



PREDICTION OF CRITICAL MICELLE CONCENTRATION - A COMPARISON OF RECENT TECHNIQUES

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ABSTRACT

Surfactants find a wide variety of commercial application in enhancing the solubility of poorly soluble solutes, especially sensitive biological compounds. In solution surfactant molecules aggregate into micelles of characteristic size and shape depending on its molecular structure and size. The concentration at which micelles start to form is called critical micelle concentration (cmc). The cmc of a surfactant in a given solvent is of great importance in understanding and predicting micelle behaviour which plays an important role for choosing suitable chemicals for specific industrial applications techniques are available in the literature to predict cmc. The early models were based on semiempirical equations. Recently, thermodynamic model and molecular thermodynamic models are used by researchers to predict cmc. This paper critically evaluates the techniques available for estimating cmc.

Key words: Critical micelle concentration, Thermodynamic modeling, Phase separation.

INTRODUCTION

Surfactants are amphiphilic molecules that contain a non polar segment, commonly called “the tail,” and a polar segment called “the head.” This characteristic, being an amphiphilic molecule, leads to aggregation. When a surfactant is dissolved at low concentrations, the molecules exist as individual entities. However, as the concentration of the surfactant increases the molecules tend to associate to form aggregates. In aqueous solutions, the hydrophobic tails of the surfactant associate, leaving the head groups (hydrophilic) exposed to the solvent. The simplest of such aggregates, with an approximately spherical shape, are called micelles. The concentration at which this change takes place is called the critical micelle concentration (cmc). Once the micelles are formed, further increase of the surfactant concentration does not significantly change the concentration of the free monomer. The surfactant added is incorporated completely into the micelles. In other words, the concentration of the free surfactant molecules remains constant after the micelles are formed.

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In non polar solvents, the hydrophilic segment can be poorly solvated, so the heads will form the interior of the aggregates. The hydrophobic segments surround the polar core and are responsible for the solubility of the aggregates. The structures formed are the so-called reverse micelles. The aggregates can be formed at low surfactant concentrations, but the aggregation numbers for reverse micelles are usually relatively small. Therefore, because of the nature of the monomer–micelle equilibrium, the cmc is not so well defined. In fact the cmc is a transition region over a small composition range, so exact determination is difficult. The cmc of a surfactant in a given solvent is thus of great help in understanding and predicting phase behavior. Some approaches have been studied to predict cmc's in aqueous solutions, but not in organic solvents. The early models are based on semiempirical equations, which relate the cmc and the properties of the surfactants, using experimentally determined constants.

Surface-active materials (surfactants) are often used in both industrial applications, e.g., enhanced oil recovery, pharmaceutical industry and biotechnology, and in daily life, e.g., as components of washing powders, shampoos, and creams. Understanding the chemical and physical properties of surfactants is very important for choosing suitable such chemicals for specific industrial applications. It is essential to have tools that can describe the physical properties and phase behavior of surfactants in both hydrophilic and hydrophobic environments.

Experimentally, the cmc can be determined, from a plot of the conductivity versus the concentration of surfactant : below the cmc there are no micelles formed and the conductivity should vary approximately linearly with surfactant concentration in a manner analogous to strong electrolytes. Above the cmc, the plot should still be linear but the slope of the line will be smaller than for concentrations below the cmc. The cmc therefore occurs at the intersection of the two linear portions of the plot of conductivity versus concentration over the entire concentration range. The cmc can also be determined by other techniques, such as spectrofluorimetry, ultrasonic absorption, surface tension, capillary electrophoresis, solubilization, micellar catalysis, self diffusion.

Nagarajan equated the cmc to that particular value where the corresponding cluster size distribution exhibits a point of inflection. As the total surfactant molar fraction X_t increases the point of inflection becomes flat and eventually exhibits a minimum and a maximum as a function of the cluster size. Ben-Naim considered that the cmc is better identified as that value of X_t for which the absolute value of d^2X_1/dX_1^2 is a maximum sX_1 is the concentration of the free surfactant chains. Bhattacharya and Mahanti⁷ defined the cmc as the intercept of a horizontal line passing through a point where $d^2X_1/dX_1^2 = 0$ and the line $X_1 = X_t$.

