B.Tech. Project Report (Final Stage)

Prediction of CMC and Surface Tension in Mixed Surfactant Solutions

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April 19, 2002 Mahesh Kumar Inakhiya

Abstract

Surfactant mixtures are commonly used in many practical surfactant applications. Surfactant Mixtures are often advantageous because they show the synergism in the system. Our B. Tech project deals with the prediction of the CMC and Surface tension in mixed surfactant system. We have reviewed total 4 model for the CMC and Surface tension prediction. We have predicted the values of CMC and Surface tension by 2 models. Predicted values are in good agreement with tha values reported in the literature.

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Acceptance Certificate

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This B.Tech Project Final stage report titled " Prediction Of CMC and Surface Tension in the Mixed Surfactant Solutions." by Mahesh Kumar Inakhiya (Roll Number: 98002033) may be accepted.

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Chapter 1

Introduction

Surfactant mixtures are commonly used in many practical surfactant applications. Mixtures are avantageous because purificaton of a singel component may be too costly or difficult and surfactant mixtures often perform better than a single surfactant. The synergistic behaviour of a surfactant mixtures may also be expolited to reduce the total amount of surfactant used in a particular application, thus reducing both cost and environmental impact. In addition, as environmental impact regulations on producing and releasing new materials become more restrictive, it may be preferable from a regulatory perspective to combine exsiting surfactants rather than to introduce new ones.

For that surfactant mixtures solution properties should be known, and for some mixtures experimental datas are not availabel.

our project dealt with the various models avaialable in the literature for the prediction of Crital micelles concentration and surface tension in mixed micelles system.

1.1 Basic definitions

Micelle: Micelle is the colloidal aggregate of amphipathic (surfactant) molecules, which occurs at a well-defined concentration known as the critical micelle concentration. The typical number of aggregated molecules in a micelle (aggregation number) is 50 to 100.

Surfactant: surfactant is a soluble compound that reduces the surface tension of liquids, or reduces interfacial tension between two liquids or a liquid and a solid. It is also known as a surface active agent. The term is derived from SURFace ACTive AgeNT. It is a compound that contains a Hydrophilic and a Hydrophobic segment.

HLB: HLB is an arbitrary scale from 0 to 40 depicting the Hydrophilic/Lipophilic Balance of a surfactant. Products with low HLB are more oil soluble. High HLB represents good water solubility. HLB is a numerically calculated number based on the surfactants molecular structure. It is not a measured parameter.

Moles of Ethylene Oxide: The Ethylene Oxide (EO) chain is the hydrophilic portion of the Surfactant molecule. The larger this portion of the molecule, the more water soluble is the non-ionic surfactant. Ethylene oxide is the reactive chemical added to base alcohols and amines to form ethoxylated non-ionic surfactants. Base Alcohol (Hydrophobic) Ethylene Oxide chain (Hydrophilic)

This surfactant contains n moles of Ethylene Oxide. Where surfactants are used to emulsify oils the Hydrophobic part of the surfactant embeds itself in the oil droplet and the Hydrophilic Ethylene oxide chain interacts with water to surround the oil droplet and form an emulsion. Surfactant are classified as follows

Nonionic Anionic

Mixed micelles: When there is more than one surfactant in the aqueous solution than the mixed micelles are formed.

Chapter 2

Prediction Of CMC

2.1 Pseudophase seperaton model-Thermodynamic Framework

2.1.1 Gibbs free energy and chemical potentials

The thermodynamic formulation used to describe the free energy of a mixed surfactant solution constitute a generalization of the one developed to describe the single surfactant solutions.[9] This formulation is for the aqueous solution of two surfactants. Considering a solution of N_W water molecules, N_A surfactant A molecules, and N_B surfactant B molecules in the thermodynamic equilibrium at temperature T and pressure P. If the concentration of the surfactant mixture exceeds its CMC, the surfactant molecules will assemble to form a distribution of mixed micelles $N_{n\alpha}$ having aggregation number n and composition α. In such a mixed micelle there are nα surfactant A molecules and $n(1-\alpha)$ surfactant B molecules. and

$$N_A = \sum_{n,\alpha} n\alpha N_{n\alpha} \tag{2.1}$$

$$N_B = \sum_{n,\alpha} n(1-\alpha) N_{n\alpha} \tag{2.2}$$

Mixed micelles of different size and composition are treated as distinct species in chemical equilibrium with each other as well as with the free monomeres in the solution.

The gibbs free energy of the mixed surfactant solution G is modeled as the sum of three contributions: the free energy of formation G_f, the free energy of mixing G_m, and the free energy of interaction G_i.

The free energy of formation is expressed as

$$G_f = N_w \mu^o{}_w + N_A \mu^o{}_A + N_B \mu^o{}_B + \sum_{n.\alpha} n N_{n\alpha} g_{mic}(sh, n, \alpha) \tag{2.3}$$

where $\mu^o{}_w(T,P)$, $\mu^o{}_A(T,P)$, and$\mu^o{}_B(T,P)$ are the standard state chemical potentials of water, surfactant A monomers and Surfactant B monomers respectively, at the solution temperature T and pressure P; $g_{mic}(sh, n, \alpha)$ is the free energy of mixed micellization, ehich represents the free emergy change per monomer associated with transferring $n\alpha$ surfactant A monomers and $n(1-\alpha)$ surfactant B monomers from water into a mixed micelles of size sh, aggeration number n, and composition α.

The free energy of mixing the formed mixed micelles, free monomers, and water is modeled by an expression of the form

$$G_m = kT[N_w ln X_w + \sum_{n,\alpha} N_{n\alpha} ln X_{n\alpha}] \tag{2.4}$$

where $X_w = N_w/(N_w + N_B + N_A)$, $X_{n\alpha} = N_{n\alpha}/(N_w + N_A + N_B)$ k is the Boltazmann constant, and T is the absolute temperature. $-G_m/T$ is an entropic contribution which reflects the number of ways in which the distribution of mixed micelles, the free monomers, and water molecules can be positioned in the solution as a function of the solution concentration and composition.

