



Equation oriented mixed micellization modeling based on asymmetric Margules-type formulations

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ABSTRACT

The determination of the composition of mixed micellar systems is a major problem since only the composition of the total micellar solution is accessible to the experimenter. A new approach is introduced in the present work based on Equation Oriented Optimization and Margules asymmetric formulations which is not restricted to the number of components and guarantees the applicability of the Gibbs–Duhem relation. The method is validated through its application to systems from literature and the quality of the solutions is tested with already published data and by comparison with other approaches. We do also show how excess properties can be predicted and that the excess entropy is not zero as assumed by the original regular and sub-regular solution theories.

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1. Introduction

The practical relevance of micelles is mainly due to their solubilization and emulsification capabilities which give them a preponderant role in fields such as pharmacy and medicine. Micelles serve as drug delivers in the body and are widely utilized in cosmetic and food industry. They also intervene in several biomedical processes such as the solubilization and transport of cholesterol in the gastrointestinal tract by means of bile salt-lecithin mixed micelles (Staggers et al., 1990).

Surfactant mixtures are used in most surfactant applications instead of pure amphiphiles because the mixtures often have enhanced properties when compared to the sum of properties of the pure components (synergism). A good description and characterization and, if possible, prediction of behavior of the micellar systems is necessary for their rational application. A proper panorama of the thermodynamic properties of micellar systems is a valuable tool for the surfactant technologist to design and select non-ideal surfactant mixtures with unique and desirable properties such as very attractive interactions that can result in critical micelle concentration of the mixture substantially lower than those of the pure surfactants.

A major problem is to determine the molar fraction of each surfactant in the aggregate since its value is fixed by the partition

equilibria of the species between the aggregate and the surrounding medium. The experimenter only has access to the total composition of the micellar solution. Therefore, the mixed micelles composition has to be experimentally determined or calculated on the basis of a thermodynamic model parameterized with physicochemical properties, mainly the critical micelles concentration (CMC).

There are two types of thermodynamic methods for micelle formation in surfactant solutions: (i) phenomenological models such as the pseudo-phase separation model and the mass-action model and (ii) molecular thermodynamic methods (see Electronic Supplementary Material, E.S.M., for the sections on Phenomenological Models and Molecular Thermodynamic Methods). These two types of methods are generally considered in literature as parallel treatments for micelle formation. The phenomenological methods mainly aim to the estimation of the mixed micelle compositions while the molecular thermodynamic theories are generally used to predict critical micelle concentrations and other properties.

In the pseudo-phase separation model, the micellar aggregate is conventionally represented as a “pseudo-phase” whose constitution depends on the composition of its environment and cannot be freely fixed by the experimenter, thus it is a “non-autonomous phase”. This is a conceptual model which does not correspond to an obligation imposed by the physical reality of the system. This approach has been quite successful in predicting the behavior of both binary nonionic and binary ionic mixtures of surfactants, particularly when they have the same hydrophilic group. However, the binary mixtures of nonionic and ionic surfactants or of surfactants with different hydrophilic groups significantly deviate from the

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ideal model. In order to deal with non-idealities, the Regular Solution Theory (RST) was developed by Holland and Rubingh (1983) on the basis of the pseudo-phase separation model and treating non-idealities via a regular solution approximation. The RST is the most frequently and systematically applied model for interpreting the behavior of surfactant mixtures. As for ideal mixtures, RST supposes a random distribution of the mixture components but with a possible interaction between them which results in an enthalpic effect. That is to say, the micellar structure is ignored and the interactions between the different surfactant molecules are accounted for by a single generalized parameter which represents an excess heat of mixing and that is related to the net (pairwise) interactions in the mixed micelles.

There is an extension of the RST which deals with multi-component nonideal mixed micellar (MRST) systems, however, as stated by the developers of these models, Holland and Rubingh (1992), the problem is addressed in a way designed to avoid the algebraic complexity that would arise from a direct extension of the binary surfactant model to multicomponent mixtures while allowing for arbitrarily accurate numerical solution of the appropriate relationships. As deduced from the original work, the multiple equations for multiple unknowns of this model were simultaneously and numerically solved for each individual mixture but, as stated by the authors, it could have been solved iteratively and sequentially.

Another remarkable feature of this generalized multicomponent procedure is that it is assumed that the activity coefficients can be expressed only by net pairwise interactions between components obtained independently from the binary mixtures. For a ternary system, the model can be synthesized into three nonlinear equations where the molar fractions of the mixture without considering the solvent (α_i), the critical micelle concentration of the pure components (cmc_i^0) and the binary interaction parameters of the binary mixtures (β_{ij}) are known and the critical micelle concentration of the mixture (CMC^{mix}) and the molar fraction of the components in the micelle (x_i) are unknown. As stated by Graciaa et al. (1989), the critical micelle concentration can be directly measured, and the model results can be easily compared with experiments.

The Margules-type equations are commonly used to represent excess molar properties mathematically in many fields such as mineralogy. For the n -component system, the excess free energy (G^{exc}) function is approximated by a p th-order Taylor series, whose constants have no thermodynamic meaning, involving $(n-1)$ independent compositional variables. The expression for G^{exc} is differentiated with respect to each compositional variable, and the resultant partial derivatives are evaluated at each of the compositional extremes to obtain the Margules parameters (activity coefficients at infinite dilution, γ_i^∞). When $p=2$, the solutions are symmetric (strictly regular) and no ternary and higher order interaction parameters exist in ternary and higher order systems. For $p=3$, the solutions are asymmetric (subregular) and no quaternary and higher order parameters exist in quaternary and higher order systems. As a special case of the latter system ($p=3$) the constituent binaries can exhibit symmetric behavior, but the expressions for G^{exc} and $RT \ln(\gamma_i)$ can contain ternary interaction parameters. Thus, the existence of non-binary interaction parameters is a result of the complexity of the Taylor series approximation to the G^{exc} function. In general, ternary interaction parameters cannot be completely defined by the binary interaction parameters. Mukhopadhyay et al. (1992) derived the Margules-type formulations for the G^{exc} and $RT \ln(\gamma_i)$ which are thermodynamically valid (i.e., they obey the Gibbs–Duhem relation and Raoult's and Henry's laws at the compositional extremes). The expression of the activity coefficient in the RST assumes that they are symmetric with respect to the surfactant composition of the aggregate and therefore, that the excess free

energy of mixing is also symmetric with respect to the surfactant composition.

