

PHYSICAL CHEMICAL STUDIES OF SHORT-CHAIN LECITHIN HOMOLOGUES. IV. A SIMPLE MODEL FOR THE INFLUENCE OF SALT AND THE ALKYL CHAIN LENGTH ON THE MICELLAR SIZE

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A simplified association model for micellisation is presented. In this model two features are incorporated: (a) There is an optimum for the change of the standard free energy per monomer upon micellisation at a certain association number. (b) At higher association numbers this free energy change becomes constant. The resulting equations for the dependence of the average micellar weight on the concentration are used to explain the experimentally observed effects of a salting-out agent (NaCl) and of the alkyl chain length of dihexanoyl-, diheptanoyl- and dioctanoyl-lecithin.

1. Introduction

In a previous paper, part II of the series [1], we found that the micellar size of dihexanoyllecithin (diC_6 -) increased only slightly with the lecithin concentration, whereas the concentration dependence of the diheptanoyllecithin micellar size was more pronounced. In part III [2] we saw that the diC_8 -micellar weight increased very steeply with the micellar concentration. We also noted that a salting-out agent (NaCl) increased the steepness of the micellar weight-concentration curve. In this paper we explain these phenomena semiquantitatively with the help of the multiple equilibrium model [3-5]. More specifically we worked out a modified open association model, based upon the work of Mukerjee [5].

2. Association model

2.1. Equations

One of the characteristic properties of many aqueous micellar solutions is the absence of appreciable amounts of aggregates with very low association numbers (i), except for some cases where the presence of dimers has been suggested [6]. This means that the as-

sociation constants (k_i) for low values of i are relatively small. At infinite dilution k_i is defined by

$$k_i = C_i / (C_{i-1} C_1); \quad i = 2, 3, \dots \quad (1)$$

where C_i equals the molar concentration of the i -mer. At higher concentrations eq. (1) still holds if the activity coefficient f_i of each micellar species (and of the monomers) is given by [1, 2]

$$\ln f_i = M_i (B_1 C + B_2 C^2 + \dots). \quad (2)$$

B_1 and B_2 are constants. C is the total solute concentration. It depends on the behaviour of k_i as a function of i whether the micellar size distribution will be wide or narrow. If the association constants for high i are all comparable in value the distribution will be wide and the average micellar size will increase with the micellar concentration. In the "open association model" k_i is assumed to be independent of i . This implies that the standard free energy change of micellisation per monomer is independent of the association number. Such a behaviour can indeed be expected for large non-ionic micelles, where the shape strongly departs from the spherical. For smaller micelles we would expect k_i to depend on i : k_i will probably increase with i up to a

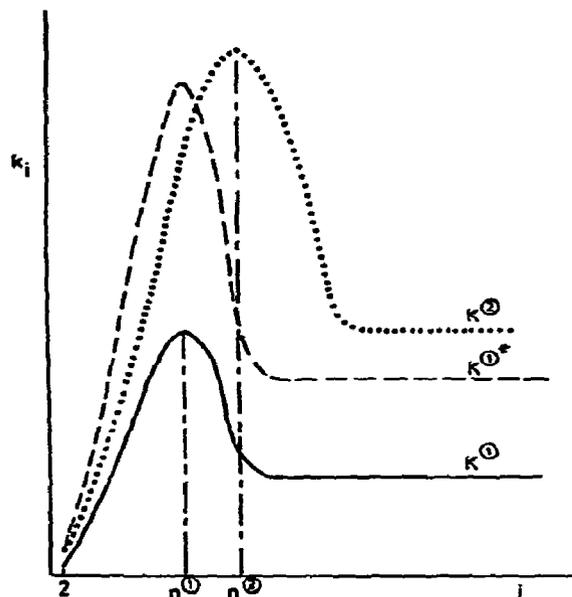


Fig. 1. A schematic picture of the dependence of the association constant k_i on the association number i . The fully drawn line represents the dependence for homologue 1 in salt free solutions. After addition of a salting-out agent the broken line (---) is obtained. The dotted line (···) represents the dependence in salt free solutions for a higher homologue.

certain value of i , where energetically favourable micelles are formed. In an extreme model we might visualize the smallest possible micelle to be a sphere with little hydrocarbon-water contact. These micelles may further grow to disks, oblate or prolate ellipsoids or cylinders if the surfactant concentration is increased. k_i might have a pronounced maximum at a certain value of i , where we assume a transition from "small" to "large" micelles. We will denote this association number by n . For nonionic surfactants, such as our zwitterionic lecithins, we may assume the value for n to be determined primarily by geometrical parameters of the monomer molecule.