The free energy of interaction reflects interaction between mixed micelles, water molecules , and free monomers in the solution. Free energy of interaction is in the following form

$$G_i = -1/2 C_{eff}(\alpha_{soln})(N_A + N_B)\phi \tag{2.5}$$

where $\phi = \phi_A + \phi_B$ is the sum of the volume fractions, ϕ_A and ϕ_B of surfactants A and B, respectively $\alpha_{soln} = N_A/(N_A + N_B)$ is the composition of the surfactant mixture, and $C_{eff}(\alpha_{soln})$ is an effective mean-field interaction parameter for the mixture which is related to the single surfactant interaction parameter C_AB through the following expression

$$C_{eff}(\alpha_{soln}) = C_{AW}\alpha_{soln} + C_{BW}(1-\alpha_{soln}) - C_{AB}\alpha_{soln}(1-\alpha_{soln})(\sqrt{\gamma_A\gamma_B}/\gamma_{eff}) \tag{2.6}$$

in equation 1.6, $\gamma_A = \Omega_A/\Omega_w$ and $\gamma_B = \Omega_B/\Omega_w$, where Ω_w, Ω_A, and Ω_B are the efffective moleculer volumes of water, surfactant A, and surfactant B, respectively, and $\gamma_{eff} = \alpha_{soln}\gamma_A + (1-\alpha_{soln})\gamma_B$. The CMC of mixed micelles can be predicted by the above free energy model through the chemical potential of water, μ_w, and the chemical potential of a mixed micelle, of aggregation number n and composition α, $\mu_{n\alpha}$, which are obtained by differentiating the gibbs free energy, eqs 1.3-1.5, with respect to N$_w and$N$_{n\alpha}$, respectively.[9] The resulting expression are given by

$$\mu_w = \left(\frac{\partial G}{\partial N_w}\right)_{T,P,N_{n\alpha}} = \mu^o{}_w + kT[ln(1-X) + X - \sum_{n,\alpha} X_{n\alpha}] + C_{eff}(\alpha_{soln})(\frac{\phi^2}{2\gamma_{eff}}) \tag{2.7}$$

$$\mu_{n\alpha} = \left(\frac{\partial G}{\partial N_{n\alpha}}\right)_{T,P,N_w,N_{n\alpha}} = n\alpha\mu^o{}_A + n(1-\alpha)\mu^o{}_B + (ng_{mic} + kT) + kT(lnX_{n\alpha}+$$

$$\text{n(X-1-}\textstyle\sum_{n\alpha} X_{n\alpha})) + n\alpha\mu^i{}_A + n(1-\alpha)\mu^i{}_B \tag{2.8}$$

where $X = X_A + X_B$, with $X_A = N_A/(N_w + N_A + N_B)$ and $X_B = N_B/(N_w + N_A + N_B)$, is the total mole fraction of surfactant in the solution, and the interaction contributions to the monomer chemical potentials are given by

$$\mu^i{}_A = \frac{\phi}{2}[C_{Aw} + \frac{\gamma_A}{\gamma_{eff}}[\alpha_{soln}C_{Aw} + (1-\alpha_{soln})C_{Bw}](1-\phi) - (1-\alpha_{soln})\frac{\sqrt{\gamma_A\gamma_B}}{\gamma_{eff}}C_{AB}(1-\phi_A)] \tag{2.9}$$

$$\mu^i{}_B = \frac{\phi}{2}[C_{Bw} + \frac{\gamma_B}{\gamma_{eff}}[\alpha_{soln}C_{Aw} + (1-\alpha_{soln})C_{Bw}](1-\phi) - \alpha_{soln}\frac{\sqrt{\gamma_A\gamma_B}}{\gamma_{eff}}C_{AB}(1-\phi_B)] \tag{2.10}$$

The chemical potentials of the surfactant A and surfactant B monomers is obtained from eq 1.8 by sunstituting $n = 1$ and $\alpha = 1$ (for A) or 0 (fro B), respectively, that is

$$\mu_A = (\mu^o{}_A + kT) + kT[lnX_{1A} + X - 1 - \sum_{n\alpha} X_{n\alpha}] + \mu^i{}_A \tag{2.11}$$

$$\mu_A = (\mu^o{}_B + kT) + kT[lnX_{1B} + X - 1 - \sum_{n\alpha} X_{n\alpha}] + \mu^i{}_B \tag{2.12}$$

where X_1A and X_1B are the mole fractions of free surfactant A and surfactant B monomers, respectively. Using eqs. 1.7-1.12 for the chemical potentials, one predicts the CMC of the mixed micellar solution in the following way.

2.2 Composition Distrubution of mixed micelles

When the mixed micellar solution is in the thrmodynamic equilibrium, the chemical potential $\mu_{n\alpha}$ of a mixed micelle of a aggregration number n and composition α is related to the chemical potentials of the free monomers through the constraints imposed by the conditions of multiple chemical equilibrium , that is
$\mu_{n\alpha} = n\alpha\mu_A + n(1-\alpha)\mu_B(2.12)$equation 2.13 implies that the chemical potential of a mixed micelle having aggregation number n and compositoin α is equal to the sum of the chemical potentials of its constituent $n\alpha$ surfactant A and $n(1-\alpha)$ surfactant B molecules. Substituting eqs 2.8, 2.11 and 2.12 in eq 2.13, one obtains the following expression for the equllibrium micellar size and composition distribution

$$X_{n\alpha} = \frac{1}{e} X_{1A}{}^{n\alpha}{}_{1A} X_{1B}{}^{n(1-\alpha)}{}_{1B} e^{-n[\beta g_{mic}(\alpha)-1]} = \frac{1}{e} X_1{}^n e^{-n\beta g_m(\alpha,\alpha_1)} (2.13)$$

where $\beta = \frac{1}{kT}$, $\beta g_m = [\beta g_{mic} - 1 - \alpha ln\alpha_1 - (1-\alpha)ln(1-\alpha_1)]$ is a modified dimensionless free energy of the mixed micellization per monomer, $X_1 = X_{1A} + X_{1B}$ is the total mole fraction of free monomers in solution.
The composition $\alpha^*(n)$, at which $X_{n\alpha}$ exhibits a maximum for a given micellar aggregation number n, is referred as the optimum composition. $\alpha^*(n)$ is function of the aggregation number n and one can obtaine it by setting the derivative of $X_{n\alpha}$ with respect to α equal to zero. By implementing this procedure one can obtain the following implicit equation

$$\beta \frac{\partial g_{mic}(n,\alpha)}{\partial \alpha}|_{\alpha^*} = ln \frac{\alpha_1}{(1-\alpha_1)} \tag{2.14}$$

using eq 2.14 one can obtain the composition for all aggregation numbers from the knowledge of α_1 and $g_{mic}(n, \alpha)$.

