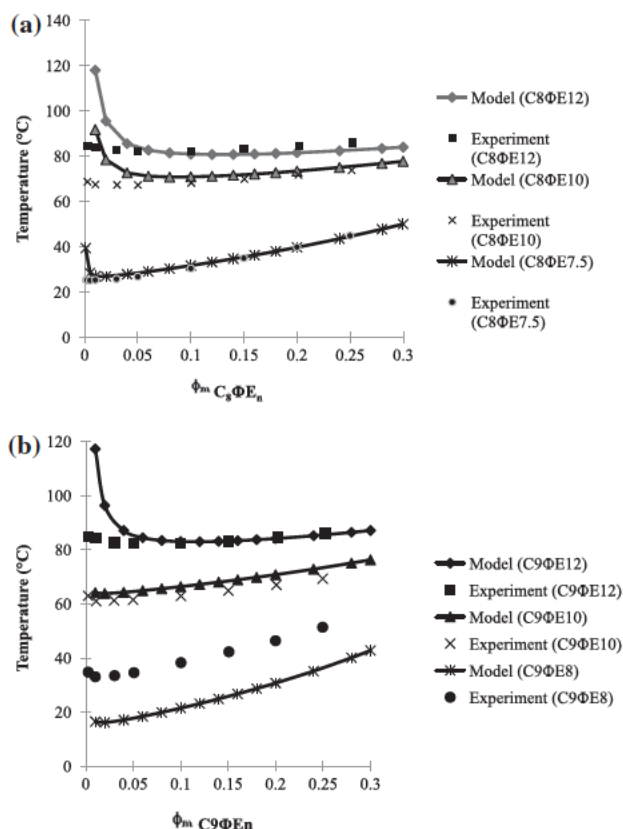


Figure 4. Cloud point curves of: a) C₈ΦE_n; b) C₉ΦE_n.

concentrations higher than 5 wt.%, except for C₉ΦE₈. It could therefore be assumed that the average value of *n* reported by the manufacturer is not so precise.

Thus, the model sensitivity to ethylene oxide number was checked for the surfactant C₉ΦE₈ (Figure 5).

One can notice in Figure 5 that a small variation of *n* changes the cloud point significantly. For this surfactant, a value of *n* = 8.4 gives the closest agreement with experimental results.

Besides, the cloud point, *T_c*, strongly depends on the micelle aggregation number, *N*. This dependence was studied for the surfactants C₈ΦE₁₀ and C₉ΦE₁₀, using Equations (21) and (25). Results are shown in Figure 6. *T_c* curves become more sensitive to the value of *N* as dilution increases. However, for surfactant concentrations greater than 0.1% (v/v), the calculated curves are practically superimposed. On the other hand, the theoretical curves approach the experimental points when *N* increases, but the best fit is obtained for *N* values greater than the generally accepted aggregation numbers. This result means that *N* could be considered as a fitting parameter. Hence, in a wide range of surfactant concentrations, the model applied to water-surfactant systems leads to very satisfactory results for values of aggregation numbers in accordance with literature values.

Polyethoxylated alcohols

Commercial C₁₂E₄

The cloud point of Simulsol P4 (commercial C₁₂E₄) is around 6 °C at 1 wt. %. Indeed, aqueous solutions of this

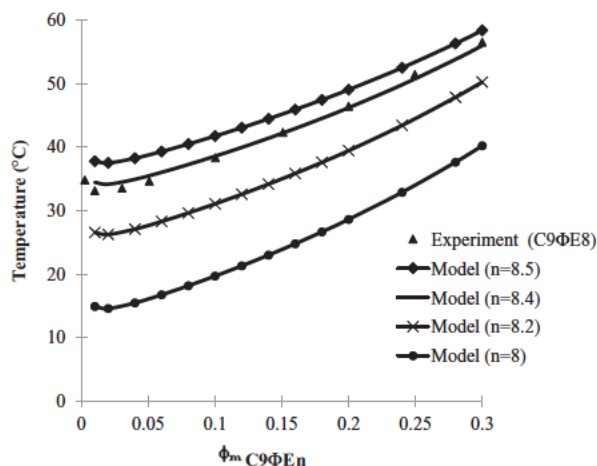


Figure 5. Curves of cloud point for C₉ΦE_n (*n* = 8 to 8.5).