The RST is usually solved iteratively, e.g. Ghosh et al. (2011). Some authors have implemented asymmetric Margules formulations for binary systems but solving the models iteratively for each mixture composition (Hao et al., 2012; Hu et al., 2007). A major issue when solving the model for each mixture composition is that the optimum values of the Margules parameters may not be probably obtained, moreover, different values are usually achieved for each mixture composition and thus, the Gibbs–Duhem equation is not fulfilled. This issue has been pointed out by Letellier et al. (2008b): “in numerous cases, the coefficient β varies with the mixture composition. The supporters of this approach justify their choice by showing that the CMC values of the mixtures follow behaviors predicted by RST”. These latter authors have developed a method to determine the compositions of the aggregates based on the strict application of the Gibbs–Duhem relation (see E.S.M.), once the assumption of the pseudo-phase is accepted. However, it seems to be quite cumbersome to extend it to systems with more than two components and it strongly depends on the precision of the numerical derivatives so the authors warn that a large set of experimental values is required. The same authors have introduced and applied the concept of nonextensive thermodynamics to describe the behavior of pure ionic surfactants at concentrations higher than the CMC (Letellier and Turmine, 2015; Letellier et al., 2008a).

The amphiphiles should follow the equal-activity relationship, and their equilibrium distributions should correspond to the minimal Gibbs energy of the solution. The optimization of the Gibbs free energy has been used to solve phase equilibrium calculations in several systems (Camarda et al., 1999; Jarungthammachote and Dutta, 2008; Nichita et al., 2002a, b; Rossi et al., 2009, 2011; Teh and Rangaiah, 2002).

In the present work we introduce a new insight into the thermodynamics of mixed micellization modeling employing the Equation Oriented Optimization approach minimizing the total free energy of micellization of the system. The method can be easily extended to multicomponent systems and ternary interaction parameters are contemplated using Margules formulations for asymmetric solutions.

2. Theory

Assuming that the surfactants in the pseudo-phase are in equilibrium with the species in solution and that the temperature and the pressure are fixed, the surfactant activity of component i in the pseudo-phase in reference to pure component as the standard state (scale for molar fractions) a_i^m is given by (see E.S.M. for the deduction):

$$a_i^m = \frac{a_i^b}{a_i^{b,0}} \quad (1)$$

where a_i^b is the activity coefficient of i in the bulk of the micellar solution (monomer) in reference to the infinitely diluted solution and $a_i^{b,0}$ is the activity of pure i in the bulk in reference to the infinitely diluted solution at the aggregation threshold.

Letellier et al. (2011) introduced a theoretical treatment of Rubingh's model that contemplates the possible dissociation of the components of the mixture in the bulk as well as in the micelle, redefining the molar fraction of the ionic surfactants in the aggregates:

$$xp_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (3)$$

where xp_i corresponds to the molar fraction of the particles and r is the number of identical and indistinguishable particles generated

by the surfactant i while x_i correspond to the stoichiometric molar fractions. In the classical RST the molar fractions in the pseudo-phase are the stoichiometric ones.

Following Letellier et al. (2011) we obtained the following relations'

For non-ionic surfactants with and without supporting electrolyte:

$$xp_i\gamma_i = \frac{CMC^{\text{mix}}\alpha_i}{cmc_i^0} \quad (4)$$

For the ionic surfactants without supporting electrolyte (see E.S.M.):

$$xp_i\gamma_i = \left[\frac{CMC^{\text{mix}}\alpha_i}{cmc_i^0} \right]^{2/r} \quad (5)$$

For the ionic surfactants with supporting electrolyte:

$$xp_i\gamma_i = \left[\frac{CMC^{\text{mix}}\alpha_i}{cmc_i^0} \right]^{1/r} \quad (6)$$

Notice that for 1:1 ionic surfactant fully ionized ($r_i=2$), the Clint's relation (see E.S.M.) is applied and $x_i = xp_i$.

Note that in the original Rubingh's model, where no dissociation of the surfactants was considered, the following relation was used:

$$cmc_i^0 x_i \gamma_i = CMC^{\text{mix}} \alpha_i \quad (7)$$

2.1. Generalized Margules formulations

It is assumed that the G^{exc} can be sufficiently approximated by a Taylor series truncated in the fourth power in the full range of $0 \leq x_i \leq 1$. Thus, the quaternary or higher order interaction parameters are neglected but they could be contemplated if a higher order polynomial ($p \geq 4$) were employed. The activity coefficients are obtained deriving G^{exc} with respect to the number of moles according to the standard relationship:

$$RT \ln(\gamma_i) = \frac{\partial \left[\left(\sum_i m_i \right) G^{\text{exc}} \right]}{\partial m_i} \quad (8)$$

For a n -component symmetric solution, where all the constituent binaries are characterized by symmetric Margules-type parameters, and the Taylor series approximating the G^{exc} function is truncated after the second power ($p=2$):

$$G^{\text{exc}} = \sum_{i < j}^n W_{ij} x_i x_j \quad (9)$$

$$RT \ln(\gamma_i) = \sum_{\substack{j=1 \\ j \neq i}}^n W_{ij} x_j - G^{\text{exc}} \quad (10)$$