Equation 2.13 for the micellar size and composition distribution is applicable to mixed micelles of all shapes, sizes,and compositions. However, as shown in equation 2.13 one needs to know

(i)the free energy of micellization $g_{mic}(n, \alpha)$ as a function of n and α or, equivalently, g_m as a function of n, α, and α_1,

(ii)the equlibrium solution monomer mole fraction X_1, and

(iii)the equilibrium solution monomer composition α_1.

condition (ii) and (iii) are equivalent to knowing the $X_{1A} = \alpha_1 X_1$ and $X_{1B} = (1 - \alpha_1)X_1$.

X_1 and α_1 (or equivalently X_{1A} and X_{1B}) is calculated by using the eq. 2.13 in two constraint imposed by the conservation of the total number of surfactant A and surfactant B molecules in solution, that is, $N_A = \sum_{n\alpha} n\alpha N_{n\alpha}$ and $N_B = \sum_{n\alpha} n(1 - \alpha)N_{n\alpha}, orequivalently$

$$X_A = \alpha_{soln}X = \alpha_1 X_1 + \sum_{n,\alpha} n\alpha X_{n\alpha} \tag{2.15}$$

$$X_B = (1 - \alpha_{soln})X = (1 - \alpha_1)X_1 + \sum_{n,\alpha} n(1 - \alpha)X_{n\alpha} \tag{2.16}$$

given g_{mic} (or equivalently g_m), and on inserting eq. 2.13 into eqs 2.15 and 2.16, one obtains two implicit equations for X_1 and α_1 as a function of X and α_{soln}. Solving these two equations simultaneously one can obtain $X_1(X, \alpha_{soln}, T, P)$ and $\alpha_1(X, \alpha_{soln}, T, P)$ which is inserted back into the eq 2.13 to calculate the entire micellar size and composition distribution $X_{n\alpha}$ as a function of X,α_{soln},T,P, and other solution conditions.

g_{mic} is calculated by following molecular model

2.2.1 Molecular model for g_{mic} calculation

The free energy of mixed micellization $g_{mic}(sh, n, \alpha, l_c)$ represents the free energy change (per monomer) associted with creating a micelle, having shape sh, aggregation number n, composition α, and core minor radius l_c, from $n\alpha$ A-type and $n(1-\alpha)$ B-type surfactant monomers.

The magnitude of g_{mic} reflects many complex physicochemical factors such as the hydrophobic effect, interfacial effects, conformational free energy changes associted with restricting the hydrophobic chains inside the micellar core, steric and electrostatic interactions between the hydrophilic moieties at the micellar core-water interface, and entropy effects associated with mixing the two surfactant species in a mixed micelle.[10]

For the evaluation of free energy contribution associated with the various physicochemical factors mentioned above, one can visualize the reversible formation of mixed micelle having shape sh, aggregation number n, composition $alpha$, and core minor radius l_c (fianl state) from $n\alpha$ surfactant A monomers and $n(1-\alpha)$ surfactant B monomers (initial state) in water, as shown in Figure 2.1. The various steps of the mixed micelles formation process is as follows:

In the first step the heads, if charged are discharged along with the conterions. Subsequently, in the second step, the bond between the head and the tail of each surfactant molecule is broken, in the thord step, the hydrocarbon tails of surfactant A and B are transferred from water to a mixtures of hydrocarbons A and B whose composition is equal to the micellar composition α. In the fourth step, an hydrocarbon droplet having shape sh and core minor radius l_c is created from the hydrocarbon mixture having composition α. That is, in this step, an interface seperating the hydrocarbon mixture from water is create. Within this hydrocarbon droplet the tails are unrestrcted and can move freely. However in a micelle, each tail is bonded to a head and therfore one of the tail ends is restricted to lie in the vicinity of the micellar core-water interface. Accordingly, in the fifth step, this restriction is imposed on the tails. So, at the end of the fifth step, the creation of micellar core has been completed. The creation of micellar corona of heads follows next. Accordingly, in the sixth step, the discharged heads are reattached to the tails at the micellar core-water interface. This involvs three operation:

Figure 2.1: Schematic representation of thought process to visualize the various physicochemical factors involved in the formation of a mixed micelle. Surfactant A is represented by a blach head and a full tail and surfactant B by a blank head and dashed tail.

recreating the bond between the head and tail, screening part of the micellar core-water interface from contact with water, and introducing steric repulsion between the heads. Finally, in the seventh step, the heads if charged, are recharged along with the associated counterions. This completes the creation of the micellar sorona and hence of the entire mixed micelle.[10]

Various contributions to the g_{mic} is related to the various physicochemical factors associates with the micellization.

These include:

(i) The hydrophobic free energy $g_{w/hc}$ associated with transferring the hydrocarbon tails from water to an hydrocarbon mixture in the third step,

(ii) The interfacial free energy g_{σ} associated with creating the micellar core-water interface in the fourth step, as well as with shielding part of that interface in the sixth step,

(iii) The configurational (packing) free energy $g_{hc/mic}$ arising from the loss in configurational degrees of freedom in the fifth step,

(iv) The steric free energy g_{st} associated with repulsive steric interactions between the heads in the sixth step, and

(v) the electrostatic free energy g_{elec} associatd with the first and the seventh steps.

The total free energy of mixed micellization $g_{mic}(sh, n, \alpha, l_c)$ is then computed by summing these five free energy contributions, that is

$$g_{mic}(sh.n, \alpha, l_c) = g_{w/hc} + g_{\sigma} + g_{hc/mic} + g_{st} + g_{elec} \tag{2.17}$$

using Eq 2.17 one can calculate the free energy of micellization for the three regular micellar shapes of spheres, infinite-sized cylinders, and infinite-sized disks or bilayers.