In fig. 1 a general picture of the dependence of k_i on the association number is presented.

In the following derivations a sharp transition between the small and the large micelles (where all association constants are taken to be equal) is assumed. This modified open association model results in

$$K_n = C_n / (C_1)^n = \prod_{i=2}^n k_i \quad (3)$$

and

$$K = C_{n+j} / (C_{n+j-1} C_1). \quad (4)$$

We now assume the concentrations of the micelles with $i < n$ to be negligible, that is we assume all k_i ($i < n$) to be small and k_n to be very large so that $K_n = \prod_{i=2}^n k_i$ obtains a suitable finite value.

The equivalent micellar concentration $E - C_1$ (micellar concentration expressed in amounts monomer per unit volume) and the weight average micellar association number N_w are found from

$$E - C_1 = \sum_{i=2}^{\infty} i C_i = \sum_{i=n+1}^{\infty} i C_i + n C_n \quad (5)$$

and

$$N_w = \frac{\sum_{i=2}^{\infty} i^2 C_i}{E - C_1} = \frac{\sum_{i=n+1}^{\infty} i^2 C_i + n^2 C_n}{E - C_1}. \quad (6)$$

Using eq. (4) and solving the resulting binomial series, in analogy to Mukerjee's procedure [5], we obtain

$$E - C_1 = C_n \left(\frac{n}{1-X} + \frac{X}{(1-X)^2} \right) \quad (7)$$

and

$$N_w = n + \frac{X}{1-X} + \frac{X}{(1-X)^2 [n + X/(1-X)]} \quad (8)$$

$$\text{where } X = K C_1. \quad (9)$$

At high concentrations in a polydisperse micellar system the following approximation will be valid: $X = 1 - \delta$ with δ approaching zero as the concentration increases.

Using this approximation for $\delta \ll 1/n$ and combining eqs. (3), (7) and (8) we find

$$\begin{aligned} N_w &= 2(K^{n-1}/K_n)^{1/2} [(E - C_1)/C_1]^{1/2} \\ &= 2(K/K_1)^{(n-1)/2} (c_m/c_1)^{1/2}, \end{aligned} \quad (10)$$

where c_m equals the total micellar concentration in mass per unit volume and c_1 is the monomer concentration (\approx CMC). K_1 is the geometric average of the

association constants for the small micelles

$$K_1 = \left(\prod_{i=2}^n k_i \right)^{1/(n-1)} \quad (11)$$

Eq. (10) is analogous to Mukerjee's [5] eq. (26); only the proportionality factor is different: Mukerjee explicitly used $n = 2$.

2.2. Salt effects

The main influences of added electrolytes on the association properties of nonionic detergents originate from salting-out and salting-in effects [7, 8]. If n is mainly determined by geometrical factors, it should be reasonably independent of the salt concentration. In this case we must look for possible effects of the salt on K/K_1 . One may expect that the net effect of addition of salt is due to salting-out of the hydrocarbon part of the free monomer molecule (effects on the micelles cancel each other to a great extent in the calculation of the association constants), leading to an increase of the standard free energy of micellisation per monomer which is independent of the micellar size. This results in an increase of all association constants k_i by the same factor f as shown in fig. 1 (broken line).

$$k_i^* = k_i f \quad (\text{for all values of } i \geq 2) \quad (12)$$

and also

$$K_1^* = K_1 f. \quad (13)$$

If this is correct eq. (10) shows that the weight average micellar weight at a given value of c_m/c_1 is independent of the salt concentration. The monomer concentration c_1^* (\approx CMC*) will of course be lowered by a factor f with respect to c_1 (in salt free solutions).

2.3. Influence of the hydrocarbon chain length

Geometrical factors will undoubtedly lead to an increase of n with increasing chain length. K and K_1 will also increase. The dependence of K/K_1 on the chain length is, however, more complicated.