For an n -component asymmetric solution with $p=3$:

$$G^{\text{exc}} = \sum_i^n \sum_{<j}^n x_i x_j [x_j W_{ij} + x_i W_{ji}] + \sum_i^n \sum_{<j}^n \sum_{<k}^n x_i x_j x_k C_{ijk} \quad (11)$$

$$RT \ln(\gamma_i) = 2 \sum_{\substack{j=1 \\ j \neq i}}^n x_i x_j W_{ji} + \sum_{\substack{j=1 \\ j \neq i}}^n x_j^2 W_{ij} + \sum_j^n \sum_{\substack{k < k \\ j \neq i \ k \neq i}}^n x_j x_k C_{ijk} - 2G^{\text{exc}} \quad (12)$$

$$C_{ijk} = \frac{1}{2} [W_{ij} + W_{ji} + W_{ki} + W_{ik} + W_{jk} + W_{kj}] - W_{ijk} \quad (13)$$

C_{ijk} contains binary interaction parameters and if it is assumed to be zero then there is no ternary interaction. The term W_{ijk} only involves the third order terms of the Taylor series and contains no binary terms and hence can be independently set to zero and thus the ternary term C_{ijk} is completely determined by the binary interaction parameters. However, it is advised not to evaluate C_{ijk} and W_{ijk} independently. The symmetric Margules formulations are recovered when $W_{ij} = W_{ji}$, that is to say, the symmetric formulations are contemplated in the asymmetric ones.

A particular case of asymmetric ($p=3$) solution appears when $W_{ij} = W_{ji}$ but $W_{ijk} \neq 0$, a special case of asymmetric solutions with ternary interactions where the constituent binaries show symmetric behavior.

It is important to notice that the RST employs the Margules formulations for binary systems ($n=2$) and symmetric solutions ($p=2$). That is to say, $W_{ij} = W_{ji} = \beta RT$ (see E.S.M.).

$$G^{\text{exc}} = x_1 x_2 \beta \quad (14)$$

$$\ln(\gamma_1) = \beta x_2 - G^{\text{exc}} = \beta x_2^2 \quad (15)$$

$$\ln(\gamma_2) = \beta x_1 - G^{\text{exc}} = \beta x_1^2 \quad (16)$$

The extension of the RST for multicomponent systems do also apply the Margules formulations for symmetric solutions ($p=2$), thus it only uses binary interactions to express the activity coefficients in the multicomponent systems (Holland and Rubingh, 1983). That is to say, it not only assumes that the binary interactions are symmetric but it also neglects ternary interactions. However, in general ternary interaction parameters cannot be completely defined by the binary interaction parameters.

In the present work we introduce the Equation Oriented Mixed Micellization Model (EOMMM) employing the Margules' formalism for the excess free energy and the activity coefficients. Due to the various sources of non-ideality in the surfactant systems, such as steric hindrances, specific interactions such as coulombic interactions, hydrogen bonding and hydrophobic/hydrophilic interactions, the Margules type formulations might not be the best formalism for a determined system. However, other alternative expressions described in literature, such as the van Laar equations (Peng, 2010), can be effortlessly implemented within this approach.

3. Equation Oriented Mixed Micellization Model (EOMMM)

Nomenclature

Sets

n	surfactant mixtures
i	components

Parameters

$\alpha_{i,n}$	molar fraction of component i in the mixture n without considering the solvent
$CMC \exp_n^{\text{mix}}$	experimentally determined critical micelle concentration of the mixture n
cmc_i	critical micelle concentration of the pure component i
MID_i	micelle ionization degree (see E.S.M.)
mg	margin allowed in $CMC \exp_n^{\text{mix}}$ ($0 \leq mg \leq 1$)

Variables

$x_{p_i,n}$	molar fraction of particles of component i in micelles of mixture n
$x_{i,n}$	stoichiometric molar fraction of component i in micelles of mixture n
$\gamma_{i,n}$	activity coefficient of component i in micelles of mixture n

W_{ij} binary Margules coefficient
 W_{ijk}, C_{ijk} ternary Margules coefficients
 G_n^{exc} excess free energy of micellization of mixture n
 G_i free energy of micellization of pure component i
 CMC^{mix} critical micelle concentration of mixture n

$$G_n^{exc} = \sum_{i < j}^n W_{ij} x_{p_{i,n}} x_{p_{j,n}} \quad \forall n$$

3.1.5. Asymmetric solution

$$\gamma_{i,n} = \exp \left(\frac{2 \sum_{j=1}^n x_{p_{i,n}} x_{p_{j,n}} W_{ji} + \sum_{j=1}^n x_{p_{j,n}}^2 W_{ij} + \sum_{j=1}^n \sum_{k=1}^n x_{p_{j,n}} x_{p_{k,n}} C_{ijk} - 2 G_n^{exc}}{RT} \right) \quad \forall n$$

3.1. Constraints

Either Eq. (4), (5) or (6) is used depending on whether the surfactant is ionic or nonionic and on the conditions (with or without supporting electrolyte):

3.1.1. Non-ionic surfactants with and without supporting electrolyte (Eq. (4))

$$x_{p_{i,n}} \gamma_{i,n} = \frac{CMC_n^{mix} \alpha_{i,n}}{cmc_i^0} \quad \forall n$$

3.1.2. Ionic surfactants without supporting electrolyte (Eq. (5))

$$x_{p_{i,n}} \gamma_{i,n} = \left[\frac{CMC_n^{mix} \alpha_{i,n}}{cmc_i^0} \right]^{2/r} \quad \forall n$$

3.1.3. Ionic surfactants with supporting electrolyte (Eq. (6))

$$x_{p_{i,n}} \gamma_{i,n} = \left[\frac{CMC_n^{mix} \alpha_{i,n}}{cmc_i^0} \right]^{1/r} \quad \forall n$$

The relation between the stoichiometric molar fractions $x_{i,n}$ and the molar fraction of the particles $x_{p_{i,n}}$ given by Eq. (3):

$$x_{p_{i,n}} \sum_i (r_i x_{i,n}) = r_i x_{i,n} \quad \forall n$$

The addition of the molar fractions of the components in the micelles:

$$\sum_i x_{p_{i,n}} = 1 \quad \forall n$$

$$\sum_i x_{i,n} = 1 \quad \forall n$$

The activity coefficients and the excess free energy of micellization of the mixtures are calculated with the Margules formulations, either for symmetric (Eqs. (9) and (10)) or asymmetric solutions (Eqs. (11)–(13)) (see E.S.M.).