Five energy contributions in the above equation is calculated in the following way:

A. Hydrophobic Free Energy

$g_{w/hc}$ represents the free energy change associated with transferring the hydrocarbon tails of surfactants A and B from water to a mixture of hydrocarbons A and B whose composition is equal to micellar composition α.[10]

For calculations

$$g_{w/hc}(\alpha) = \alpha {g^{A}}_{w/hc} + (1-\alpha){g^{B}}_{w/hc} + kT[\alpha ln\alpha + (1-\alpha)ln(1-\alpha)] \tag{2.18}$$

where

$${g^{A}}_{w/hc} = [(4.09 - 1.05n_{cA})(298/T) - (4.62 + 0.44n_{cA})]kT \tag{2.19}$$

and

$$g^{B}{}_{w/hc} = [(4.09 - 1.05n_{cB})(298/T) - (4.62 + 0.44n_{cB})]kT \tag{2.20}$$

B. Interfacial Free Energy

The interfacial free energy g_σ reflects the contribution to g_{mic} associated with the creating a micellar core-water interface.[10]

For calculations

$$g_\sigma = \alpha\sigma_A(a - a_{0A}) + (1-\alpha)\sigma_B(a - a_{0B}) \tag{2.21}$$

where σ_A and σ_B are the curvature-dependent interfacial tensions between hydrocarbons A and B, respectively, a_{0A} and a_{0B} are the corresponding interfacial areas per surfactant molecule screened by the heads (approximately equal to 21 A^{o2} each for single tail surfactants), and $a = Sv/l_c$ is the available interfacial area per surfactant molecule, where S is shape factor (3 for spheres, 2 for cylinders, and 1 for disks or bilayers), $v = \alpha v_A + (1-\alpha)v_B$ is an average tail volume, where

$$v_A = 27.4 + 26.9(n_{cA} - 1) \tag{2.22}$$

and

$$v_B = 27.4 + 26.9(n_{cB} - 1) \tag{2.23}$$

σ_A and σ_B are calculated from the following eqs.

$$\sigma_A = \sigma_{0A}[1 - (S-1)\delta_A/l_c] \tag{2.24}$$

and

$$\sigma_B = \sigma_{0B}[1 - (S-1)\delta_B/l_c] \tag{2.25}$$

where σ_{0A} and σ_{0B} are the interfacial tensions at a planar interface between water and hydrocarbons A and B. δ_A and δ_B are the Tolman distance corresponding to hydrocarbons A and B. It is calculatd as follows. for C_{11}, $\delta = 2.25A^o$ and for C_n, $\delta(n) = \delta(11)l_{max}(n)/l_{max}(11)$, where $l_{max}(n) = 1.54 + 1.265n$, n is number of carbon atoms.

C.Packing Free Energy

In a mixed micelle, the nonpolar hudrocarbons tails bonded to the heads , and therfore the tail ends which are attached to the heads are restricted to lie in the vicinity of the micellar core-water interface. This results in a loss of conformational degree of freedom, and the associated free energy change $g_{hc/mic}$ is evaluated using a single chain mean field model.[10]

For calculation purpose,

$$-\frac{g_{hc/mic}}{kT} = (Z_A/Z^{free}{}_A) + (1-\alpha)ln(Z_B/Z^{free}{}_B) + \rho_{hc}\sum_{i=1}^{L} F_i V_i \tag{2.26}$$

where Z is the partition function associated with the single chain of type A or B, F_i is the mean field, ρ_{hc} is density of CH_2 groups in the micellar core.

D.Steric Free Energy

The steric free energy contributoin is calculated by treating the heads present at interface as a localized monolayer, which reflects the fact that each head is physically attached to a tail at the interface.[10]

For calculations

$$g_{st} = -kTln\left[1 - \frac{\alpha a_{hA} + (1-\alpha)a_{hB}}{a}\right] \tag{2.27}$$

where a_{hA} and a_{hB} are the average cross sectional area of head A and B, respectively.

E. Electrostatic Free Energy

Electrostatic free energy contribution is often very small. So it is generally not included in the g_{mic} calculations.

2.2.2 CMC prediction

At very low surfactant concentration most of the surfactant molecules exist as free monomers. However, as the total concentration of surfactant is increased, keeping its composition constant, micelles begin to form beyond a certain threshold concentration known as Critical micellar concentration (CMC). Beyond the CMC most of the added surfactant remains in the micellar form, and the total monomer concentration remains practically constant. The first micelle that form has a composition close to the optimum value α^*, because at $\alpha = \alpha^*$ the free energy of micellization exhibits a maximum. The mole fraction of these micelles can therfore be expressed, using $\alpha = \alpha^*$ in eq. 12.3 as

$$X_{n\alpha^*} = \frac{1}{e}\left(\frac{X_1}{e^{\beta g_m(\alpha^*,\alpha_1)}}\right)^n \tag{2.28}$$

Using the expression for the g_m one finds that

$$ln(cmc) \approx \beta g_m(sh, \alpha^*, \alpha_1) = \beta g^B{}_{mic} + \beta g^{AB}{}_{mic}\alpha^{*2} + ln\left(\frac{1-\alpha^*}{1-\alpha_1}\right) - 1 \tag{2.29}$$

where sh corresponds to the shape of the optimum micelle, and α^* is obtained from the following equation

$$\beta(g^A{}_{mic} - g^B{}_{mic}) + \beta g^{AB}{}_{mic}(1-2\alpha^*) + ln\frac{\alpha^*}{1-\alpha^*} = ln\frac{\alpha_1}{1-\alpha_1} \tag{2.30}$$

By combining the Eqs. 2.18 and 2.19 one obtains the

$$\frac{1}{cmc} = \frac{\alpha_1}{f_A cmc_A} + \frac{1-\alpha_1}{f_B cmc_B} \tag{2.31}$$

where

$lnf_A = \beta g^{AB}{}_{mic}(1-\alpha^*)^2$,

$lnf_B = \beta g^{AB}{}_{mic}(\alpha^*)^2$,

$ln(cmc_A) = \beta g^A{}_{mic} - 1$,

and $ln(cmc_B) = \beta g^B{}_{mic} - 1$.

so one can predict the mixtures CMC from a knowledge of $g^A{}_{mic}$, $g^B{}_{mic}$, and $g^{AB}{}_{mic}$.

2.3 Regular solution approximation model

2.3.1 Ideal Treatment

When two surfactant with the same head group but with deiiferent chain lengths are mixed, then there is no net interaction between the surfactant species. There is interacton between the head groups of the surfactants in the mixed micelles,byt since the head groups are of the same kind this interaction is not different for the different surfactant species so becaues of this the net interaction is zero.[5]

CMC of a surfactant is an average of the CMC's of the single surfactants,

$$CMC = x_1 CMC_1 + (1 - x_1) CMC_2 \tag{2.32}$$

where CMC is the critical micelle concentration of the surfactant mixture and the CMC_i are the critical micelle concentration of the single surfactant species and x_1 is the fraction of the surfactant 1 in the whole system, *i.e.* where

$$x_1 = \frac{C_1}{C_1 + C_2} \tag{2.33}$$

C_1 and C_2 are the molar surfactant concentrations of respective species.