Correlations of the CMC

Linear relationships between the logarithm of the cmc and the size of a homologous series of surfactants have been known for decades. The limitations of applicability of these relationships are that the coefficients must be recalculated for each homologous series. More general relationship would be of value in establishing specific quantitative aspects of Molecular structure that influence CMC, as well as allowing predication of cmc for molecules not yet synthesized.

A quantitative structure property relationship (QSPR) study of the cmc of nonionic surfactants introduced a multiple regression between log cmc and three descriptors based on molecular topology and constitution.¹

$$\log_{10} \text{cmc} = -1.80 - 0.567t - \text{KH0} + 1.054t - \text{ASIC2} + 7.51 \text{RNNO}$$

$$R^2 = 0.983, F = 1433, S^2 = 0.0313, N = 77$$

In this regression, t- KH0 is the zero Order Kier and Hall molecular connectivity index for the hydrophobic fragment (surfactant tail), which correlates highly with both molecular volume ($r = 0.979$) and surface area ($r = 0.971$). t-ASIC2 is the second order average information content index for the hydrophobic fragment, which captures some of the information on the complexity (branching and unsaturation) of the hydrophobic tail. RNNO is the relative number of nitrogen and oxygen atoms, representing the contribution of the hydrophilic head group.

For anionic surfactants

$$\log_{10} \text{cmc} = (1.89 \pm 0.11) - (0.314 \pm 0.010) t\text{-sum-KH0} - (0.034 \pm 0.003) \text{TDIP} - (1.45 \pm 0.18) h\text{-sum-RNC}$$

$$R^2 = 0.940, F = 597, s^2 = 0.0472, N = 119$$

The most significant descriptor is t-sum-KH0, the sum of Kier and Hall molecular connectivity indices of zeroth order over all hydrophobic fragments. The second descriptor, the dipole of the molecule (TDIP), is calculated by from the quantum chemical charge distribution in the molecule. It has less dependency on the cmc. The third descriptor, h-sum-RNC, is the sum of the relative numbers of carbon atoms over all hydrophilic fragments.

For anionic surfactants with simple sulfates and sulfonates

$$\log_{10} \text{cmc} = (2.42 \pm 0.07) - (.537 \pm 0.009) \text{KH1} - (0.019 \pm 0.002) \text{KS3} + (0.096 \pm 0.005) \text{HGP}$$

$$R^2 = 0.988, F = 1691, s^2 = 0.0068, N = 68$$

KH1 is the first Order Kier and Hall molecular connectivity index.

Single - chain mean -field theory

A single-chain mean -field theory² is used to predict the cmc of binary mixtures. The cmc of two symmetric nonionic amphiphiles is calculated as a function of temperature in order to analyze the validity of the ideal mixing assumption.

Cmc is located by plotting the volume fraction of free chain ϕ_1 against the total amphiphile concentration, ϕ_t .

$$\phi_t = \phi_1 + \phi_N$$

where ϕ_t is the volume fraction of the spherical micelle with $N > 1$; N is the No. of amphiphiles

constituted in the spherical micelle ; ϕ_t is total chain volume fraction and ϕ_1 is free chain volume fraction.

Excluded volume effects facilitate aggregation are responsible for in cmc. At low total chain volume fraction ϕ_1 ϕ_1 is same as ϕ_t indicating that the amphiphile molecules are in solution as free chains. On increasing ϕ_1 the free chain concentration starts to be less than ϕ_t and then saturates, at point of cmc where micelles start to appear. As temperature increases, cmc values start to increase. This is because the higher temperature requires a higher concentration of free amphiphile chains before the cmc is reached.

Thermodynamic models

Thermodynamic models have been employed to describe the phase behavior of surfactant solutions in an attempt to predict cmc.

Phase separation model

The phase separation model represents micellization as equilibrium between two pseudophases, the micelles and the monomers in solution. The cmc can be calculated through the standard free energy of micellization. This model qualitative understanding of the micellar solution but it cannot provide information on the size of the micelle.

