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ORIGINAL CONTRIBUTION

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Markov chain model of mixed surfactant systems

I. New expression for the non-ideal interaction parameter

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Abstract A new model of mixed surfactant systems have been developed in the work presented. It includes two parameters only connected directly with the Gibbs free energy of the surfactant aggregation. They can be determined using both the aggregation equilibrium constant values or the phase composition data. It has been shown also the relation between these new parameters and the same of the regular solution approximation and the alternative models. The possibility to describe the available experimental information about the micelle composition as a function of the singly dispersed surfactant mixture composition better than by the other models has been shown also.

Key words Mixed surfactant system – non-ideal interaction parameter – regular solution approximation model – Markov chain model – conditional probability – transition matrix

Introduction

The polydispersity of commercial surfactants, synergetic behaviour of mixed surfactant systems and the possibility to control their physical properties and stability by a variation of the surfactant composition [1, 2] are the reasons for a growing applied interest in these systems. In addition it is noteworthy that the functional molecular aggregation formed in nature are composed of two or more kinds of surface-active chemical species [3, 4]. Therefore, the studies of mixed micelles, mixed films or mixed surfactant phase organization are essential not only for developing the surfactant abilities in the applied aspect, but also for comprehending some functions of biological systems. This situation has led to an enormous challenge to understand the interaction mechanism between different components in the mixed surfactant systems which controls the performance of these systems. From the first pseudo-phase separation model [5–7] the mixed surfactant system simulation passes through the ideal-mixed formation model [8–11] and came to the non-ideal one [12–19]. Introducing the regular solution approximation in the last model, the molecular non-ideality interaction parameter (β) has been determined as an energy interaction difference between equal (H_{11}, H_{22}) and non-equal (H_{12}) surfactant molecules; $\beta = (H_{11} + H_{22} - 2H_{12})/RT$ [13]. Two sets of β-values for surfactant pairs are tabulated; β^{m} – for mixed micelles and β^{s} – for mixed monolayers [13, 20]. As the mixed surfactant system behaviour is well above the ideal one, the calculation of the aggregation number, CMC and composition of these systems using these β-values is a general approach for a surfactant synergism description [13, 21–23]. In spite of a good correspondence between the calculated and the experimental data for a number of mixed surfactant systems [24–27] it is clear now that the considerable deviation between them for many others [15, 28–30] is a result of a general limitation of the regular solution approach – zero value of the mixing entropy [13, 31]. This is a reason for a series of alternatives to regular solution approach (an improved pseudophase separation model [32–35], mass action model [36, 37], several molecular models [38–43]) which have been developed. Their advantage is that they account for the Gibbs free energy of mixing, but their limited application up to now comes from their multi-parameter approaches and the more special requirements for the estimation of the Gibbs free energy of mixing.

The new model, developed in this work, keeps the above mentioned advantage of the alternatives and at the same time includes only two parameters which are connected directly with the Gibbs free energy of surfactant aggregation. They can be determined easily using both the aggregation equilibrium constant values or the phase composition data. It is shown that the logarithm of each of them is just the difference between the Gibbs free energies of the two surfactant additions to a given surfactant aggregate active center. The above mentioned parameter expression is a logarithm of the new two parameter production at a partial case certainly when mixing entropy is zero.

Results

Theoretical background of the model

Despite the model is free from surfactant number limitation, the general expressions will be derived for a bicomponent surfactant mixture. It will be shown later that there is quite an easy expansion of the method to three- and more-component surfactant mixtures. There are four different equilibrium reactions at bicomponent surfactant aggregation

$$\sim S_1 + S_1 \xrightleftharpoons[k_{11,b}]{k_{11,f}} \sim S_1S_1; \quad K_{11} = k_{11,f}/k_{11,b} \tag{1}$$

$$\sim S_1 + S_2 \xrightleftharpoons[k_{12,b}]{k_{12,f}} \sim S_1S_2; \quad K_{12} = k_{12,f}/k_{12,b} \tag{2}$$

$$\sim S_2 + S_1 \xrightleftharpoons[k_{21,b}]{k_{21,f}} \sim S_2S_1; \quad K_{21} = k_{21,f}/k_{21,b} \tag{3}$$

$$\sim S_2 + S_2 \xrightleftharpoons[k_{22,b}]{k_{22,f}} \sim S_2S_2; \quad K_{22} = k_{22,f}/k_{22,b} \tag{4}$$

where S_i, $\sim S_j$, $\sim S_iS_j$, $k_{ij,f}$, $k_{ij,b}$ and K_{ij} ($i = 1, 2$) are i-th surfactant molecule, j-th aggregate active center, ij-th dyad aggregate active center, forward and back reaction rate constants and equilibrium constants respectively. According to this model the aggregate active centre and the aggregate diad active centre are the last and the pair of the last and next to last addited to the aggregate surfactant molecules. These aggregate components can be expected to be in a specific more active state than the other ones because of the uncompensated intermolecular forces. Their exited state is just the reason for their participation in the back deaggregation reactions (1–4). Hence they determine both the aggregate affinity to the different surfactant molecules and the equilibrium constant values (1–4). By the aggregate dyad active center concentrations

$$[\sim S_1S_1] = K_{11}[\sim S_1][S_1] \tag{5}$$

$$[\sim S_1S_2] = K_{12}[\sim S_1][S_2] \tag{6}$$

$$[\sim S_2S_1] = K_{21}[\sim S_2][S_1] \tag{7}$$

$$[\sim S_2S_2] = K_{22}[\sim S_2][S_2] \tag{8}$$

it is possible to express the conditional probabilities for both conservation and alteration of the surfactant aggregate active center in each aggregation step.