3.1.4. Symmetric solution

$$\gamma_{i,n} = \exp \left(\sum_{\substack{j=1 \\ j \neq i}}^n \frac{W_{ij} x_{p_{j,n}} - G_n^{exc}}{RT} \right) \quad \forall n$$

$$C_{ijk} = \frac{1}{2} [W_{ij} + W_{ji} + W_{ki} + W_{ik} + W_{jk} + W_{kj}] - W_{ijk}$$

$$G_n^{exc} = x_{p_{1,n}} x_{p_{2,n}} (x_{p_{2,n}} W_{12} + x_{p_{1,n}} W_{21}) + x_{p_{1,n}} x_{p_{3,n}} (x_{p_{3,n}} W_{13} + x_{p_{1,n}} W_{31}) + x_{p_{2,n}} x_{p_{3,n}} (x_{p_{3,n}} W_{23} + x_{p_{2,n}} W_{32}) + x_{p_{1,n}} x_{p_{2,n}} x_{p_{3,n}} C_{123} \quad \forall n$$

3.2. Objective function

The objective function is the minimization of the total free energy, that is to say, the sum of the free energies of all the mixtures considered.

$$\min \sum_n \left(G_n^{exc} + \sum_i x_{i,n} G_i + RT \sum_i x_{p_{i,n}} \ln x_{i,n} \right)$$

The free energy of micellization of pure surfactant i was obtained using the mass-action model (see E.S.M.)

$$G_i = RT(2 - MID_i) \ln \left(\frac{cmc_i}{55.55} \right)$$

3.3. Bounds over variables

$$0 \leq x_{p_{i,n}} \leq 1$$

$$\alpha_{i,n} \Rightarrow x_{i,n}$$

$$CMC \exp_n^{mix}(1 - mg) \leq CMC_n^{mix} \leq CMC \exp_n^{mix}(1 + mg)$$

Proper lower and upper bounds have to be given to $\gamma_{i,n}$, W_{ij} and the total free energy of micellization in order to the solver to be able to find the global optimum.

The mathematical model has been solved with GAMS (General Algebraic Modeling System) Rev 23.4.3. GAMS is a high-level modeling system for mathematical programming and optimization. It consists of a language compiler and a stable of integrated high-performance solvers. It is tailored for complex, large scale modeling applications. GAMS is a very well-known tool in fields like Process System Engineering, Economic Science and Operation Research. (See E.S.M. for an example of EOMMM model input file). The Equation Oriented Optimization approach simultaneously solves the equation system in order to find the minimum/maximum of an objective function subject to a set of constraints. The presented problem belongs to the non-linear programming class (NLP) and was solved to global optimality with BARON 12.4 and CONOPT 3.14.

Many authors solve the RST model for each mixture. That is to say, they simultaneously solve Eqs. (7), (9) and (10) and the addition of the molar fractions of all the components in the micelles in order to obtain W_{ij} ($=\beta RT$), the values of x_i and γ_i (for each

mixture: number of equations = $2 \times$ number of components + 1; number of unknowns = $2 \times$ number of components + 1). However, a different value of W_{ij} is obtained for each mixture, implying a different expression for the excess free energy of micellization in each mixture and the unfulfillment of the Gibbs–Duhem equation. Therefore, fitting the estimated and the experimental CMC of the mixture is not an enough criteria to determine $x_{i,n}$, $\gamma_{i,n}$ and the Margules parameters because there are multiple solutions. Therefore, in order to decrease the number of degrees of freedom, it is necessary to minimize the total free energy of micellization. This problem is in fact a multiobjective optimization since the total free energy of micellization has to be minimized while minimizing the error between the experimental and estimated CMCs of the mixture. To attain this, the mg parameter was varied in order to obtain the minimum value that allowed a feasible solution of the problem. This takes into account that experimentally determined CMC depend on the method employed and that in fact the CMC itself is not a well-determined concentration value but a concentration interval.

4. Results and discussion

In order to validate our method, we applied it to systems obtained from literature and tested the quality of the solutions with already published data and/or with other approaches. We do also show how our method can be easily applied to multicomponent systems.

4.1. Case study 1: binary mixture Hyamine ($i=1$) – DTAB ($i=2$)

In a binary system studied by Rodríguez et al. (2012) composed of Hyamine (Hy) – dodecyltrimethylammonium bromide (DTAB), the molar fractions of the surfactants in the micelles were experimentally determined. We are now comparing those molar fractions with the estimated by the EOMMM considering symmetric and asymmetric solutions. We are also comparing these results with the usually applied procedure in which the equations considering symmetric solutions are solved simultaneously for each individual mixture (RST), and the method developed by Letellier et al. (2008b). The experimental data are given in Table 1 in the E.S.M.

Fig. 1 and Fig. 1 in the E.S.M. resemble those obtained for liquid–vapor equilibrium (Smith et al., 1989) while it is evident that the slopes of the logarithms of the activity coefficients in Fig. 2 in the E.S.M. do not obey the Gibbs–Duhem relation. Table 1 shows that the estimated molar fractions obtained with the EOMMM procedure considering asymmetric Margules formulations has an average relative error of 24.84% while it is 33.33% when symmetric Margules formulations is applied and 36.34% with the RST model. Both EOMMM procedures (symmetric and asymmetric) were solved with $mg=0.10$. Fig. 3 in the E.S.M. shows the experimental, the ideal and the obtained with EOMMM CMCs. The Margules parameters for the asymmetric case are $W_{12} = -8836.50$ (J/mol) and $W_{21} = -2204.19$ (J/mol) and for the symmetric case $W = -5371.64$ (J/mol) ($\beta = -2.17$ in kT units). However, when the system of equations is solved individually