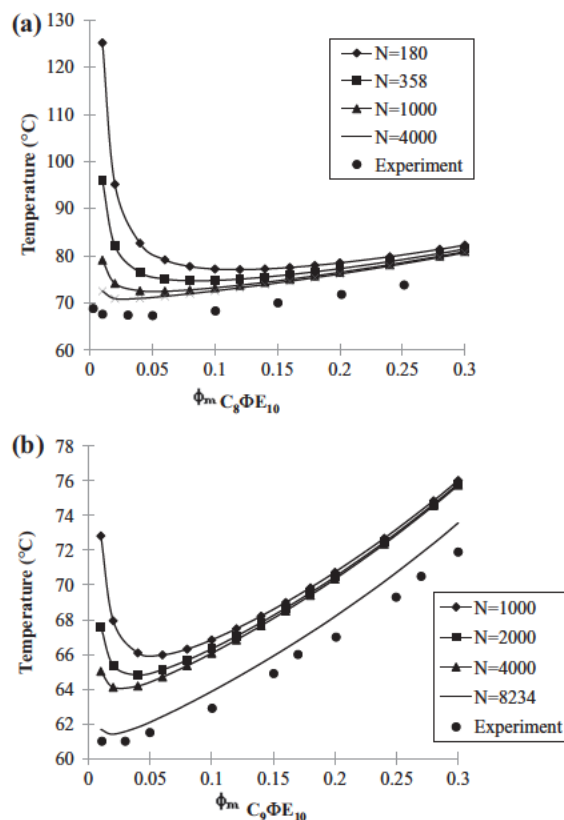


Figure 6. Cloud point temperature dependence with *N*: (a) C₈ΦE₁₀; (b) C₉ΦE₁₀.

surfactant are already turbid at room temperature at this concentration. The Flory-Huggins-Rupert model was used to calculate the demixing curve of this surfactant and compare it with the experimental one. The commercial surfactant was produced as a mixture of 16 surfactants (C₁₂E_n, *n* = 1–16) and 10% of residual dodecan-1-ol (Figure 2).

Using Equations (15) and (16), we calculate the terms $\sum_{i=1}^n x_{i+1} H_{1(i+1)}$ (equal to 1327.940 cal/mol) and $\sum_{i=1}^n x_{i+1} S_{1(i+1)}$ (equal to 5.604 cal/mol K). The term $\sum_{i,j=2, j>i}^n x_i x_j w_{ij}$ was adjusted to be equal to 70 cal/mol for this commercial surfactant.

The demixing curve found by the thermodynamic model adapted for complex non ionic surfactant systems

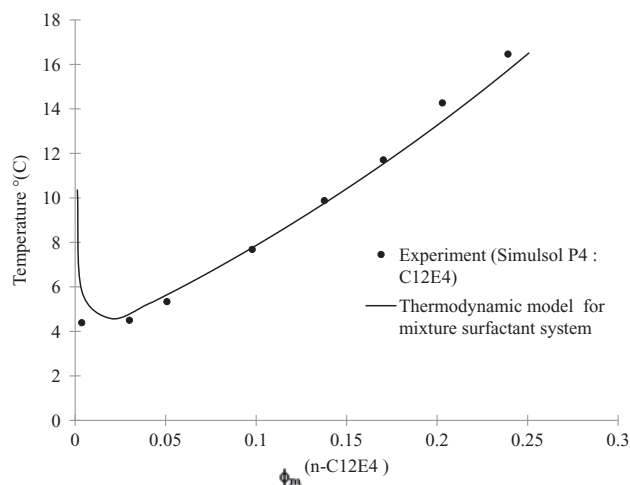


Figure 7. Comparison between the miscibility curve calculated by the Flory Huggins Rupert model adapted for mixture surfactant system (Equation 20) and the experimental curve of commercial $C_{12}E_4$ (Simulsol P4).