$$\begin{aligned} p_{11} &= p(\sim S_1/S_1) \\ &= [\sim S_1S_1]/([\sim S_1S_1] + [\sim S_1S_2]) \end{aligned} \tag{9}$$

$$\begin{aligned} p_{12} &= p(\sim S_1/S_2) \\ &= [\sim S_1S_2]/([\sim S_1S_1] + [\sim S_1S_2]) = 1 - p_{11} \end{aligned} \tag{10}$$

$$\begin{aligned} p_{21} &= p(\sim S_2/S_1) \\ &= [\sim S_2S_1]/([\sim S_2S_1] + [\sim S_2S_2]) = 1 - p_{22} \end{aligned} \tag{11}$$

$$\begin{aligned} p_{22} &= p(\sim S_2/S_2) \\ &= [\sim S_2S_2]/([\sim S_2S_2] + [\sim S_2S_1]). \end{aligned} \tag{12}$$

The probability expressions by the equilibrium constants and surfactant concentrations in a solution are produced introducing the relations (5–8) for the dyad concentrations in Eqs. (9–12).

$$p_{11} = g_1[S_1]/(g_1[S_1] + [S_2]) \tag{13}$$

$$p_{12} = [S_2]/(g_1[S_1] + [S_2]) \tag{14}$$

$$p_{21} = [S_1]/(g_2[S_2] + [S_1]) \tag{15}$$

$$p_{22} = g_2[S_2]/(g_2[S_2] + [S_1]) \tag{16}$$

where

$$g_1 = K_{11}/K_{12} \tag{17}$$

$$g_2 = K_{22}/K_{21} \tag{18}$$

are the retious of the corresponding competing reaction equilibrium constants. Each of them accounts for the differences between the standard Gibbs energies of the competing reactions of a given aggregate active centre to the both surfactant molecules. It is now worthwhile to mention that the discussed probabilities can be estimated by the experimental determined quantities $[S_i]$ and g_i ($i = 1, 2$).

If the surfactant aggregation process is treated as a Markov one, then each aggregate active center conforms with the corresponding Markov chain state. It means that the last surfactant molecule added to the surfactant aggregate determines the nature and activity of the surfactant aggregate. The above determined probabilities form the Markov chain transition matrix

$$P = \begin{array}{c|cc} & S_1 & S_2 \\ \hline S_1 & p_{11} & p_{12} \\ S_2 & p_{21} & p_{22} \end{array} \qquad (19)$$

From the finite Markov chains theory [44] it follows that the elements of the eigen vector ($\acute{I}$) of P ($\acute{I}P = \acute{I}$) are the mole fractions of surfactants (x_i, $i = 1, 2$) in the produced surfactant aggregates.

$$\acute{I}_1 = x_1 = p_{21}/(p_{21} + p_{12}) \qquad (20)$$

$$\acute{I}_2 = x_2 = p_{21}/(p_{21} + p_{12}) \qquad (21)$$

So, from Eqs. (14, 16) and the last two ones, the following equation

$$\frac{x_1}{x_2} = \frac{p_{21}}{p_{12}} = \frac{\acute{A}_1}{\acute{A}_2} \cdot \frac{g_1\acute{A}_1 + \acute{A}_2}{g_2\acute{A}_2 + \acute{A}_1} \qquad (22)$$

is derived, where $\acute{A}_i = [S_i]/([S_i] + [S_j])$, $(i, j = 1, 2; i \neq j)$ are the mole fractions of surfactants in a solution. The structure of this solution is the same as for the bicomponent copolymer composition equation [45]. The essential difference between them is that the g_i ($i = 1, 2$) constants are the relations between the equilibrium constants while the copolymerization constants are the relations between the propagation rate constants. The structure similarity is a result of the propagation addition mechanism of both processes. It allows the use of numerous of the developed methods for the determination of the copolymerization constants for the determination of the g_i ($i = 1, 2$) values. One of them is the linearization of Eq. (22) and determination of g_1 and g_2 from the intercepts and slopes of the experimental straight lines

$$\frac{v-1}{w} = g_1 - \frac{v}{w^2} g_2 \qquad (23)$$

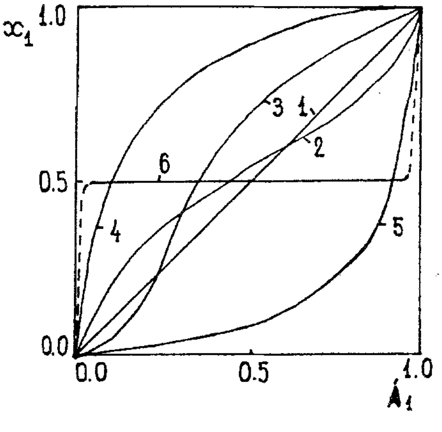
or

$$w\left(1 - \frac{1}{v}\right) = -g_2 + \frac{w^2}{v} g_1 \qquad (24)$$

where $v = x_1/x_2$ and $w = \acute{A}_1/\acute{A}_2$. It is clear from these equations that for the experimental determination of g_i ($i = 1, 2$) values by this method, the dependence of the surfactant aggregate composition on the solution surfactant composition is necessary. The determination of this dependence could be performed by one of numerous methods developed to this end [46, 47]. The other method for the determination of the g_i ($i = 1, 2$) values is based on the definition Eqs. (17, 18) and requires the independent determination of the equilibrium constant (K_{ij}; $i, j = 1, 2$) values.