The area per molecule measured at the surface of the hydrocarbon core of densely packed spherical

micelles with a diameter proportional to the chain length is independent of the chain length. In larger elongated micelles of the same packing density and diameter the area per molecule will be smaller than in the case of spherical micelles. Therefore the packing of the parts of the chain close to the head groups will be more constrained (smaller number of possible configurations) for large micelles than for small ones. On elongating the chains this effect will become relatively less important, leading to an increase of K/K_1 with increasing chain length (see dotted curve in fig. 1).

For ionic surfactants the repulsive forces are thought to reside mainly in the polar parts, which extend away from the hydrocarbon core surface. The area per head group, measured at some distance outside the core, in small densely packed spherical micelles decreases on elongation of the alkyl chain length. The repulsive forces will therefore increase with the chain length. The area per head group in elongated micelles will be less dependent on the chain length. K/K_1 will therefore increase for ionic surfactants. For zwitterionic micelles the situation is more complicated since depending on the orientation of the dipoles attractive or repulsive forces exist. A decrease in the area per head group changes the electrostatic interactions and the number of possible configurations of the polar parts. Probably the radius of curvature of the micellar surface is also very important. A general rule for the dependence of K/K_1 on the chain length is difficult to derive.

A slight increase of K/K_1 together with the increase in n will lead to a much steeper increase of N_w with $(c_m/c_1)^{1/2}$ for higher surfactant homologues.

3. Interpretation of the experimental data in terms of this association model

We will now apply this association model to the results of the micellar weight determinations given in part II and III of this series [1, 2]. In fig. 2 we have plotted the weight average association number of the three homologues (diC₆-, diC₇-, diC₈-) as a function of $(c_m/c_1)^{1/2}$. On the basis of these data, n , K and K_1 can in principal be determined. The accurate evaluation, especially of n and K_1 is hampered by the uncertainties in the thermodynamic nonideality and the difficulties of measuring at low micellar concentrations.

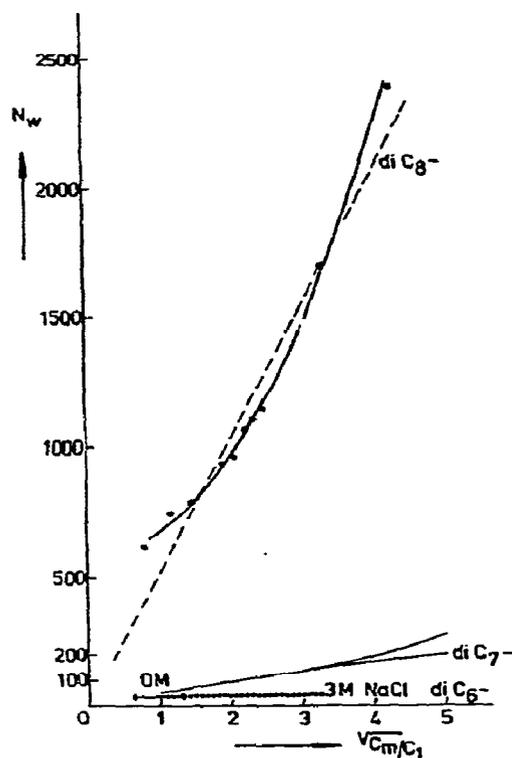


Fig. 2. The idealised weight average association number for three lecithin homologues as a function of the square root of the ratio of the micellar and monomer concentration. The data were taken from parts II and III of this series [1, 2]. The broken line for diC_8^- was calculated from $N_w = 2.38 \times 10^7 / 526.5 (c_m/c_1)^{1/2}$ (the first term from the curve fitting performed in part III [2]). The two lines for diC_7^- originate from two micellar models (part II [1], fig. 15, curve I and II). The fully drawn line for diC_6^- refers to NaCl free solutions while the dotted line refers to solutions containing 3M NaCl.

Dihexanoyllecithin. The weight average micellar weight increases slightly with the micellar concentration. The system is therefore relatively monodisperse and because $X = KC_1$ is too small compared to unity the approximate eq. (10) cannot be applied (a numerical value for X will be given later on). The parameters n , K and K_1 were therefore obtained by numerical curve fitting procedures (least squares) using eqs. (3), (7) and (8). The experimental data were first corrected for nonideality using the excluded volume of rigid non-interacting particles [1]. The geometrical model

in which all micelles are assumed to be spheres (part II, model I, fig. 11) is incompatible with this association model (polydisperse system with k_i independent of i for $i > n$). We therefore used the data where the micelles were visualised as spherocylinders with little hydrocarbon-water contact. The two sets of values for the parameters n , K and K_1 , given in table 1 (a) and (b), were calculated using outer radii of 15Å and 18Å respectively (part II, model II, figs. 13 and 14). From table I we also see that addition of 3M NaCl has virtually no influence on n and K/K_1 in accordance with our assumptions (section 2.2).