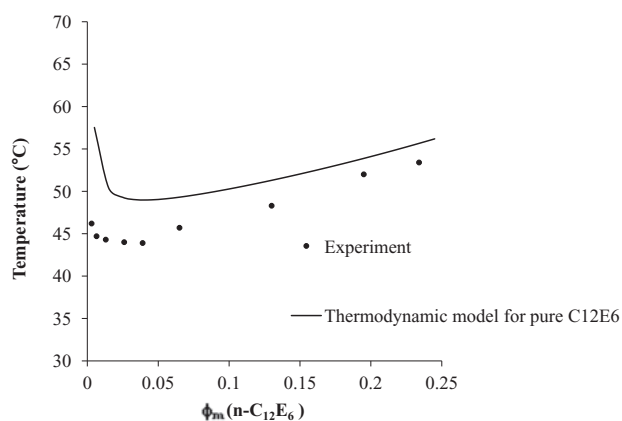


Figure 8. Comparison between the pure $C_{12}E_6$ miscibility curve calculated by the Flory Huggins Rupert model (Equation 17) and the experimental curve of commercial $C_{12}E_6$.

(Equation 20) is shown in Figure 7. This curve almost coincides with the experimental demixing curve. At low surfactant concentration (less than 10% by volume), the experimental curve is below that calculated using Equation 20; this may be due to dodecan-1-ol which decreases the cloud point of nonionic surfactants.^[32]

Commercial $C_{12}E_6$

The simplest method is to use Equation (17) and calculate the cloud point using the average formula ($C_{12}E_6$) given by the manufacturer, supposing that this surfactant is a pure chemical species. In this case, the experimental and calculated curves are quite different, as shown in Figure 8.

However, the chromatogram provided for the pilot-plant $C_{12}E_6$ sample shows that it is a mixture of 18 surfactants ($C_{12}E_n$, $n=1-18$) and 4% of residual dodecan-1-ol (Figure 3).

Flory-Huggins-Rupert model adapted for complex surfactant mixture was applied to commercial $C_{12}E_6$. From Equations (15) and (16), we can calculate the

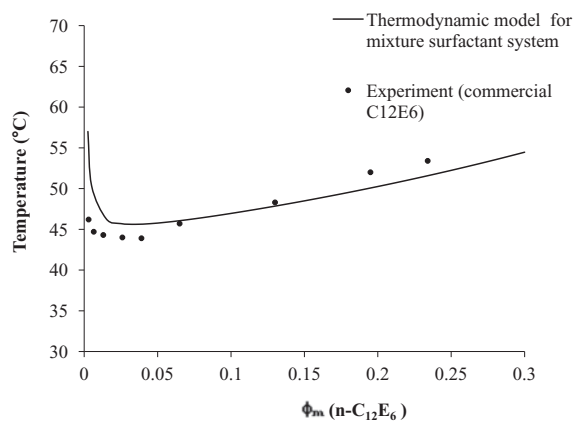


Figure 9. Comparison between the miscibility curve calculated by the Flory Huggins Rupert model adapted for mixture surfactant system (Equation 20) and the experimental curve of commercial $C_{12}E_6$.

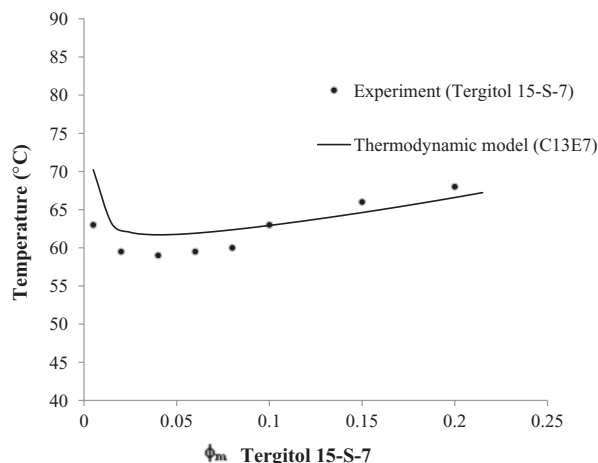


Figure 10. Comparison between the $C_{13}E_7$ miscibility curve calculated by the Flory Huggins Rupert model (Equations 13 and 17) and the experimental curve of Tergitol 15 S-7.