The Eqs. (20–22) allows the prediction of the surfactant aggregate composition if the g_i ($i = 1, 2$) values and the solution surfactant composition are known. The control of this composition can be realized by the variation of both surfactant monomer composition and g_i ($i = 1, 2$) values (for example by alteration of pH, ionic strength, solvent nature etc.). The curves on Fig. 1 show the influence of g_i ($i = 1, 2$) value combinations of the "$x_1 - \acute{A}_1$" dependence. Curve 1 on this figure shows the case when $g_1 = g_2 = 1$. This is azeotropic surfactant aggregation and the aggregate composition is equal to that of a surfactant solution. Curve 6 characterizes the other extreme case – the alternating aggregation when every kind of aggregate propagating active center prefers the other type surfactant molecule. The aggregate composition is equimolar ($x_1 = x_2 = 0.5$) at any surfactant solution composition and the surfactant molecules in aggregate form the correct alternating sequences ($\sim S_1 - S_2 - S_1 - S_2$). Curve 2 characterizes the cases which are close to the alternating aggregation process but as $g_i \neq 0$ ($i = 1, 2$) the possibilities for the addition of the surfactant molecules to the same kind of aggregate propagating active center does not go to zero. Hence, there is not the extreme alteration of the two kinds of molecules in the surfactant aggregates. The opposite case is the surfactant aggregation when every kind of aggregate propagation active center prefers the same kind

Fig. 1 Dependences of the surfactant 1 mole fraction in the surfactant aggregate (x_1) on the mole fraction of the same surfactant in the surfactant mixture ($\acute{A}_1$) at different combination of g_i ($i = 1, 2$) values: 1. Curve 1; $g_1 = g_2 = 1$. 2. Curve 2; $g_1 < 1$; $g_2 < 1$. 3. Curve 3; $g_1 > 1$; $g_2 > 1$; 4. Curve 4; $g_1 > 1$; $g_2 < 1$. 5. Curve 5; $g_1 < 1$; $g_2 > 1$. 6. Curve 6; $g_1 = g_2 = 0$



surfactant molecule (curve 3 of the figure). There is a possibility for the formation of the two kinds of monosurfactant aggregates which depends on the degree of g_i $(i = 1, 2)$ value deflection from unity ($g_i > 1$ $(i = 1, 2)$). At last, the curves 4 and 5 are produced at the aggregation processes when one of both kinds surfactant molecules is preferred (S_1 for a curve 4 and S_2 for a curve 5) from the both kinds aggregate of propagating active centers and so the aggregates are enriched by the same kind of surfactant in comparison with the surfactant solution.

The method allows easy derivation of similar relations to Eqs. (20–22), describing the dependence of surfactant aggregate composition on the surfactant solution, for three- and more-component surfactant mixtures. It is necessary only to treat $(n \times n)$ transition matrix P and n-component vector $\acute{I}$ $(n \geq 3)$ in this case instead of (2×2) matrix P and two-component vector $\acute{I}$. For an example, if $n = 3$

$$x_1 = \acute{I}_1 = [p_{31}(1 + p_{32} - p_{22}) - p_{32}(p_{31} - p_{21})]/D \tag{25}$$

$$x_2 = \acute{I}_2 = [p_{32}(1 + p_{31} - p_{11}) - p_{31}(p_{32} - p_{12})]/D \tag{26}$$

$$x_3 = \acute{I}_3 = 1 - \acute{I}_1 - \acute{I}_2 \tag{27}$$

where

$$\begin{aligned} D = {} & (1 + p_{31} - p_{11})(1 + p_{32} - p_{22}) \\ & - (p_{31} - p_{21})(p_{32} - p_{12}) \end{aligned} \tag{28}$$

$$p_{ij} = ([S_j]/g_{ij}) / \sum_{k}^{3} [S_k]/g_{ik} \; (i, j = 1, 2, 3) \tag{29}$$

$$g_{ij} = K_{ii}/K_{ij} \; (i, j = 1, 2, 3) \tag{30}$$

The relations [25–27] are similar to Eqs. (20,21). There is a possibility to obtain two independent composition equations (x_1/x_2 and x_1/x_3 for an example) similar to Eq. (22). The number of g_{ij} parameters is six ($g_{ii} = 1$, $i = 1, 2, 3$) in this case and not two as it is at the bicomponent surfactant aggregation. They can be subdivided into three pairs (g_{ij}; $i, j = 1, 2$; 1, 3 and 2, 3) and the values of each of them can be determined from the equations, similar to Eq. (22) or its linear forms (Eqs. 23, 24) describing the corresponding bicomponent surfactant aggregation processes.