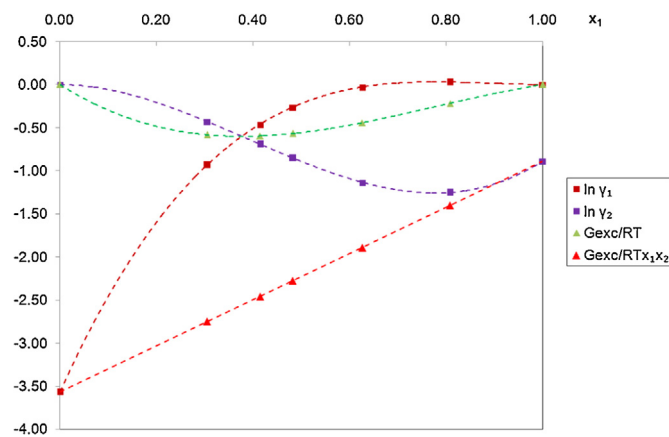


Fig. 1. Natural logarithm of the activity coefficients for Hyamine (■) and DTAB (■); excess free energy of micellization (▲) and excess free energy of micellization divided the molar fractions in the micelles ($x_1 = x_{Hy}$ and $x_2 = x_{DTAB}$) (▲) as a function of the molar fraction of Hy in the micelles obtained considering Margules formulations for asymmetric solutions with the EOMMM procedure. Dashed lines are trend lines.

for each mixture, the values of W were 0; -5446.80 ; -4156.48 ; -4309.07 ; -5875.62 ; -5496.45 and 0 for the mixtures with $\alpha_{DTAB} = 0$; 0.25; 0.5; 0.75; 0.85; 0.95 and 1 respectively. Fig. 4 in the E.S.M. shows the total and the ideal free energies and Fig. 5 in the E.S.M. shows the molar fractions in the micelles (x_i) as a function of the total molar fractions (α_i) of hyamine obtained with EOMMM (asymmetric and symmetric) and RST.

Table 2 in the E.S.M. shows the calculation of the molar fractions according to Letellier et al. (2008b) using Eqs. (3) and (4) in the E.S.M. with the derivatives numerically calculated. The average relative error is 40.63% and 35.84% when backward and central finite differences respectively are used. A fourth order polynomial was used to interpolate the activity of Hy as a function of the activity of DTAB (Fig. 6 in the E.S.M.). Table 3 in the E.S.M. shows the molar fractions of the derivatives obtained deriving analytically this polynomial, the molar fractions in the micelles of Hy and the relative errors. In this case the average relative error was 52.65%.

This example shows that, as stated by Letellier et al. (2008b), it is a thermodynamic mistake adopting a priori model behavior. The asymmetric formulations contemplates the symmetric ones, therefore they will always be more accurate (or at least equal) and they will always provide an equal or lower minimum in the objective function than the symmetric ones (see Fig. 4 in the E.S.M.). The sub-regular solution model has also been applied in binary alloys to explain the asymmetry in the heat of mixing (Llewellyn Leach, 1967).

The method proposed by Letellier et al. (2008b) is less accurate than ours in the present case because, as it is based in numerical differentiation, it requires a large set of experimental values evenly distributed in order to have good precision. At this point, we want to emphasize the advantage of our approach: we are not assuming a model of behavior but we only assume that the excess free energy

Table 1

Experimental and estimated molar fractions obtained with the EOMMM procedure considering symmetric and asymmetric Margules formulations and with the RST.

α_{DTAB}	Symmetric			Asymmetric		RST	
	Experimental x_{DTAB}	x_{DTAB}	Rel. error %	x_{DTAB}	Rel. error %	x_{DTAB}	Rel. error %
0.25	0.325	0.197	39.29	0.192	40.93	0.177	45.36
0.50	0.471	0.310	34.09	0.374	20.65	0.287	38.94
0.75	0.705	0.438	37.91	0.517	26.62	0.430	38.91
0.85	0.659	0.514	22.04	0.585	11.17	0.513	22.14
Average			33.33		24.84		36.34

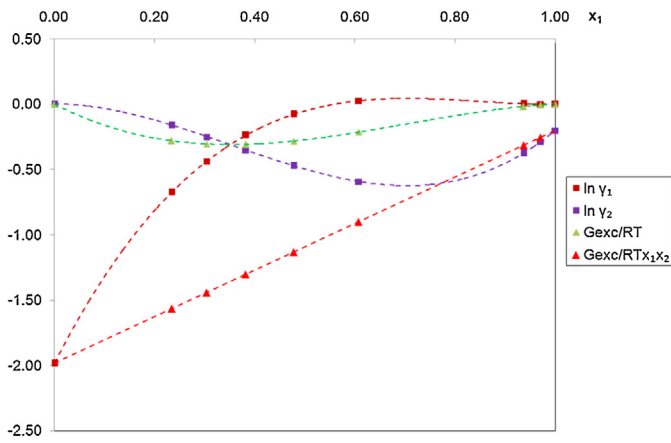


Fig. 2. Natural logarithm of the activity coefficients for Brij (■) and DTAB (■); excess free energy of micellization (▲) and excess free energy of micellization divided the molar fractions in the micelles ($x_1 = x_{Brij}$ and $x_2 = x_{DTAB}$) (▲) as a function of the molar fraction of Brij in the micelles obtained considering Margules formulations for asymmetric solutions and $r_{DTAB} = 1$ with the EOMMM procedure. Dashed lines are trend lines.

(G^{exc}) function can be properly approximated by a p th-order Taylor series and base our model in the analytically differentiation of G^{exc} to obtain the activity coefficient.

4.2. Case study 2: binary mixture Brij ($i = 1$)–DTAB ($i = 2$) in the presence of supporting electrolyte

The experimental values of Brij–DTAB mixtures in saline sodium (0.3 mol/L NaBr) have been previously published (Letellier et al., 2008b).

