



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

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## ARTICLE INFO

### Article history:

Received 21 August 2015

Received in revised form

28 December 2015

Accepted 30 December 2015

Available online 21 January 2016

### Keywords:

Mixed micelles

Margules formulations

Regular solution theory

Mathematical modeling

## 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 ( $\alpha_i$ ), the critical micelle concentration of the pure components ( $cmc_i^0$ ) and the binary interaction parameters of the binary mixtures ( $\beta_{ij}$ ) 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,  $\gamma_i^\infty$ ). 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  $\beta$  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

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