Relation of the model developed to other models

Relation to ideal mixing model

From the general equation of the ideal mixing model

$$x_i = \frac{C_{\mathrm{mix}}^{\mathrm{cmc}}}{C_i^{\mathrm{cmc}}} \; (i = 1, 2, \ldots) \tag{31}$$

($C_{\mathrm{mix}}^{\mathrm{cmc}}$, C_i^{cmc} are the critical micelle concentrations of the surfactant mixture and i-th surfactant respectively) and from Eq. (20) or Eq. (21) it is possible to derive the relation between g_i $(i = 1, 2)$ values, $C_{\mathrm{mix}}^{\mathrm{cmc}}$ and C_i^{cmc}. If $i = 1$ this expression is

$$\frac{C_{\mathrm{mix}}^{\mathrm{cmc}}}{C_1^{\mathrm{cmc}}} \cdot \frac{\acute{A}_1^2}{\acute{A}_2} = -g_2 + \left[1 - \frac{\acute{A}_1 C_{\mathrm{mix}}^{\mathrm{cmc}}}{C_1^{\mathrm{cmc}}}\right] \left(\frac{\acute{A}_1}{\acute{A}_2}\right)^2 g_1 \, . \tag{32}$$

Similar relation between g_i $(i = 1, 2)$ values, $C_{\mathrm{mix}}^{\mathrm{cmc}}$ and C_2^{cmc} can be derived too. These linear forms can be applied also for the determination of g_i $(i = 1, 2)$ values for ideal bicomponent surfactant mixtures using $C_{\mathrm{mix}}^{\mathrm{cmc}}$ and C_i^{cmc} $(i = 1, 2)$.

Relation to non-ideal regular solution approximation model

Introducing the activity coefficients

$$f_1 = \exp[\beta(1 - x_1)]^2 \tag{33}$$

$$f_2 = \exp[\beta x_1^2] \tag{34}$$

in Eqs. (31) the general relations of the non-ideal regular solvent approximation model are derived [13]:

$$x_1 = \acute{A}_1 C_{\mathrm{mix}}^{\mathrm{cmc}} / C_1^{\mathrm{cmc}} \exp[\beta(1 - x_1)^2] \tag{35}$$

$$x_2 = \acute{A}_2 C_{\mathrm{mix}}^{\mathrm{cmc}} / C_2^{\mathrm{cmc}} \exp[\beta(1 - x_1)^2] \tag{36}$$

Combining them with Eqs. (20, 21) the following linear relations between g_i, C_i^{cmc} $(i = 1, 2)$, $C_{\mathrm{mix}}^{\mathrm{cmc}}$, x_1 and x_2 are derived:

$$(\acute{A}_1/\acute{A}_2)[1 - (\acute{A}_1/\acute{A}_2)]\tilde{o}_1 = g_2 - (\acute{A}_1/\acute{A}_2)^2 \tilde{o}_1 g_1 \tag{37}$$

$$(\acute{A}_2/\acute{A}_1)(\tilde{o}_2 - 1) = g_1 + (\acute{A}_2/\acute{A}_1)^2 \tilde{o}_2 g_2 \tag{38}$$

where

$$\tilde{o}_1 = \{\exp[\beta(1 - x_1)^2] C_1^{\mathrm{cmc}} / \acute{A}_1 C_{\mathrm{mix}}^{\mathrm{cmc}}\} - 1 \tag{39}$$

$$\tilde{o}_2 = [C_2^{\mathrm{cmc}} \exp(\beta x_1^2) / \acute{A}_2 C_{\mathrm{mix}}^{\mathrm{cmc}}] - 1 \, . \tag{40}$$

They can be used also for the determination of those g_i $(i = 1, 2)$ values which describe the relation between the surfactant aggregate and surfactant solution compositions, in the case when the aggregation process is described by the non-linear regular solution approximation model. Again these expressions are interesting for they show the quite complex dependences between β and g_i $(i = 1, 2)$ parameters which are proposed here, even for this partial case.

A more common relation between g_i $(i = 1, 2)$ and β follows from the definition Eqs. (17, 18) for g_i $(i = 1, 2)$, using the relation between the equilibrium constant and standard reaction Gibbs energy.

$$g_i = K_{ii}/K_{ij} = \exp[-(\Delta G^\circ_{ii} - \Delta G^\circ_{ij})/RT]; \quad i,j = 1,2;\ i \neq j\ . \quad (41)$$