If ${x_1}^m$ represents the mole fraction of surfactant 1 in micelle itself and not in the whoole system, then the CMC of a surfactant mixture is

$$CMC = {x_1}^m CMC_1 + (1 - {x_1}^m) CMC_2 \tag{2.34}$$

where ${x_1}^m$ is the mole fraction of surfactant 1 in micelles. the molar composition ${x_1}^m$ of mixed micelle is given by

$${x_1}^m = \frac{x_1 CMC_2}{x_1 CMC_2 + (1 - x_1) CMC_2} \tag{2.35}$$

2.3.2 Genaral Treatment

In many systems surfactants of different kinds are mixed, such as anionic and nonionics. Here the nonionic surfactants shield the repulsion between the head groups of the anionic surfactants in the micelle and hence there is a net interaction between the two type of surfactant. Another example is of mixtures of anionic and cationic surfactants, where exists a very srtrong interacton between the surfactants. For these type of mixtures the CMC is given by following equation

$$CMC = {x_1}^m f_1 CMC_1 + (1 - {x_1}^m) f_2 CMC_2 \tag{2.36}$$

where f_1 and f_2 are the activity coefficients of the surfactants in the micelle. For calculation of these activity coefficients following equation are used

$$lnf_1 = (1 - {x_1}^m)^2\beta \tag{2.37}$$

$$lnf_2 = ({x_1}^m)^2\beta \tag{2.38}$$

where β is an interaction parameter, quantifying the net interaction between the surfactant species in the micelle. Positive β valur imply that there is a net repulsion between two surfactant components while negative β value imply a net attraction. If β is zero the activity coefficient will be unity and equation 2.25 will revert to equation 2.23. Negative β values are most commonly found, significant for a net attraction between the surfactant species. Positive β values also exixts *e.g.* mixtures of noramal hydrocarbon-based surfactants with fluorinated ones.

in terms of solution compositions

$$\frac{1}{CMC} = \frac{x_1}{f_1 CMC_1} + \frac{1 - x_1}{f_2 CMC_2} \tag{2.39}$$

and

$${x_1}^m = \frac{x_1 f_1 CMC_2}{x_1 f_2 CMC_2 + (1 - x_1) f_1 CMC_1} \tag{2.40}$$

For variuos surfactant mixtures β values are given in Table 2.1.[7]

β values

Chapter 3

Prediction of Surface tension

The ability of surfactants to adsorb at liquid interfaces is an important property as surfactant compositions are widely used for many technological processes, such as detergents, foam and emulsion stabilizers, etc. These compositions are usually mixtures of homologues or surfactants of different nature, e.g. non-ionic surfactants with ionics, ionic surfactants with zwitterionic ones, or anionic and cationic surfactants All models proposed so far for the prediction of mixture properties dealt with the predictions of surface or interfacial tensions of mixed solutions from known characteristics of the individual compounds. Therefore, in all equations of state proposed for mixed surface layers, the isotherm parameters of pure compounds were involved

This model predicts the surface tension of a surfactant mixture from the surface tension values or isotherm parameters of individual solution by the use of one simple equation.This equation can be applied not only to ideal mixtures of homologues, but also to surfactants which exhibit a non-ideal surface behaviour.

3.1 Rigorous Model

Equations of state for surface layers, adsorption isotherms and surface tension isotherms can be derived by equating the expressions for the chemical potentials at the surface ${\mu_i}^s$,

$$\mu_i{}^s = \mu_i{}^{os} + RTlnf_1{}^s x_i{}^s - \gamma\omega_i \tag{3.1}$$

to those in the solution bulk

$$\mu i^\alpha = \mu_i{}^o\alpha + RTlnf_i{}^\alpha x_i{}^\alpha \tag{3.2}$$

where R is the gas law constant, T is the temperature, γ is surface tension, $\$\mathrm{itf}_i$ are the activity coefficients, x_i are the molar fractions, ω_i are the partial molar surface areas. The superscript'α' refers to the bulk solution, and 's' to the surface; the standard chemical potentials $\mu_i{}^o\alpha$ and $\mu_i{}^{os}$ depend on pressure and temperature. This method yields the equation of state and adsorption isotherm for mixture of two non-ionic surfactants (i=1,2) in non-ideal surface layers:[1]

$$\pi = -\frac{RT}{\omega_o}[ln(1-\theta_1-\theta_2)+\theta_1\left(1-\frac{1}{n_1}\right)+\theta_2\left(1-\frac{1}{n_2}\right)+a_1\theta_1{}^2+a_2\theta_2{}^2+2a_{12}\theta_1\theta_2] \tag{3.3}$$

$$b_1c_1 = \frac{\theta_1}{(1-\theta_1-\theta_2)^{n_1}}exp(-2a_1\theta_1-2a_{12}\theta_2)exp[(1-n_1)(a_1\theta_1{}^2+a_2\theta_2{}^2+2a_{12}\theta_1\theta_2)] \tag{3.4}$$

$$b_2c_2 = \frac{\theta_2}{(1-\theta_1-\theta_2)^{n_2}}exp(-2a_2\theta_1-2a_{12}\theta_1)exp[(1-n_2)(a_1\theta_1{}^2+a_2\theta_2{}^2+2a_{12}\theta_1\theta_2)] \tag{3.5}$$

Here $\theta_i = \Gamma_i\omega_i$ is the monolayer coverage, Γ_i is the adsorption, $\pi = \gamma_0 - \gamma$ is the surface pressure,γ_0 is the surface tension of solvent, $ni = \omega_i/\omega_0, \omega_i$ and ω_0 are the partial molar surface areas of the surfactant and solvent, respectively, a_1, a_2 and a_{12} are the constants of intermolecular interactions, b_i is the adsorption constant, c_i is the surfactant concentration in the solution bulk. Choosing the dividing surface after LucassenReynders (i.e. assuming $\omega_0 = \omega$ and $\Gamma_0 + \Gamma_1 + \Gamma_2 = 1/\omega$, where ω is the mean molar area of both surfactants, 1 and 2), one can eliminate the contributions which result from the entropic non-ideality of the solvent, thus reducing Eq. (3) to a much simpler form[1]

$$\pi = -\frac{RT}{\omega}[ln(1-\theta_1-\theta_2)+\alpha_1{\theta_1}^2+a_2{\theta_2}^2+2a_{12}\theta_1\theta_2] \tag{3.6}$$

where

$$\omega = \frac{\omega_1\Gamma_1+\omega_2\Gamma_1}{\Gamma_1+\Gamma_2} \tag{3.7}$$

while the choice of the dividing surface after LucassenReynders does not affect the form of the adsorption isotherms, the values of n_1 should now be calculated as $n_i = \omega_i/\omega$. To apply (3.4), (3.5), (3.6) and (3.7), one should possess information about the adsorption characteristics of the individual surfactants (b_i, a_i, ω_i). If no specific interaction exists between the molecules of different species, then one can approximately assume $a_{12} = (a_1 + a_2)/2$.