The “critical micellar concentration of mixture” is calculated as in the work of Letellier et al. (2011):

$$\Delta\theta_{cmc} = CMC - \alpha_1 cmc_1^0 - \alpha_2 cmc_2^0 \quad (17)$$

The values of $\Delta\theta_{cmc}$ (see Fig. 7 in the E.S.M.) with the experimental CMC are superimposed with the $\Delta\theta_{cmc}$ with the ideal CMC when $r_{DTAB} = 1.5$ (the variations of the CMC of the mixtures were well described in Letellier et al. (2011) with $r_{DTAB} = 1.4$ by supposing an ideal model). However, r_{DTAB} has to be approximately 1 in order to have negative excess energies of micellization in all the mixtures as shown in Fig. 2. See Figs. 8 and 9 in the E.S.M. for excess free energy of micellization and activity coefficients when $r_{DTAB} = 1$ and $r_{DTAB} = 1.5$, respectively. Thus, as expected by the law of mass action, when there is a supporting electrolyte the ionic surfactant has a low ionization degree.

4.3. Case study 3: binary mixture C_8E_4 ($i = 1$)–SDS ($i = 2$)

The system sodium dodecyl sulphate (SDS) and *O*-n-octyltetraethylene glycol (C_8E_4) has been previously studied by Hey et al. (1985) and the enthalpies of mixed-micelle formation have been obtained calorimetrically. It has been determined that SDS and the mixtures with $\alpha_{SDS} \geq 0.6$ as well as the pure SDS have small micellization heats. For pure C_8E_4 the heat of micellization is $H_{C_8E_4} = 13.5 \pm 1.5$ kJ/mol.

Our model does not assume that the excess entropy is zero. Therefore, it can be calculated as:

$$G^{exc} = H^{exc} - TS^{exc} = H - \sum_i x_i H_i - TS^{exc} \quad (18)$$

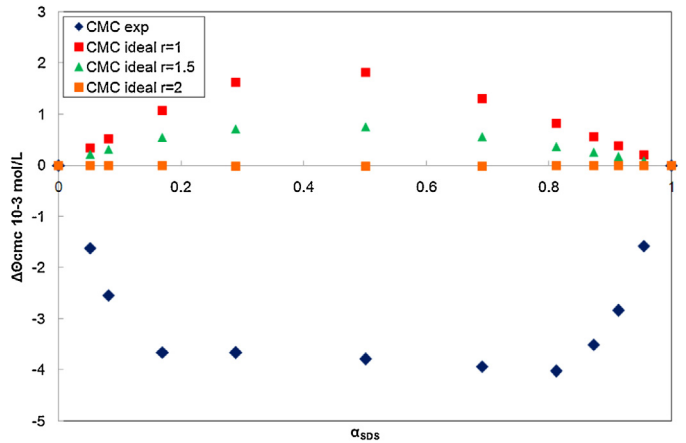


Fig. 3. Variation of the critical micellar concentration mixture ($\Delta\theta_{cmc}$) with α_{SDS} for the experimental CMC and the ideal CMC with different values of r_{SDS} .

The ideal CMC was obtained with Eq. (44) in the E.S.M. $\Delta\theta_{cmc}$ is equal 0 for all the mixtures when $r_{SDS} = 1.986$ and it is slightly below zero for $r_{SDS} = 2$ when synergistic effects are neglected since it was assumed that there are no interactions between the components of the mixture (ideality). When $\Delta\theta_{cmc}$ is calculated with the experimental CMC it is evident that there is synergy between the components manifested by considerably negative values of $\Delta\theta_{cmc}$ (see Fig. 3).

The EOMMM was applied with asymmetric Margules formulations and $mg = 0.10$, which is within the experimental error for the CMC values determined by Hey et al. (1985).

When $r_{SDS} = 2$ (SDS totally dissociated) the Margules parameters obtained were: $W_{12} = -6997.54$ and $W_{21} = -8051.40$ (J/mol). The excess entropy and excess enthalpy (see Figs. 4–6) were calculated according to Eq. (17) with the heats of micellization H (difference between mixed and unmixed systems) reported in Table 5 in the E.S.M.

Therefore, there is a range of r_{SDS} from approximately $r_{SDS} = 1.5$ to 1 where the excess entropy is higher than the excess free energy for a range of compositions indicating antagonism toward the mixed micelle formation. As Fig. 2 shows that the system is synergistic for the whole range of compositions, this range of r_{SDS} can be discarded and the real r_{SDS} value must probably be between 2 and 1.5.

The regular solution model proposed by Hildebrand and Scott (1950) did not take into account the problem of excess entropy

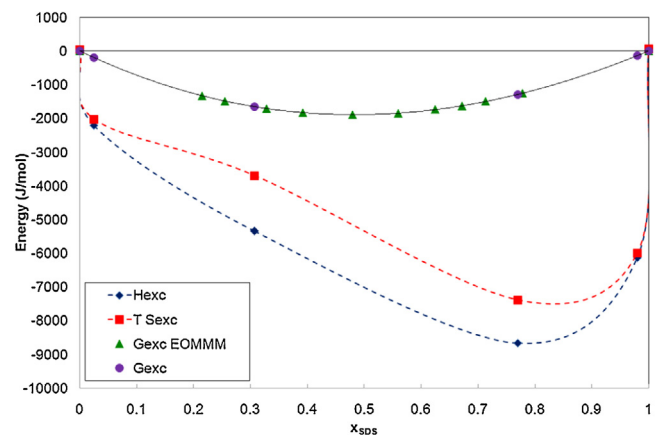


Fig. 4. Excess properties in the experimental mixtures reported by Hey et al. (1985) and free energy calculated with EOMMM obtained with $r_{SDS} = 2$.

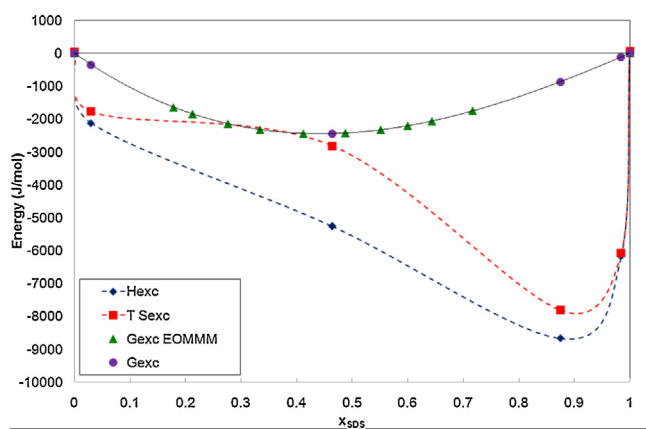


Fig. 5. Excess properties in the experimental mixtures reported by Hey et al. (1985) and free energy calculated with EOMMM obtained with $r_{SDS} = 1.5$.