These expressions show that the developed model is free from the regular solution approximation limitation as g_i ($i = 1, 2$) parameters account for the change of the aggregation free energy and not only of the aggregation enthalpy. This is the general advantage of the new model. From the product

$$g_1 g_2 = \exp[-(\Delta G^\circ_{11} + \Delta G^\circ_{22} - \Delta G^\circ_{12} - \Delta G^\circ_{21})/RT] \quad (42)$$

it follows that

$$\ln g_1 g_2 = -\beta \quad (43)$$

if $\Delta S^\circ_{ij} = 0$ ($i,j = 1, 2$) and $\Delta H^\circ_{12} = \Delta H^\circ_{21}$. The last conditions underline both the considerable limitations of the regular solution approximation model and the versatility of the new one. It is worthwhile to mention one more advantage of the new model, connected with the introduction of two (g_1, g_2) molecular interaction parameters instead of one (β), as in the regular solution approximation model. It has already been shown that the common mixing free energy is subdivided into four parts in accordance with the above mentioned four equilibrium aggregation reactions (1–4). Each g_i ($i = 1, 2$) value depends on the difference between the standard free energies of the two possible competitive equilibrium reactions to a given aggregate active center. So, g_i ($i = 1, 2$) values allow not only to predict and to control the aggregate composition (Eq. 22), but to obtain more detailed information about the relation between surfactant molecular structure and molecular interaction during surfactant aggregation. The importance of this possibility is not less than that mentioned above, applied significantly to control aggregate composition. Actually the fact that each g_i value depends only on the difference $\Delta G^\circ_{ii} - \Delta G^\circ_{ij}$ ($i = 1, 2; j \neq i$) allows a direct comparison of the molecular amphiphyle characteristics of the two (S_i and S_j) surfactants and their influence on the addition reactions to the i-th aggregation active center. Perhaps after a determination of numerous g_i values, it will be possible to resolve the challenge to calculate the g_1 values from the molecular amphiphile characteristics of the surfactants.

In conclusion of this comparison, it will be interesting to note the fact that in both the ideal mixture model and the nonideal regular solution approximation model, the calculations use the C_i^{cmc} ($i = 1, 2$). But pure surfactant is practically not. That is why the surfactant purification degree considerably influences the values. The method discussed is also free from this defect.

Relation to some alternatives to regular solution approximation model

The common peculiarity of the discussed model and the different alternatives to regular solution approximation models (ARSAM) [38, 39, 41, 43, 48, 49, 50] is that they account for the surfactant molecular but not phase characteristics. It turned out to be a fruitful way to overcome the mixing entropy zero value limitation. But the large number of the ARSAM parameters limits their application and outlined the versatility of the model developed. However the relation between these models asks a special treatment and will be a subject of a future publication.

Calculation of the mixed micelle composition as a function of the singly dispersed surfactant mixture using g_i ($i = 1, 2$) values

The experimental data in the literature for surfactant monomer-micelle composition of different kinds surfactant mixtures is used to calculate the g_i ($i = 1, 2$) values and to verify the correspondence between the experimental and calculated composition curves. Different kinds of surfactant mixture are chosen for which a deviation between experimental and calculated by the non-ideal regular solution approximation model composition, is discovered.

Example I

The aggregation behaviour of binary mixture of decyl methyl sulfoxide ($C_{10}SO$, S_1) and decyl dimethyl phosphene oxide ($C_{10}PO$, S_2) at 24 °C in 1 mM Na_2CO_3 was considered as an ideal one ($\beta = 0$) by Holland and Rubingh [15]. But more precisely calculations by the Nagarajan molecular alternative model of the regular solution approximation one [50] show little deviation from ideal mixing conditions. In Fig. 2 the micelle compositions calculated by both the Nagarajan and the developed models are compared. One can see a full coincidence between two curves if $g_1 = 2.72$ and $g_2 = 0.33$ values are used for a calculation of the x_1–$\hat{A}_1$ curve by the discussed model. These values are calculated by Eq. (23) using the experimental [15] and Nagarajan [50] data for x_1 values (Fig. 3). From the surfactant tail identity it follows that the discussed deviation from ideality is a result of the surfactant head group influencing the surfactant molecular interaction. More precisely, as $g_1 > g_2$, $g_1 > 1$ while $g_2 < 1$ this deviation can be explained by the more considerable steric hindrance between $-PO(CH_3)_2$ head groups than between $-SOCH_3$ and $-PO(CH_3)_2$ ones ($K_{22} < K_{21}$ and $g_2 < 1$). That is why the

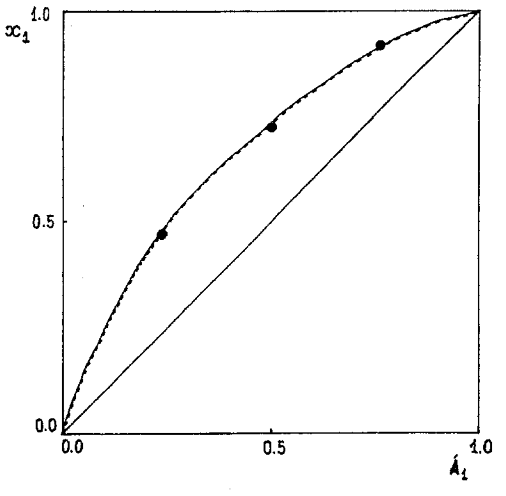


Fig. 2 Mole fraction of $C_{10}SO$ in mixed $C_{10}SO$ (S_1) – $C_{10}PO$ (S_2) micelles (x_1) as a function of the mole fraction of $C_{10}SO$ (A_1) in the singly dispersed surfactant mixture. —— Nagarajan [50] model results. ---- Markov chain model results. ● Experimental results [15]