The values of b_i, ω_i, a_i for the individual surfactant is calculated via best fit between experimental surface tension isotherm for individual solution, and the Frumkin model:[2,3]

$$\pi = -\frac{RT}{\omega_1}[ln(1-\theta_i)+a_i{\theta_i}^2] \tag{3.8}$$

$$b_ic_i = \frac{\theta_i}{(1-\theta_i}exp(-2a_i\theta_i) \tag{3.9}$$

eqs 3.8 and 3.9 comes from the eqs 3.3 and 3.4 for $\theta_2 = 0$, provided that $\omega_o = \omega_i$.

For some systems the value of a_{12} bears an element of uncertainty as $a_{12} \neq (a_1 + a_2)/2$ ($e.g.$ mixture of $C_{10}EO_5$ with SDS in 0.01 M NaCl, and mixture of betaine homologues BHB12+BHB16), and calculations using (3.4), (3.5), (3.6) and (3.7) cannot ensure a correct description of the experimental results for any mixture of surfactant. For that type of syemtems one much simpler theoretical models, which additionally account for processes actually taking place in the adsorption layer, can be used instead of the complicated set of (3.4), (3.5), (3.6) and (3.7) assuming that $a_{12} = (a_1 + a_2)/2$. Moreover, the use of this model does not require any preliminary consideration of isotherms of individual solutions, but rather involves information about the surface tension at certain surfactant concentrations.

For that, an exact expression is being derived which relates the surface pressure of a surfactant mixture with the surface pressure of individual solutions. For an ideal ($a_1 = a_2 = a_{12} = 0$) mixture of homologues $\omega = \omega_1 = \omega_2$), Eq. (3.6) can be rewritten in the following form:

$$\pi = \frac{RT}{\omega} ln \left(\frac{\theta_1}{1-\theta_1-\theta_2} + \frac{\theta_2}{1-\theta_1-\theta_2} + 1 \right) = \frac{RT}{\omega} ln(b_1c_1 + b_2c_2 + 1) \quad (3.10)$$

Using the corresponding equations for the individual surfactants 1 and 2 (in the following the subscript 0 refers to the individual solution),

$$\pi_i = -\frac{RT}{\omega} ln(1-\theta_{oi}) = \frac{RT}{\omega} ln(1 + b_ic_i) \quad (3.11)$$

$$b_ic_i = \frac{\theta_{oi}}{(1-\theta_{oi})} \quad (3.12)$$

and substituting the terms bici in Eq. (3.10) by the corresponding products from Eq. (3.11), one can express the equation of state [Eq. (3.10)] as[1]

$$exp\overline{\pi} = exp\overline{\pi_1} + exp\overline{\pi_2} - 1 \quad (3.13)$$

$\overline{\pi} = \pi\omega/RT$, $\overline{\pi_1} = \pi_1\omega/RT$, and $\overline{\pi_2} = \pi_2\omega/RT$ are the dimensionless surface pressures of the mixture and individual solutions of components 1 and 2, respectively, at identical surfactant concentrations as in the mixture.

The use of Eq. (3.13) requires only the knowledge of one pair of experimental values of surface pressure (tension) of individual solutions. The only parameter of the isotherm in Eq. (3.13), the molar area ω , can be either calculated from the molecular geometry of the surfactant, or determined experimentally from the limiting slope of the γ vs. lnc curve for the individual surfactant (slope of the surface tension isotherm near the CMC or solubility limit). Moreover, it was shown that calculations according to Eq. (3.13) are quite insensitive with respect to the choice of ω. Therefore for estimation one can assume that this parameter is equal to the value typical for the surfactant type considered, e.g.$(1.2 \div 2.0) \times 10^5 m^2/mol$ for fatty alcohols, acids, ethers and most anionic and cationic surfactants.

3.2 Simple Model

3.2.1 Non Ideal Mixture of homologues

The equation of state and adsorption isotherm for a non-ideal surface layer of two surfactants with the same molar areas are Eq. (3.6) and

$$b_i c_i = \frac{\theta_i}{(1 - \theta_1 - \theta_2)} exp(-2a_i\theta_i - 2a_{12}\theta_i) \tag{3.14}$$

It can be shown that Eq. (3.13) can be used also for the approximate description of non-ideal mixtures of surfactants. The π value in Eq. (3.6) are being expressed via the terms $b_i c_i$ using the expressions for isotherms Eq. 3.14. These products are being expressed via the π_i values for individual solutions using (3.8) and (3.9). This leads to a (dimensionless) equation of state for a mixed surface layer:

$$exp\overline{\pi} = k_1 exp\overline{\pi_1} + k_2 exp\overline{\pi_2} - k_3 \tag{3.15}$$

here

$k_1 = exp[a_1({\theta_{o1}}^2 - {\theta_1}^2 + 2\theta_1 - 2\theta_{o1}) - a_2{\theta_2}^2]$,

$k_2 = exp[a_2({\theta_{o2}}^2 - {\theta_2}^2 + 2\theta_2 - 2\theta_{[o2]}) - a_1{\theta_1}^2]$ and

$k_3 = exp(2a_1\theta_1 - a_1{\theta_1}^2 - a_2{\theta_2}^2) + exp(2a_2\theta_2 - a_1{\theta_1}^2 - a_2{\theta_2}^2) - exp(-a_1{\theta_1}^2 - a_2{\theta_2}^2)$,

the subscript 0 refers to the coverage for the individual solution. Eq. (3.15) and the expressions for k_i is obtained by (3.6) and (3.14) for $a_{12} = 0$. If the more correct expression $a12 = (a_1 + a_2)/2$ is introduced, then the resulting equation converts into the Eq. (3.15), but the expressions for ki become more cumbersome. Analysing the values of k_i one can see that, as the signs of the terms in the expression are opposite, and assuming only small deviations from ideality, one obtains the approximation $k1 \cong k_2 \cong k_3 \cong 1$. If the condition $a_{12} = (a_1 + a_2)/2$ is imposed, all coefficients k_i are also become approximately equal to 1. Therefore Eq. (3.15) which describes a non-ideal surface layer can be approximately transformed into Eq. (3.13) derived for an ideal mixture of homologues. For ideal surface layers, as $a_1 = a_2 = 0$ and thus $k_1 = k_2 = k_3 = 1$, Eq. (3.15) coincides exactly with Eq. (3.13).[1]

3.2.2 Mixtures of ionic homologues

Mixtures of an ionic and a non-ionic surfactant are quite similar to those considered above, because the contribution of the DEL to the surface pressure for an ionic surfactant can be treated approximately as a non-ideality factor.[1] If the solution of an individual ionic surfactant and their mixtures are studied at fixed ionic strength (which is usually accomplished by addition of an indifferent electrolyte), then the surface pressure of a mixed solution, similarly to non-ionic surfactants, is calculated from the data obtained for individual solutions according to Eq. (3.13)

It is known that mixtures of ionic surfactants for any arbitrary ionic strength can be satisfactorily described by the Langmuir or Frumkin equation of state and isotherm if, instead of the concentrations of ionic surfactants, the electroneutral combination of the corresponding ions is considered.