terms $\sum_{i=1}^n x_{i+1} H_{1(i+1)}$ (equal to 2803.769 cal/mol) and $\sum_{i=1}^n x_{i+1} S_{1(i+1)}$ (equal to 8.955 cal/mol K). On the other hand, the term $\sum_{i,j=2, j>i}^n x_i x_j w_{ij}$ is not simple to calculate, because it requires knowledge of the free enthalpies of interaction of all the possible combinations between the surfactants molecules of the mixture. The presence of dodecan-1-ol in the mixture complicates calculation, its free interaction energy with the surfactants in the micelles being probably different from that of the surfactant molecules between them. At this stage, this term remains an adjustable parameter. The value of $\sum_{i,j=2, j>i}^n x_i x_j w_{ij} \approx 280$ cal/mol leads to a smaller deviation (<10% on average between calculated and experimental results as shown in Figure 9. Again at low surfactant concentration (less than 10% by volume), the experimental curve is below that calculated using Equation (20);

Tergitol 15-S-7

Let us try to find the pure straight-chain alcohol ethoxylate showing the cloud point curve as close as possible to that of Tergitol 15-S-7. Since branched, or middle-functionalized,

chains are equivalent to shorter straight chains, as an approximation, the average formula, $C_{13}E_7$, was assumed for this commercial surfactant. Equation (17) was used to calculate the cloud point. Small deviations between calculated and experimental values (Figure 10) justify the displayed formula.

Conclusion

The cloud point phenomenon has been studied using the Flory-Huggins theory, which was investigated by various authors and applied in particular by Rupert^[9] to polyethoxylated alcohols. In this theory, an analogy between cloud point phenomenon and phase separation in polymer solutions was assumed. This theory interprets the clouding phenomenon for pure surfactant systems adequately. In this work, the cloud point curves of commercial polyethoxylated surfactants, which consist of a mixture of several pure surfactants, such as octylphenol, nonylphenol and alcohol ethoxylates, commercial $C_{12}E_4$ and $C_{12}E_6$ and Tergitol 15-S-7 (average formula: $C_{12-14}H_{25-29}O[CH_2CH_2O]_7H$), were quite well predicted. This approach also correlates enthalpy and entropy of interaction with the structure of the surfactant. But, finally, at this stage, in spite of the effort considering the multicomponent feature of any commercial surfactant, the prediction of clouding properties still remains a challenge and it is still necessary to keep a fitting parameter allowing to take into account the complexity of the surfactant formula.