Mass action model

Cmc values provide a measure of the chemical potential change during the micellization process. It suggests that micelles be considered as chemical aggregates of amphiphiles bound together as a result of multiple chemical equilibria. Chemical equilibrium constant K for the aggregation is given by -

$$\Delta\mu_0 = RT \ln(\text{cmc})$$



$$K = 1/\text{cmc}$$

$$K = e^{(-\Delta\mu_0/RT)}$$

Both models assume activity coefficients equal to unity for the monomers in solution taking advantage of low concentrations of monomeric amphiphiles in aqueous solution. For Surfactant system, the activities of the two conformations of amphiphiles should be the same at cmc and their activities should be in unison

$$a_s^{\text{cmc}} = a_m = 1$$

$$a_s^{\text{cmc}} = x_s^{\text{cmc}} \cdot \gamma_s^{\text{cmc}}$$

Activity coefficients of monomeric amphiphiles are functions of surfactant segment compositions and solvent composition. Therefore cmc is also functions of surfactant segment compositions and solvent composition.

Molecular model of mixed micellization

Simplified working model of a developed molecular –thermodynamic theory of mixed surfactant solutions is presented and can be utilized to predict cmc's of binary surfactant mixtures in which one of the surfactant is zwitterionic (Isaac Reif and Daniel Blankschtein, 2001). The complete theory is based on a thermodynamic framework which accounts for mixed micelle formation, the solution of mixing, and the interactions between the various species present in solution. It was designed to take advantage of some of the results of thermodynamic theory, while reducing the number of required inputs and simplifying the complexity of the calculations. It is much easier to use. It requires as inputs only the pure surfactant chemical structures and cmc's, solution conditions, temperature and the concentration of added salt. The following expression was derived to relate the cmc of a binary mixture, cmc_{mix} to the cmc's of the pure surfactants, cmc_A and cmc_B

$$1/cmc_{mix} = \alpha_1/f_A cmc_A + (1-\alpha_1)/f_B cmc_B.$$

Where, cmc_A , critical micelle concentrations of the single surfactant A. cmc_B is critical concentration of surfactant B.

$$Cmc_A = \exp[(g_{mic}^A - 1)/kT].$$

$$Cmc_B = \exp[(g_{mic}^B - 1)/kT].$$

Where g_{mic}^A and g_{mic}^B are the free energies of micellization of the single surfactants A and B respectively. α_1 is the solution monomer composition and f_A and f_B are the activity of surfactants A and B respectively.

$$f_A = \exp [\beta_{AB} (1-\alpha^*)^2/kT]$$

$$f_B = \exp [\beta_{AB} (\alpha^*)^2/kT].$$

β_{AB} is the binary interaction parameter, a constant, independent of the mixed micelle composition. α^* is the optical micelle composition at which the free energy of mixed micellization is reduced, k is the Boltzmann constant, and T is the absolute temperature. The theory is limited to binary mixtures in which both surfactants have linear hydrocarbon tails and heads of similar size. It should be applied when electrostatic interactions dominate the nonidealities associated with mixed micelle formation.

NRTL method

Segment-based local composition NRTL (nonrandom two-liquid) model is proposed to

determine activity coefficients and to determine cmc from the activity coefficients (Renon and Prausnitz, 1986). NRTL model is derived to account for the solution nonideality of aqueous nonionic surfactant solutions. The temperature-dependent interaction parameters of the NRTL model are obtained from the correlation of binary water-poly(ethylene glycol) system vapor-liquid equilibrium (VLE) data and water + hydrocarbon liquid-liquid equilibrium (LLE) data. The NRTL equation contains three parameters for a binary system and is written as

$$G^E/RT = G_{21}\tau_{21}/(x_1 + x_2 G_{21}) + G_{12}\tau_{12}/(x_2 + x_1 G_{12})$$

$$\ln\gamma_1 = x_2^2[\tau_{21}(G_{21}/x_1 + x_2 G_{21})^2 + G_{12}\tau_{12}/(x_2 + x_1 G_{12})^2]$$

$$\ln\gamma_2 = x_1^2[\tau_{12}(G_{21}/x_2 + x_1 G_{12})^2 + G_{12}\tau_{12}/(x_1 + x_2 G_{21})^2]$$

$$G_{12} = \exp(-\alpha\tau_{12})$$

$$G_{21} = \exp(-\alpha\tau_{21})$$

$$\tau_{12} = b_{12}/RT$$

$$\tau_{21} = b_{21}/RT$$

Where α , b_{21} and b_{12} parameters specific to a particular pair of species are independent of composition and temperature.