Considering a solution containing a mixture of two anionic (or cationic) surfactants, e.g. the two homologues R_1X and R_2X with a common counterion X^+, with or without addition of an electrolyte XY. In such systems the counterion concentration of X^+ is given by the sum of the concentrations of R_1X, R_2X and XY. For an ideal surface layer ($a_1 = a_2 = a_{12} = 0$) the following surface pressure isotherm is obtained:

$$\pi = \frac{RT}{\omega_{RX}} ln[((b_1 f_{1\pm})^2 c_{R_1X} c_{X^-} + (b_2 f_{2\pm})^2 c_{R_2X} c_{X^-})^{1/2} + 1] \tag{3.16}$$

$$\pi_i = \frac{RT}{\omega_{R_iX}} ln[((b_1 f_{1\pm}{}^2 c_{R_iX} c_{X^-})^{1/2} + 1] \tag{3.17}$$

Combining (6.16) and (6.17), one obtains the expression which describes the surface tension of a mixed solution

$$exp\overline{\pi} = ((exp\overline{\pi_1} - 1)^2 + (exp\overline{\pi_2} - 1)^2)^1 + 1 \tag{3.18}$$

Unlike the cases of non-ionic surfactants or ionic surfactants in the presence of electrolyte excess, when the calculations according to Eq. (3.13) are made, one should choose the concentrations (activities) of the individual solutions to ensure that the products of the concentrations of the corresponding surface-active ions and counterions in the individual solutions and in the mixture of surfactants are equal. For example, assuming that the R_1X concentration in the mixture is c_1, and the concentration of R_2X is c_2, then the surface pressure in the individual solutions is determined for the concentrations $c_{01} = [c_1(c_1 + c_2)]^{1/2}$ and $c_{02} = [c21(c_1 + c_2)]^{1/2}$, respectively. This means, the increase of the counterion concentrations in the surfactant mixture due to the addition of the second surfactant's counterion has to be taken into account. Similarly the influence of small additions of indifferent electrolyte with a common counterion has also to be considered.[1]

The account for non-ideality of the components in the surface layer of an ionics mixture does not affect the form of Eq. (3.18). Thus, Eq. (3.13) in the case of counterion excess, and Eq. (3.18) in the case where no indifferent electrolyte is added (and the correction of the concentrations in the individual solutions as described above) are allowed an approximate description of non-ideal mixtures of ionic surfactants with identical values of the molar areas of the components.

3.2.3 Mixture of components with different molar areas

The surfactants with essentially different molar areas are often present simultaneously in a mixture. The equation of state for the ideal mixture of two surfactants with different ω_i is also expressed by Eq. (3.10) in the form

$$\pi = -\frac{RT}{\omega} ln(1 - \theta_1 - \theta_2) \tag{3.19}$$

However, the ω value is no longer a constant but depends on the corresponding partial molar areas ω_i and adsorptions of components 1 and 2, and is given by Eq. (3.7). For this mixture, the adsorption isotherms are

$$b_i c_i = \frac{\theta_i}{(1 - \theta_1 - \theta_2)^{n_i}} \tag{3.20}$$

where $n_i = \omega_i/\omega$. Following the lines of the preceding sections, one can use Eq. (3.20) to substitute the $b_i c_i$ terms in Eq. (3.19), and then by the corresponding values of $b_i c_i$ for individual solutions from Eq. (3.11). This again results in Eq. (3.15) where the coefficients are being defined by

$k_1 = (1 - \theta_1 - \theta_2)^{1-n_1}$,

$k_2 = (1 - \theta_1 - \theta_2)^{1-n_2}$ and

$k_1 = (1 - \theta_1 - \theta_2)^{1-n_1} - (1 - \theta_1 - \theta_2)^{1-n_2}$.

If the values n_i are close to 1, then the coefficients k_i can be approximated to be 1, i.e. Eq. (3.13) is valid also for this case. The dimensionless pressures in Eq. (3.13) are $\overline{\pi} = \pi\omega/RT$, $\overline{\pi_1} = \pi_1\omega/RT$ and $\overline{\pi_2} = \pi_2\omega/RT$. To determine the average of ω for the mixture, the same substitution procedure for $b_i c_i$ is used and Eq. (3.7) becomes

$$\omega = \frac{\omega_1(exp\overline{\pi_1} - 1) + \omega_2(exp\overline{\pi_2} - 1)(1 - \theta_1 - \theta_2)^{n_2-n_1}}{exp\overline{\pi_1} - 1 + exp\overline{\pi_2} - 1)(1 - \theta_1 - \theta_2)^{n_2-n_1}} \tag{3.21}$$

Estimations using this equation show that even if the difference between the ω_i values is relatively small, but the surface coverage is medium or large, the term $(1 - \theta_1 - \theta_2)^{n_2-n_1}$ cannot be omitted. However, one can use other expressions for the mean area, which do not involve unknown quantities. As the adsorption is roughly proportional to the surface pressure (for extremely diluted surface layers $\pi = RT\Gamma$), then the mean molar area, Eq. (3.7), is given by

$$\omega = \frac{\omega_1\pi_1 + \omega_2\pi_2}{\pi_1 + \pi_2} = \omega_1\frac{\overline{\pi_1} + \overline{\pi_2}}{\overline{\pi_1} + \overline{\pi_2}(\omega_1/\omega_2)} \tag{3.22}$$

Assuming that the adsorptions of surfactants characterized by different molar areas in a densely packed layer (at sufficiently large π) are roughly inverse proportional to ω_i, instead of Eq. (3.22) one obtain

$$\omega = \frac{\omega_1\pi_1/\omega_1 + \omega_2\pi_2/\omega_2}{\pi_1/\omega_1 + \pi_2/\omega_2} = \omega_1\frac{\pi_1 + \pi_2}{\pi_1 + \pi_2(\omega_1/\omega_2)} \tag{3.23}$$

Both models provide quite a satisfactory description of surfactant mixtures with essentially (more than twice) different values of the molar areas of the components.