References

- [1] Flory, P. J. Thermodynamics of High Polymer Solutions. *J. Chem. Phys.* **1942**, *10*, 51–61. DOI: [10.1063/1.1723621](https://doi.org/10.1063/1.1723621).
- [2] Flory, P. J. Phase Equilibria in Polymer Systems. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, Chapter XIII, 1953; pp 578–580.
- [3] Huggins, M. L. Solutions of Long Chain Compounds. *J. Chem. Phys.* **1941**, *9*, 440–440. DOI: [10.1063/1.1750930](https://doi.org/10.1063/1.1750930).
- [4] Kjellander, R. Phase Separation of Non ionic Surfactant Solution a Treatment of the Micellar Interaction and Form. *J. Chem. Soc., Faraday Trans. 2.* **1982**, *78*, 2025–2042. DOI: [10.1039/F29827802025](https://doi.org/10.1039/F29827802025).
- [5] Leng, C. A. Interacting CnEm Non Ionic Micellar Systems. *J. Chem. Soc., Faraday Trans. 2.* **1985**, *81*, 145–158. DOI: [10.1039/F29858100145](https://doi.org/10.1039/F29858100145).
- [6] Evans, H.; Tildesley, D. J.; Leng, C. A. Theories of Cloud Curve Phase Separation in Nonionic Alkyl Polyoxyethylene Micellar Solution. *J. Chem. Soc., Faraday Trans. 2.* **1987**, *83*, 1525–1541. DOI: [10.1039/F29878301525](https://doi.org/10.1039/F29878301525).
- [7] Goldfarb, J.; Sepulveda, L. Application of a Theory of Polymer Solutions to the Cloud Points of Nonionic Detergents. *J. Colloid Interface Sci.* **1969**, *31*, 454–459. DOI: [10.1016/0021-9797\(69\)90046-0](https://doi.org/10.1016/0021-9797(69)90046-0).
- [8] Weckström, K.; Zulauf, M. Lower Consolute Boundaries of a Poly (Oxyethylene) Surfactant in Aqueous Solutions of Monovalent Salts. *J. Chem. Soc., Faraday Trans. 1.* **1985**, *81*, 2947–2958.
- [9] Rupert, L. A. M. A Thermodynamic Model of Clouding in Water/Alcohol Ethoxylate Mixtures. *J. Colloid Interface Sci.* **1992**, *153*, 92–105. DOI: [10.1016/0021-9797\(92\)90300-B](https://doi.org/10.1016/0021-9797(92)90300-B).
- [10] Nakagawa, T. In *Nonionic Surfactants: Physical Chemistry*, chap. 15; M. J. Schick, Ed.; Marcel Dekker: New York, 1967.
- [11] Degiorgio, V. In *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*; Corti, M., Degiorgio, V., Eds.; North Holland: Amsterdam; 1985; pp 303–335.
- [12] Hinze, W. L.; Pramauro, E. A Critical Review of Surfactant Mediated Phase Separation (Cloud Point Extraction): Theory and Application. *Crit. Rev. Anal. Chem.* **1993**, *24*, 133–177. DOI: [10.1080/10408349308048821](https://doi.org/10.1080/10408349308048821).
- [13] Lindman, B.; Wennerstroem, H. Nonionic Micellar Growth with Increasing Temperature. *J. Phys. Chem.* **1991**, *95*, 6053–6054. DOI: [10.1021/j100168a063](https://doi.org/10.1021/j100168a063).
- [14] Inoue, T.; Ohmura, H.; Murata, D. Cloud Point Temperature of Polyoxyethylene Type Non Ionic Surfactants and Their Mixtures. *J. Colloid Interface. Sci.* **2003**, *258*, 374–382. DOI: [10.1016/S0021-9797\(02\)00162-5](https://doi.org/10.1016/S0021-9797(02)00162-5).
- [15] Watanabe, H.; Tanaka, H. A Nonionic Surfactant as a New Solvent for Liquid Liquid Extraction of Zinc (II) with 1 (2 Pyridylazo) 2 Naphtol. *Talanta* **1978**, *25*, 585–589. DOI: [10.1016/0039-9140\(78\)80151-9](https://doi.org/10.1016/0039-9140(78)80151-9).
- [16] Gullickson, N. D.; Scamehorn, J. F.; Harwell, J. H. *Liquid Coacervate Extraction. In Surfactant Based Separation Processes. Surfactant Science Series*; Marcel Dekker: New York; 1989; Vol. 33, pp 141–152.
- [17] Quina, F.; Hinze, W. L. Surfactant Mediated Cloud Point Extraction: An Environmentally Benign Alternative Separation Approach. *Ind. Eng. Chem. Res.* **1999**, *38*, 4150–4168. DOI: [10.1021/ie980389n](https://doi.org/10.1021/ie980389n).
- [18] Akita, S.; Takeuchi, H. Cloud Point Extraction of Organic Compounds from Aqueous Solution with Non Ionic Surfactant. *Sep. Sci. Technol.* **1995**, *30*, 833–835. DOI: [10.1080/01496399508013895](https://doi.org/10.1080/01496399508013895).