Advantage: cmc values of some aqueous polyoxyethylene alcohol solutions are successfully predicted by this method.

Unifac method

Universal functional activity coefficient model (UNIFAC) is a group contribution method for the estimation of activity coefficients. Comprehensive studies of UNIFAC have been presented by several researchers, but not for surfactant solutions. Several versions of UNIFAC with different group interaction parameters are readily available in the literature. Because of the extensive use of UNIFAC in the chemical industry and its large amount of group parameters, it appears very interesting to explore its applicability to surfactant systems. The UNIFAC model was first published in 1975 by Fredenslund, Jones and Prausnitz, a group of chemical engineering researchers from the University of California. Subsequently they and other authors have published a wide range of UNIFAC papers, extending the capabilities of the model; this has been by the development of new or revision of existing UNIFAC model parameters.

The UNIFAC method has proved to be a reliable method for predicting activity coefficients in liquid mixtures and thus many phenomena dependent on them. It is based on the UNIFAC adopts a group contribution approach to the description of liquid mixtures, with the behavior of the molecules predicted from parameters for the chemical groups they contain and the interactions between them. The process of surfactant aggregation can be seen as an extreme case of local composition changes. The groups in the core of the micelle interact so favorably

with each other that they are surrounded by their own kind. Thus, there are grounds for hoping that UNIFAC might correctly predict aggregation to micelles. The group parameters used in UNIFAC are derived principally from data for mixtures of small molecules that will not show strong aggregation. A UNIFAC group contribution method is used to predict activity coefficients for each species present in a liquid mixture of a given composition. The activity coefficients are relative to the pure liquid standard state.

The UNIFAC method considers the Gibbs energy of a solution as the sum of two terms: a combinatorial term that accounts for differences in the size and shape of the molecules and a residual term that accounts mainly for the effects that arise from energetic interactions between groups. The molecules are represented as combinations of chemical groups, and the interaction parameters for each type of group have been compiled by regression of phase equilibrium data

Chemical activity

The activity coefficient of the components in a system is a correction factor that accounts for deviations of real systems from that of an Ideal solution, which can either be measured via experiment or estimated from chemical models (such as UNIFAC). By adding a correction factor, known as the activity (a_i , the activity of the i^{th} component) to the liquid phase fraction of a liquid mixture, some of the effects of the real solution can be accounted for. The activity of a real chemical is a function of the thermodynamic state of the system, i.e. temperature and pressure. Equipped with the activity coefficients and knowledge of the constituents and their relative amounts, phenomena such as phase separation and vapour-liquid equilibria can be calculated. UNIFAC attempts to be a general model for the successful prediction of activity coefficients. The UNIFAC model splits up the activity coefficient for each species in the system into two components; a combinatorial γ^c and a residual component γ^r . For the i^{th} molecule, the activity coefficients are broken down as per the following equation:

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^r$$

In the UNIFAC model, there are three main parameters required to determine the activity for each molecule in the system. Firstly there are the group surface area R and volume contributions Q obtained from the Van der Waals surface area and volumes. These parameters depend purely upon the individual functional groups on the host molecules. Finally there is the binary interaction parameter τ_{ij} , which is related to the interaction energy U_i of molecular pairs (equation in "residual" section). These parameters must be obtained either through experiments, via data fitting or molecular simulation.