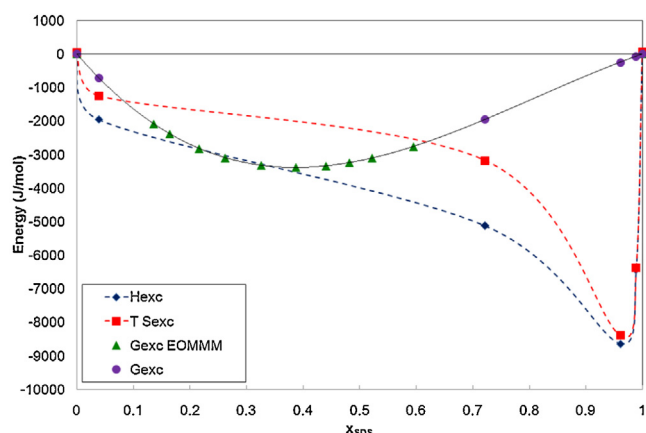


Fig. 6. Excess properties in the experimental mixtures reported by Hey et al. (1985) and free energy calculated with EOMMM obtained with $r_{SDS} = 1$.

$S^{exc} \neq 0$ into consideration. Neither did the sub-regular solution model developed by Hardy (1953). However it is well-known that some molten solutions and alloys can have either positive or negative S^{exc} because the mixing of components cannot be completely

random. Moreover, the mixing entropy is significantly influenced by the atom profile, dimension direction, and so on, as stated by Chen et al. (2002). In case of mixed micelles, other factors causing nonzero excess entropy may be steric hindrances, specific interactions such as columbic interactions, hydrogen bonding and hydrophobic/hydrophilic interactions. Therefore, the excess entropy of mixed micelles, as real solutions, may not equal to zero.

4.4. Case study 4: Ternary system $C_{10}TAB$ ($i = 1$)– $C_{12}TAB$ ($i = 2$)– $C_{14}TAB$ ($i = 3$)

In order to show the ease of the extensibility of our method to systems with more than two components, we applied it to a ternary system of homologues: decyltrimethylammonium bromide ($C_{10}TAB$); dodecyltrimethylammonium bromide ($C_{12}TAB$) and tetradecyltrimethylammonium bromide ($C_{14}TAB$). This system has been studied by Schulz et al. (2013) and experimental data has been extracted from their work.

The EOMMM was solved for the complete triangular diagram considering 70 mixtures with $mg = 0.4$. Fig. 7 shows the estimated CMC and Figs. 10 and 11 in the E.S.M. show the experimental and the ideal CMCs, respectively. The CMC values (experimental, estimated and ideal) for each of the 70 mixtures are reported in Table 6 in the E.S.M. The average relative error for the estimated CMC is 21.6%.

The Margules parameters obtained are $W_{12} = -10301.66$ (J/mol); $W_{21} = 1214.73$ (J/mol); $W_{13} = -7175.55$ (J/mol); $W_{31} = 10553.37$ (J/mol); $W_{32} = 12142.72$ (J/mol); $W_{23} = -8878.93$ (J/mol); $W_{123} = 37666.09$ (J/mol) and $C_{123} = -38888.75$ (J/mol). It is worth to highlight that the ternary parameters are too large to be neglected in the model.

It would be expected that homologues mixtures were ideal, as assumed in the original RST. However, as shown in Fig. 8, the excess free energy is close to zero only for mixtures with $\alpha_{C_{12}TAB} \leq 0.4$. Fig. 9 shows that the micelles are in general richer in $C_{14}TAB$ in concordance with its lower CMC ($cmc_{C_{14}TAB}^0 = 0.0041$ mol/L; $cmc_{C_{12}TAB}^0 = 0.0145$ mol/L and $cmc_{C_{10}TAB}^0 = 0.067$ mol/L). Figs. 15 and 16 in the E.S.M. show the molar fractions in the micelles of $C_{10}TAB$ and $C_{12}TAB$, respectively. The natural logarithms of the activity coefficients are shown in Figs. 13 and 14 of the E.S.M.

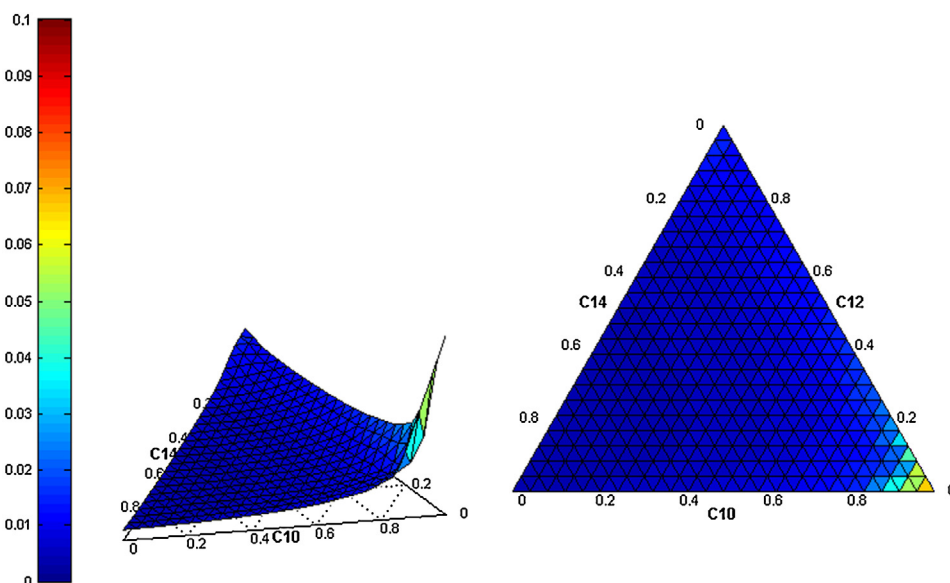


Fig. 7. CMC estimated with EOMMM.