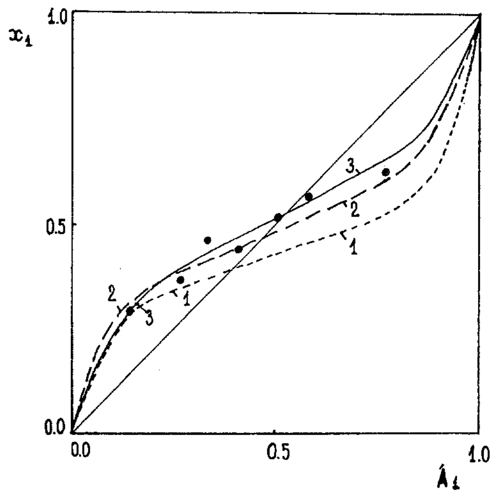


Fig. 4 Mole fraction of NPE 50 (S_1) in mixed NPE 50 (S_1) – DBS (S_2) micelles as a function of NPE 50 mole fraction in a singly dispersed surfactant mixture at 27 °C. The experimental data (points) are from ref. [48]. The curves are calculated by the regular solution approximation model ($\beta = -2.4$, curve 1), Osborne-Lee and Schechter model ($w = -0.4$; $z = 2$; $R = 5.2$, curve 2 [43]) and Markov chain model ($g_1 = 0.30$; $g_2 = 0.28$, curve 3)

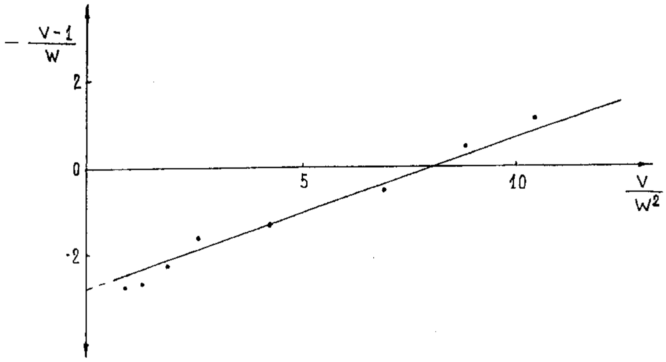


Fig. 3 Linearization of the Nagarajan [50] and experimental [15] data for $C_{10}SO$ (S_1) and $C_{10}PO$ (S_2) surfactant mixture in 0. 1 mM Na_2CO_3 at 25 °C in the Eq. (23) coordinates for a g_i ($i = 1, 2$) value determination

g_i ($i = 1, 2$) values are quantitatively measured for these steric hindrances of this type of surfactant aggregation.

It is interesting to note that in a correspondence with Eq. (43), $\beta = -\ln(2.72 \times 0.33) = -0.11$. This value is very close to zero and explains the Holland and Rubingh [15] success in describing their experimental data by the ideal pseudophase model. At the same time the obtained results show the sensitivity of the proposed method to such molecular surfactant differences as one methyl group in the surfactant head groups and to reflect these differences quite sharply.

Example II

Figure 4 shows the experimental [48] dependence of mole fraction of nonyl phenol ethoxylated with 50 average ethylene oxide units (NPE 50, S_1) in mixed micelles with decyl benzene sulfonate (DBS, S_2), with mole fraction NPE 50 in the singly dispersed surfactants at 27 °C. These experimental results are compared to the calculated results by the regular solution approximation model ($\beta = -2.4$, cuirve 1), the Osborne-Lee-Schechter [43] model ($w = -0.5$; $z = 2$; $R = 5.0$; curve 2) and the Markov chain model ($g_1 = 0.30$; $g_2 = 0.28$; curve 3). One can see that the calculated by the Osborne-Lee-Schlechter and Markov chain model curves are far closer to the experimental points than the curve calculated by the regular solution approximation model. The g_i ($i = 1, 2$) values are determined (graphically or analytically) from the same experimental data using the linear form of Eq. (22). There are two different reasons for a deviation from ideality of this mixed surfactant system. The first is the repulsion between the negatively charged DBS head groups and the second – is the steric hindrance between the NPE 50 head groups. As a result of the former, $K_{22} < K_{21}$ and $g_2 < 1$, whilst the latter caused and $K_{11} < K_{12}$ and $g_1 < 1$. The influence of the small difference between the two surfactant tails on the surfactant aggregation is probably negligible in this case, in comparison with the above mentioned two effects of the surfactant head group interaction. The measure of the significance of these effects is the deviation of the g_i

($i = 1, 2$) values from unity or $-\ln(g_1 g_2)$ from zero ($-\ln g_1 g_2 = 2.48$ in this case).

From the comparison of the Osborne–Lee–Schlechter model curve (curve 2 of Fig. 4) and the Markov chain model (curve 3 of Fig. 4) it is clear that the latter is closer to the experimental points than the former. But the general advantage of the Markov chain model is that the g_i ($i = 1, 2$) values are determined directly from the experimental data and that their physical nature is more clear.