3.3 Other Model

The Joos relationship for the equation of state to describe the mixed adsorption behaviour is given by following equation (This relation for surfactants in concentration up to about $10^{-2} mol/liter$)[4]

$$exp\left(\frac{-\pi}{RT{\Gamma_0}^\infty}\right)+exp\left(\frac{-\pi}{RT{\Gamma_1}^\infty}\right)\frac{C_1}{a_1}+exp\left(\frac{-\pi}{RT{\Gamma_2}^\infty}\right)\frac{C_2}{a_2}=1 \tag{3.24}$$

where ${\Gamma_0}^\infty$, ${\Gamma_1}^\infty$ and ${\Gamma_2}^\infty$ are the maximum adsorption of the solvent, and surfactant 1 and 2, respectively, π is the surface pressure, R is the gas law constant and T is the absolute temperature. The parameters a_1 and a_2 are expressed as

$$a_1 = exp\left(\frac{{\mu_1}^S-{\mu_1}^B}{RT}\right)\omega \tag{3.25}$$

$$a_2 = exp\left(\frac{{\mu_2}^S-{\mu_2}^B}{RT}\right)\omega \tag{3.26}$$

where μ^S is the chemical potential in the surface under standard conditions, μ^B is the chemical potential in the bulk under standard conditions and ω is the number of the moles of water per litre. Eq/ 3.24 gives good results for the systems of nonionic or ionic surfactants in the presence of a swamping electrolyte.

If one of the surfactant is a 1:1 electrolyte type A^+ and B^-, then its activity is close to 10^-2M. Therefore for an aqueous solution including one nonionic and one ionic surfactant type 1:1 electrolyte in the absence of a swamping electrolyte, eq 3.24 is approximately written in the form

$$exp\left(\frac{-\pi}{RT{\Gamma_0}^\infty}\right)+exp\left(\frac{-\pi}{RT{\Gamma_1}^\infty}\right)\frac{C_1}{a_1}+exp\left(\frac{-\pi}{2RT{\Gamma_2}^\infty}\right)\frac{C_2}{{a_2}^*}=1 \tag{3.27}$$

where

$${a_2}^* = exp\left(\frac{{\mu_2}^S-{\mu_2}^B}{2RT}\right)\omega \tag{3.28}$$

assuming that $C_2C_1 = b = const$ and $C_{tot} = C_1 + C_2 = C_1(1+b)$ gives

$$exp\left(\frac{-\pi}{RT{\Gamma_0}^\infty}\right)+[exp\left(\frac{-\pi}{RT{\Gamma_1}^\infty}\right)\frac{1}{a_1}+exp\left(\frac{-\pi}{2RT{\Gamma_2}^\infty}\right)\frac{b}{{a_2}^*}]\frac{C_{tot}}{1+b}=1 \tag{3.29}$$

The values of ${\Gamma_0}^\infty$, ${\Gamma_1}^\infty$, ${\Gamma_2}^\infty$, a_1 and ${a_2}^*$ used in eq 3.29 are calculate from the data for the individual surfactants on the assumption that $C_1 = 0$ or $C_2 = 0$. So by using eq 3.29 one can calculate the value of surface pressure.

Chapter 4

Results

In the previous chapter it was seen that suitable models were taken from the literature reports, therby making a precise data analysis in an attempt to compare the experimental results with those coming out from the literature survey.

4.1 CMC prediction

For CMC prediction the following model was used:

$$CMC = x_1{}^m f_1 CMC_1 + (1 - x_1{}^m) f_2 CMC_2 \tag{4.1}$$

where f_1 and f_2 are the activity coefficients of the surfactants in the micelle. For calculation of these activity coefficients following equation are used[5]

$$lnf_1 = (1 - x_1{}^m)^2 \beta \tag{4.2}$$

$$lnf_2 = (x_1{}^m)^2 \beta \tag{4.3}$$

in terms of solution compositions

$$\frac{1}{CMC} = \frac{x_1}{f_1 CMC_1} + \frac{1 - x_1}{f_2 CMC_2} \tag{4.4}$$

and

$$ {x_1}^m = \frac{x_1 f_1 \mathit{CMC_2}}{x_1 f_2 \mathit{CMC_2} + (\mathit{1} - \mathit{x_1}) f_1 \mathit{CMC_1}} \tag{4.5} $$

Results are attached

4.2 Surface Tension Prediction

For surface tension prediction following model was used

$$ \pi = -\frac{RT}{\omega}[ln(1 - \theta_1 - \theta_2) + \alpha_1 {\theta_1}^2 + a_2 {\theta_2}^2 + 2a_{12}\theta_1\theta_2] \tag{4.6} $$

where

$$ \omega = \frac{\omega_1 \Gamma_1 + \omega_2 \Gamma_1}{\Gamma_1 + \Gamma_2} \tag{4.7} $$

Here $a_{12} = \frac{a_1 + a_2}{2}$ if this is not valid then following eqs is used[1]

$$ exp\overline{\pi} = exp\overline{\pi_1} + exp\overline{\pi_2} - 1 \tag{4.8} $$

For individual solutions surface tension isotherm Frumkin model is used

$$ \pi = -\frac{RT}{\omega_1}[ln(1 - \theta_i) + a_i {\theta_i}^2] \tag{4.9} $$

$$ b_i c_i = \frac{\theta_i}{(1 - \theta_i} exp(-2a_i\theta_i) \tag{4.10} $$

Results are attached

Chapter 5

Conclusions

We have used 2 models for the CMC prediction and Surface tension prediction.

Model used for CMC prediction is the pseudophase separation model. In this approach the micelles are treated as a separate, infinite phase in the equlibrium with the monomer phase. We have predicted the values of CMC for the $SDS - C_8E_4$, SDS-DeTAB and $C_{12}SO_4Na - C_{12}E_8$ system. Results are good agreement with experimental data reported in the literature.

We have predicted the Surface tension values for the 1-heptanol-1-octanol, SDS-1-butanol, SDS-1-nonanol systems. and thess values match from the expermental values.

So we can colclude that one can predict the values of Surface tension and CMC for a surfactant mixture by using various models availabel in literature.

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