- [19] De Barros Neto, E. L. Extraction liquide liquide à deux phases aqueuses: Systèmes Phénol/Tensioactif polyéthoxylés. Thesis, Institut National Polytechnique, Toulouse, 1999.
- [20] Purkait, M. K.; Dasgupta, S.; De, S. Performance of TX 100 and TX 114 for the Separation of Chrysoidine Dye Using Cloud Point Extraction. *J. Hazard. Mater.* **2006**, *137*, 827–835. DOI: [10.1016/j.jhazmat.2006.03.003](https://doi.org/10.1016/j.jhazmat.2006.03.003).
- [21] Xie, S.; Paa, M. C.; Li, C. F.; Xiao, D.; Choi, M. M. F. Separation and Preconcentration of Persistent Organic Pollutants by Cloud Point Extraction. *J. Chromatogr. A* **2010**, *1217*, 2306–2317. DOI: [10.1016/j.chroma.2009.11.075](https://doi.org/10.1016/j.chroma.2009.11.075).
- [22] Haddou, B.; Canselier, J. P.; Gourdon, C. Use of Cloud Point Extraction with Ethoxylated Surfactants for Organic Pollution Removal. In *The Role of Colloidal Systems in Environmental Protection*, Fanun, M., Ed., Elsevier: Amsterdam, Chap. 5, pp 97–142. DOI: [10.1016/B978-0-444-63283-8.00005-3](https://doi.org/10.1016/B978-0-444-63283-8.00005-3).
- [23] Talbi, Z.; Haddou, B.; Ghoulas, H.; Kameche, M.; Derriche, Z.; Gourdon, C. Cationic Dye Removal from Aqueous Solutions Using Ionic Liquid and Nonionic Surfactant Ionic Liquid Systems: A Comparative Study Based upon Experimental Design. *Chem. Eng. Comm.* **2014**, *201*, 41–52. DOI: [10.1080/00986445.2012.759563](https://doi.org/10.1080/00986445.2012.759563).
- [24] Ghoulas, H.; Haddou, B.; Kameche, M.; Louhibi, L.; Derriche, Z.; Canselier, J. P.; Gourdon, C. Cloud Point Extraction of α Amino Acids. *Sep. Sci. Technol.* **2014**, *49*, 2142–2150. DOI: [10.1080/01496395.2014.919322](https://doi.org/10.1080/01496395.2014.919322).
- [25] Ghoulas, H.; Haddou, B.; Kameche, M.; Canselier, J. P.; Gourdon, C. Removal of Tannic Acid from Aqueous Solution by Cloud Point Extraction and Investigation of Surfactant Regeneration by Microemulsion Extraction. *J. Surfact. Deterg.* **2016**, *19*, 57–66. DOI: [10.1007/s11743-015-1764-9](https://doi.org/10.1007/s11743-015-1764-9).
- [26] Habbal, B.; Haddou, S.; Kameche, M.; Derriche, Z.; Canselier, J. P.; Gourdon, C. Cloud Point or Ionic Liquid Extraction of Furfural from Aqueous Solution: A comparative Study Based upon Experimental Design. *Desalination Water Treat.* **2016**, *57*, 23770–23778. DOI: [10.1080/19443994.2015.1133322](https://doi.org/10.1080/19443994.2015.1133322).
- [27] Benkhedja, H.; Canselier, J. P.; Gourdon, C.; Haddou, B. Cloud Point Extraction of Phenol and Benzenoid Alcohols: Scaling up of the Process in a Mixer Settler. *J. Water Proc. Eng.* **2017**, *18*, 202–212. DOI: [10.1016/j.jwpe.2017.06.016](https://doi.org/10.1016/j.jwpe.2017.06.016).

- [28] Barry, B. W.; Russel, G. F. J. Prediction of Micellar Molecular Weights and Thermodynamics of Micellization of Alkyltrimethylammonium Salts. *J. Colloid Interface Sci.* **1972**, *40*, 174–194. DOI: [10.1016/0021-9797\(72\)90007-0](https://doi.org/10.1016/0021-9797(72)90007-0).
- [29] Van Os, N. M. *Nonionic Surfactants: Organic Chemistry*; Marcel Dekker: New York; 1998.
- [30] Lumry, R. On the Interpretation of Data from Isothermal Processes. In *Methods in Enzymology*; Ackers, G. K., Johnson, M. L., Eds; Academic Press: New York; 1995; Vol. 259, pp 628–720.
- [31] Chen, L. J.; Lin, Y. S.; Huang, C. C. Effect of Hydrophobic Chain Length of Surfactant of Enthalpy Entropy Compensation in Micellization. *J. Phys. Chem. B.* **1998**, *102*, 4350–4356. DOI: [10.1021/jp9804345](https://doi.org/10.1021/jp9804345).
- [32] Maclay, M. N. Factors Affecting the Solubility of Nonionic Emulsifiers. *J. Colloid Interface Sci.* **1956**, *11*, 272–285.