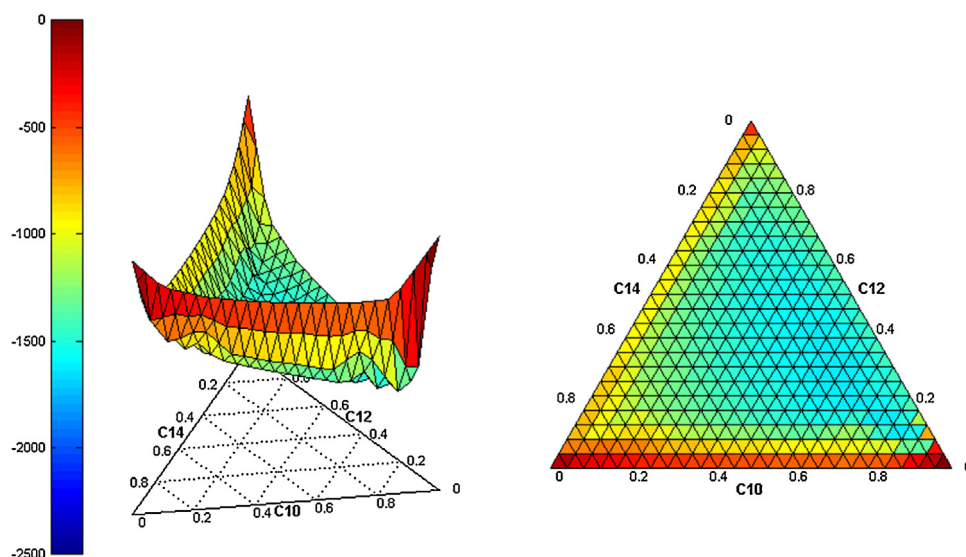


Fig. 8. G^{exc} obtained with EOMMM.

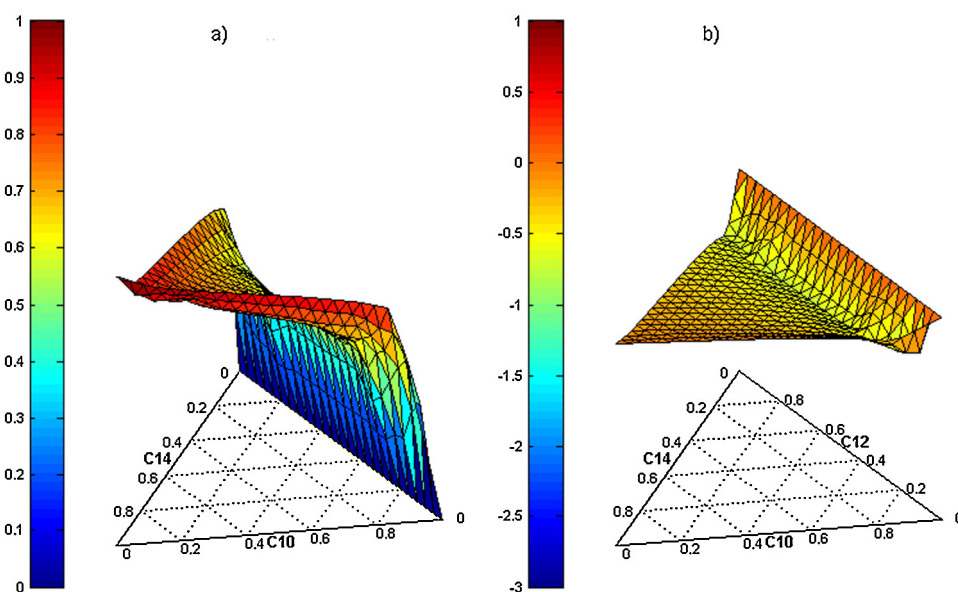


Fig. 9. (a) molar fraction in the micelles of $C_{14}\text{TAB}$ ($x_{C_{14}\text{TAB}}$), (b) natural logarithm of the activity coefficient of $C_{14}\text{TAB}$ ($\ln \gamma_{C_{14}\text{TAB}}$).

5. Conclusions

We have proposed a method to obtain the composition of mixed micellar systems which is based on the assumptions that the pseudo-phase model is valid and that the excess free energy (G^{exc}) function can be properly approximated by a p th-order Taylor series. The approach is based in the analytical differentiation of G^{exc} to obtain the activity coefficient, thus assuring the applicability of the Gibbs–Duhem relation. Its applicability is not restricted to the number of components and it is straightforward extended to multicomponents. Since it is based in analytical differentiation it gives quite accurate results even with few experimental values. By solving the problem to global optimality, a unique set of Margules parameters, compositions of the aggregates and activity coefficients is obtained which minimizes the total free energy of micellization. The method has been validated and tested with literature data and by comparison with other methodologies. Moreover, we do also show how other excess properties can be achieved and demonstrate that the excess entropy of

micellization is not zero as assumed by the original regular and sub-regular theories.

Among the activity coefficient models (see E.S.M.), the NRTL model provides a versatile thermodynamic framework to describe the solution non-ideality of mixed micelles systems (Chen, 1996). However, the compositions of the pseudo micelle phase need to be known. The molecular thermodynamic models (such as Achard, UNQUAC and UNIFAC) could be used to calculate the activity coefficients to be introduced in the RST. However, it has been recognized as a main drawback that the original RST deals with ionic surfactants as non-dissociated components (Cheng, 2003). In our method we have contemplated the dissociation of ionic surfactants through the r parameter. Therefore, we think that both methods could complement each other and that it is worthwhile to devote future work to explore congruent implementations of new versions of the RST with molecular thermodynamic concepts. The Equation Oriented Optimization is versatile enough to allow the inclusion of different thermodynamic expressions of the activity coefficients to improve the predicted values of the mixed micelles compositions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.compchemeng.2015.12.026>.

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