Combinatorial

The combinatorial component of the activity is contributed to by several terms in its equation (below), and is the same as for the UNIQUAC model.

$$\ln\gamma_i^c = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + L_i - \frac{\phi_i}{x_i}\sum_{j=1}^n x_j L_j$$

θ_i and ϕ_i are the molar weighted segment and area *fractional* components for the i^{th} molecule in the total system and are defined by the following equation; L_i is a compound parameter of r , z and q . z is the coordination number of the system, but the model is found to be relatively insensitive to its value and is frequently quoted as a constant having the value of 10.

$$\theta_i = \frac{x_i q_i}{\sum_{j=1} x_j q_j} ; \phi_i = \frac{x_i r_i}{\sum_{j=1} x_j r_j} ; L_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) ; z = 10$$

r_i and q_i are calculated from the group surface area and volume contributions R and Q (Usually obtained via tabulated values) as well as the number of occurrences of the functional group on each molecule ν_k such that:

Residual

The residual component of the activity γ^r is due to interactions between groups present in the system, with the original paper referring to the concept of a "solution-of-groups". The residual component of the activity for the i^{th} molecule containing n unique functional groups can be written as follows:

$$\ln \gamma_i^r = \sum_{\nu_k^{(i)}}^n [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

where $\Gamma_k^{(i)}$ is the activity of an isolated group in a solution consisting only of molecules of type i . The formulation of the residual activity ensures that the condition for the limiting case of a single molecule in a pure component solution, the activity is equal to 1; as by the definition of $\Gamma_k^{(i)}$, one finds that $\ln \Gamma_k - \ln \Gamma_k^{(i)}$ will be zero. The following formula is used for both Γ_k and $\Gamma_k^{(i)}$

$$\ln \Gamma_k = Q_k \left[1 - \ln \sum_m \Theta_m \Psi_{mk} - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right]$$

In this formula Θ_m is the summation of the area fraction of group m , over all the different groups and is somewhat similar in form, but not the same as θ_i . Ψ_{mn} is the group interaction parameter and is a measure of the interaction energy between groups. This is calculated using an Arrhenius equation (albeit with a pseudo-constant of value 1). X_n is the group mole fraction, which is the number of groups n in the solution divided by the total number of groups.

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

$$\Psi_{mn} = \exp - \left[\frac{U_{mn} - U_{nm}}{RT} \right] ; X_n = \frac{\sum_j \nu_m^j x_j}{\sum_j \sum_n \nu_n^j x_j}$$

U_{mn} is the energy of interaction between groups m and n , with SI units of joules per mole and R is the ideal gas constant. Note that it is not the case that $U_{mn} = U_{nm}$, giving rise to a non-reflexive parameter. The equation for the group interaction parameter can be simplified to the following:

$$\Psi_{mn} = \exp \frac{-a_{mn}}{T}$$

Thus a_{mn} still represents the net energy of interaction between groups m and n ,

For the prediction of the cmc the phase separation approach was used, where the micellar phase is approximated as a second liquid phase resulting from the liquid–liquid equilibrium between the solvent and the surfactant, with the necessary activity coefficients predicted by UNIFAC.

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Using these equations, the cmc values of different aqueous nonionic surfactant solutions have been predicted with the five different versions of UNIFAC.

The original UNIFAC VLE, modified UNIFAC VLE, UNIFAC LLE, the linear temperature dependent UNIFAC VLE, and water-UNIFAC methods predict qualitatively correct the observed trend of the hydrophobic chain for aqueous nonionic surfactant solutions but fail to predict the trend of the hydrophilic chain. By introduction of a new group, the oxyethylene group ($\text{CH}_2\text{CH}_2\text{O}$), and estimation of its interaction parameters from vapor-liquid equilibrium data, the original UNIFAC VLE method can provide good prediction for micelle formation for water + polyoxyethylene alcohol systems for both the hydrophobic and hydrophilic trends. Because of the large amount of UNIFAC interaction parameters that are readily available in the literature, the UNIFAC model should be in principle applicable to other nonionic surfactant solutions. New functional group parameters are introduced and estimated from available phase equilibrium data. The most promising model was the modified UNIFAC of B. L. Larsen, P. Rasmussen, and A. Fredenslund. Since most nonionic surfactants contain oxyethylene chains, a new set of parameters was evaluated for this group, leading to satisfactory predictions.

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