In NaCl free solutions the monomer concentration ($\approx \text{CMC}$) is largely determined by K_1 and is around 7 mg/ml [1, 8]. With $K = 56 \text{ l mole}^{-1}$ we find X to be 0.83 ($M = 471.5$). The standard free energy of micellisation per monomer (ΔG°) is in this case calculated from $-[RT(n-1)/n] \ln K_1$. For the higher homologues the monomer concentration rapidly approaches $1/K$ leading to $\Delta G^\circ = -RT \ln K$. Since K_1 is smaller than K we would expect the difference in ΔG° between diC_7^- and diC_6^- to be larger than the difference between successive higher homologues. This effect has indeed been observed (part I of this series, fig. 5) [8].

Diheptanoyllecithin. In our previous paper [1] we already saw that a plot of N_w versus $(c_m/c_1)^{1/2}$ was essentially independent of the salt concentration (part II, figs. 16 and 17). Using eqs. (3), (7) and (8) we can in principle find values for n , K and K_1 , but many different combinations of values give virtually the same micellar weight-concentration dependence except for the very low concentration range ($c_m/c_1 \leq 1$) where the experimental accuracy is low. The data given in table 1 were obtained using the two micellar models (for the calculation of the excluded volume): (c) compact spherocylindrical micelles with radii of 19Å, which disregards the hydrocarbon-water interface (part II, model I, fig. 15, curve I) and (d) micelles with radii of 16Å and hydrocarbon cores (core radius 9.1Å) with as little water contact as possible (part II, model II, fig. 15, curve II). Especially in this latter case the range of applicable values n and K_1 is very large. The two limiting sets of data are given in table 1 (diC_7^- d). The results from the micellar model with outer radii of 19Å and little hydrocarbon-water contact (core radius 9.1Å) are incompatible with the present association model, since the curve of N_w versus $(c_m/c_1)^{1/2}$ is curved upwards (part II, fig. 17). This

Table 1
Parameters of the association model for three lecithin homologues

Lecithin	NaCl conc. (mole ℓ^{-1})	K (ℓ mole $^{-1}$)	K/K_1	n
diC ₆ - (a)	—	58	1.05 (\pm 0.02)	28.0 (\mp 0.4)
	3	332	1.055 (\pm 0.01)	27.2 (\mp 0.4)
diC ₆ - (b)	—	60	1.107 (\pm 0.01)	26.9 (\mp 0.5)
	3	337	1.09 (\pm 0.01)	26.2 (\mp 0.6)
diC ₇ - (c)	—	700	1.22 (\pm 0.01)	30.9 (\mp 1)
diC ₇ - (d)	—	700 {	> 1.25	< 29.7
			< 679	> 2
diC ₈ -	—	4050 {	> 1.1	< 117
			< 66400	> 2

The errors in K are about 5 to 10% and stem from the inaccuracy of the CMC determinations [1, 2, 8]. The errors in brackets in column 4 and 5 give the coupled ranges of acceptable values for K/K_1 and n .

effect may be due to the neglect of higher virial terms.

Diocanoyllecithin. In this case eq. (10) is, for low values of n , a very good approximation of the combined eqs. (3), (7) and (8) and the range of applicable combinations of n and K_1 is therefore still larger. The two limiting sets are again given in table 1. Assuming for instance n to equal 40 or 50 we obtain K/K_1 to be 1.33 or 1.26 respectively. These values seem in the right order of magnitude as compared to the results from dihexanoyl- and diheptanoyllecithin.

4. Conclusions

The association model elaborated in this paper fits all our experimental observations regarding the influence of added salt and the chain length on the concentration dependence of the micellar weight of the lecithin homologues. Accurate determination of n from the theory is only possible if experiments are ex-

tended to micellar concentrations which are low in respect to the CMC, which was impossible for dioctanoyllecithin. Analysis on diheptanoyllecithin is hampered by the large influence of uncertainties in the thermodynamic nonideality corrections.

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