Example III

As an example of the anionic–anionic nonideal mixed surfactant system which will be analyzed by the proposed method is the sodium decyl sulfate (SDeS, S_1) – sodium dodecyl sulfate (SDS, S_2) mixture. It was studied in several laboratories [11,51]. As the head groups of both the surfactants are the same, the non-ideality would be related to the differences between the surfactant tails. The calculations by the Nagarajan [50] and Markov chain models of the mole fraction of SDeS in the mixed micelles at 25 °C as a function of the mole fraction of the same surfactant in the singly dispersed surfactant mixture are compared with the experimental data [51] in Fig. 5. One can see the very good correlation between the experimental and calculated values by both methods. But the calculations by the Markov chain model curve ($g_1 = 0.1$; $g_2 = 6.5$) are closer to the experimental points than those calculated by the Nagarajan model. The attempt to calculate this dependence by the regular solution approximation model failed for the variety of the β – values calculated on the base of CMC_{S1}, CMC_{S2} and CMC_{mix}.

As could be expected $g_1 < 1$ because SDeS tail is shorter than SDS one and $K_{11} < K_{12}$. For the same reason $K_{22} > K_{21}$, and $g_2 > 1$. The situation is the same as for the $KC_8 + KC_{14}$ or $KC_8 + KC_{10}$ mixed micelles when the close to zero β-value ($-\ln g_1 g_2 = 0.43$) shield the real nonideality of this mixed surfactant system.

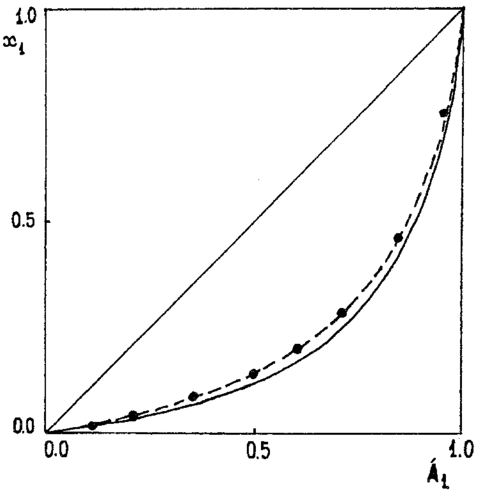


Fig. 5 Dependence of the mole fraction of SDeS in mixed SDeS (S_1) + SDS (S_2) micelles on the S_1 mole fraction in a singly dispersed surfactant mixture at 25 °C. The curves are calculated by the Nagarajan model [50] (continuous line) and by the Markov chain model (dotted line). The experimental data shown by the points are from ref. [51]

Example IV

Depending on the hydrophobic tail lengths, mixtures of anionic and cationic surfactants precipitate, or form mixed surfactant micelles or bilayer vesicles in curtain concentrations and compositions. Both phenomena are of large theoretical and applied interest and are now under active investigation [52–54]. The electrostatic repulsion between the same charged head groups and the electrostatic interaction between the different charged ones is a reason for $K_{ii} \ll K_{ij}$ and $g_i \ll 1$ ($i = 1, 2$; $i = j$). As a consequence the mixed micelles with an approximately equimolar composition is formed regardless of the composition of the singly dispersed surfactant mixture. It is interesting to follow the additional effect of the tail length on the alternating tendency in the mixing micelle formation between trialkyl ammonium bromides and sodium alkylsulfates. Some months ago this work was made by Yu and Zhao [55] for $C_mN^+(C_2H_5)_3$, Br (S_1) and $C_nSO_4^-$, Na$^+$ (S_2) surfactant mixtures with different m/n ratios (m/n = 10/10, 8/8, 8/10, 8/12 and 7/12) in 0.1 M NaBr at 25 °C. At first, it was established that there was considerable deviation of the calculations by the regular solution approximation mixed micelle composition from the experimental ones (Fig. 6). The calculations by Markov chain model curves are far closer to the experimental points than the regular solution model curves as one can see in Fig. 6.

The relationship between the g_i ($i = 1, 2$) values and m/n ratio values is presented in Table 1. One can see the smaller correlation between the m/n ratio the smaller the g_1 and greater the g_2 values become. This relationship is the result of the one direction joint effect of the steric hindrance between the S_1 head groups and of the decrease of the S_1–S_1 and S_1–S_2 tail hydrophobic interaction with the reduction of the m/n value. That is why K_{11} decreases but K_{12} increases with the decrease in m/n whilst K_{22} increases and K_{21} decreases in the same situation (m/n reduction). It will be interesting to study the same kind of mixed surfactant micelles when the m/n ratio increases and both the above mentioned effects act in opposite directions.

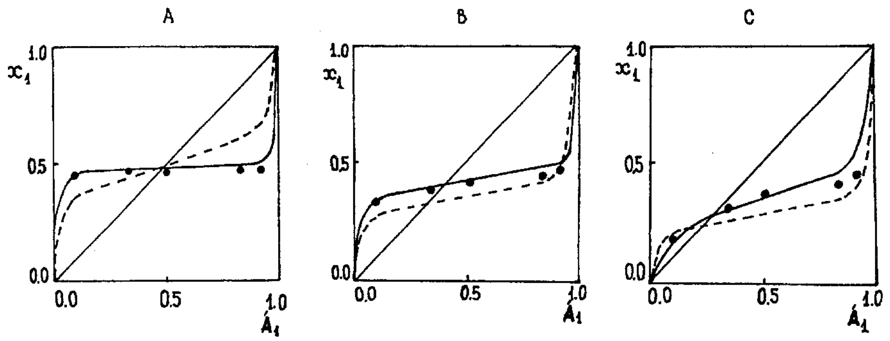


Fig. 6 Mole fraction of $C_mN^+(C_2H_5)_3$, Br^- in a mixed $C_mN^+(C_2H_5)_3$, Br^- (S_1) - $C_nSO_4^-$, Na^+ (S_2) micelles at 25 °C in 0.1 M NaBr as a function of S_1 mole fraction in a singly dispersed surfactant mixture ($\hat{A}_1$), obtained experimentally [55] (points) and calculated by the regular solution approximation (dotted lines) [55] and Markov chain (continuous lines) models. Fig. 9a. $m/n = 10/10$; Fig. 9b. $m/n = 8/10$; Fig. 9c. $m/n = 8/12$

Table 1 Correspondence between m/n ratio and g_i ($i = 1, 2$) values for the $C_mN^+(C_2H_5)_3$, Br^- (S_1) + $C_nSO_4^-$, Na^+ (S_2) mixed micelles in 0.1 M NaBr at 25 °C

N	Cationic surfactant (S_1)	Anionic surfactant (S_2)	m/n	g_1	g_2	$-\ln g_1 g_2$
1.	$C_{10}N^+(C_2H_5)_3$, Br^-	$C_{10}SO_4^-$, Na^+	10/10 = 1, 0	$3 \cdot 10^{-3}$	$2.5 \cdot 10^{-2}$	7.51
2.	$C_8N^+(C_2H_5)_3$, Br^-	$C_{10}SO_4^-$, Na^+	8/10 = 0.8	$1 \cdot 10^{-3}$	$1.5 \cdot 10^{-1}$	8.80
3.	$C_8N^+(C_2H_5)_3$, Br^-	$C_{12}SO_4^-$, Na^+	8/12 = 0.67	$1 \cdot 10^{-4}$	$6.8 \cdot 10^{-1}$	9.60

On the other hand, the hydrophobic interaction has an opposite effect on the electrostatic interaction effect provided in this manner a basic alternating tendency in the surfactant addition to the forming micelles as in this case. Actually, the lower the m/n ratio the stronger the hydrophobic interaction between S_2 tails and the more considerable the deviation of the micelle composition from the equimolar one.

It is worthwhile to mention that this analysis of the weaker hydrophobic interaction compared the electrostatic effect on the mixed $S_1 + S_2$ micelles in this case, is impossible to make in the case of the regular solution approximation model. Indeed the decrease of the value ($-\ln g_1 g_2$ decrease in Table 1) shows that the approach of the $S_1 + S_2$ surfactant mixture to the ideal mixture behaviour with the m/n value decreasing, but it is impossible to relate this approach to definite surfactant molecular characteristics. The Markov chain model enables this relations to be made quantitatively.

Conclusion

From the last part of the Results and discussion section it is clear that the experimental information about the micelle composition as a function of the singly dispersed surfactant mixture composition can be described, with good confidence, by the Markov chain model proposed here. It is worthwhile to mention that using this model the mixture micelle composition curves can be produced for the system whose behaviour is not described by the regular solution approximation model or the surfactant molecular characteristics necessary for calculations by the molecular models (Nagarajan et al. [50], Osborne-Lee et al. [43] etc.) are not available. In this case the confidence between the calculated and the experimental results is much better than that of the regular solution approximation model and a little better or equal than that of the molecular models. At the same time, the necessary initial information for the application of the Markov chain model is less than that for the other models (CMC which can be determined by one of the numerous experimental methods [11, 55, 56, 57–63] and the initial surfactant concentrations).

The g_i ($i = 1, 2$) values are unity for the ideal mixed surfactant system behaviour and reflect the nonideality better than the parameters. There are two general differences between the β and g_i ($i = 1, 2$) parameters. The first one is that g_i ($i = 1, 2$) parameters include the entropy effect on the surfactant aggregation while the β parameter accounts for the enthalpy effect only. The second is that g_i ($i = 1, 2$) parameters allow the decomposition of the nonideality of the mixed surfactant system behaviour in two parts and to relate each of them to two surfactant molecules. This is a very useful peculiarity of the discussed models it allows a more precise analysis of the nonideal behaviour and approaches this model to molecular ones. Moreover the special nonideality when $\beta = 0$, $g_1 g_2 = 1$, but $g_1 \neq 1$ and $g_2 \neq 1$ can be revealed also. In this connection it is important to note that the next stage of the proposed model development is the introduction of new generalized surfactant molecular characteristics allowing the calculation of g_i ($i = 1, 2$) values without any experimental information. Then the possibility of prediction of the Markov chain model will increase considerably.

The general assumption of the Markov chain model is that the preference of the forming surfactant aggregate to one or another surfactant molecule depends on the molecular characteristics of the last surfactant molecule added to a forming aggregate. This suggestion separates the Markov chain model from other models which are the modification of the classical pseudophase model for micelle formation [6, 64]. It requires an independent verification and probably will be a subject of many critical remarks. For all that it defends itself through the possibility of the Markov chain model to describe the mixed surfactant system behaviour better than other models. Now it seems an unrealistic assumption, but for the purpose to describe and predict the mixed surfactant system behaviour it is a good approximation. At the same time it is a good theoretical challenger also.

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