SIZE, SHAPE AND SIZE DISTRIBUTION OF MICELLES IN AQUEOUS SOLUTIONS OF SHORT-CHAIN LECITHIN HOMOLOGUES

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Micelle formation in dilute aqueous solutions of three synthetic lecithin homologues with equal fatty acid ester chains of 6, 7 or 8 carbon atoms is described. The average micellar weight increases with lecithin concentration. This effect becomes more pronounced on increasing the lipid chain length and the concentration of the salting-out electrolyte NaCl. This phenomenon is in agreement with a stepwise open association equilibrium model in which the standard free energy of micellization per monomer is independent of the micellar size (above a certain minimum size), but increases with the chain length and salt content.

I. INTRODUCTION

Studies on the association of lipid molecules are of great importance to come to understand the large numbers of problems encountered in research on biological membranes and lipid-protein interactions. The interactions between lipids and proteins can strongly depend on the structure of the individual lipid molecules. In some enzymatic reactions (1) it is the association structure of the lipid that plays a very important part. To obtain a better understanding of the factors governing lipid association, we studied lecithin homologues containing two hydrocarbon chains of equal length (2). To this end we synthesized lecithin molecules with fatty acid ester chains of 6, 7 and 8 carbon atoms. The structure of the diheptanoyl-lecithin (= di-C_7) is shown in Fig.1.

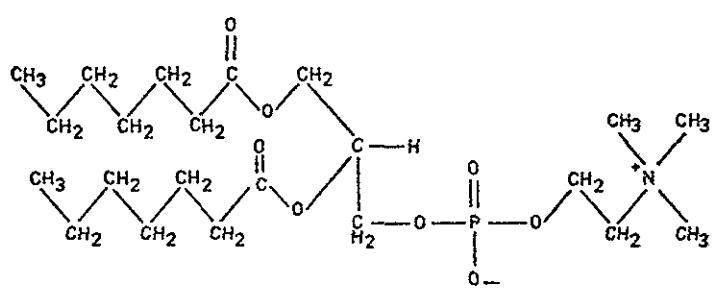

Fig.1. Diheptanoyllecithin (= di-C_7)

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The di-C_9 is the lowest homologue that associates into the familiar lamellar structures at very low concentrations. The lecithins with chains of 6 or 7 carbon atoms, on the other hand, show normal micelle formation (2b). Di-C_8 is a borderline case: depending on the electrolyte content, a phase separation occurs (2c), salting-out and salting-in being observed at high concentrations.

Electrolytes at high concentrations (C_s) also have an influence on the critical micelle concentrations (CMC) and their effect can be expressed by (2a)

$$\log(CMC)_{C_s} = \log(CMC)_{C_s=0} - k\,C_s \qquad [1]$$

in the following table (1) we give a few relevant data for the CMC's of the synthetic lecithins and the effect of NaCl.

TABLE 1
Critical Micelle Concentrations of the Lecithin Homologues and the Effect of NaCl Addition (see eq.[1])

	$(CMC)_{C_s=0}$ in g/l	k_{NaCl} in l/mol
di-C_6	6.9	0.26
di-C_7	0.71	0.21
di-C_8	0.14	
di-C_9	0.016	

From a purely physical chemical point of view, too, the micelle formation of these compounds is of importance, since the molecules (i) contain two hydrocarbon chains and (ii) have no net charge, which simplifies the interpretation of thermodynamic data. This last property is especially important in connection with the demonstration of micellar size distributions . With ionic surfactants, the large deviations from thermodynamic ideality caused by the repulsive forces originating from electrical charges obscure the size distributions of the micelles.

This paper will first deal with an association model giving rise to polydisperse micellar systems (2d). Specifically, we will discuss the dependence of the average micellar size on the concentration and chain length of the surfactants and on the salt concentration. We then deal with the interpretation of light scattering and sedimentation equilibrium experiments on

di-C_6 and di-C_7 in terms of average micellar weights. Here thermodynamic nonideality is taken into account on the basis of the excluded volume of rigid particles and association is described in terms of the mass action law. Thereafter, we will describe micelle formation of the di-C_8 homologue. This lipid associates into very large micelles and a strong angular dependence of the light scattering was observed. The results for the different lecithins will then be discussed in terms of our theory for the formation of polydisperse micelles.

II. MODEL FOR MICELLAR POLYDISPERSITY

Our model for micellar polydispersity is based on association equilibria between monomers and micelles (2d). The theory is an extension of the work of Mukerjee (3).

We define the equilibrium constants, k_i, with the following equation:

$$L_{i-1} + L_1 \rightleftarrows L_i \quad ; \; k_i = \frac{C_i}{C_{i-1} \times C_1} = \frac{C_i}{\prod_2^i k_i (C_1)^i} \qquad [2]$$

where L_1 represents a monomer molecule and L_i a micelle with association number i. C_i stands for the micellar concentration in amounts per unit volume. This equation holds at very low concentrations and also at higher concentrations if the chemical potential (μ_i) of each species can be described by eq.[3], as is often a good approximation.

$$\mu_i = \mu_i^o(P,T,c') + RT \ln c_i + RTM_i (B_1 c_t + B_2 c_t^2 + \ldots) \qquad [3]$$

The standard condition is defined at constant pressure, temperature and concentration of all other solute components. c_t is the total lipid concentration, now in mass per unit volume. B_1, B_2, etc. are constants and independent of the molecular weight M_i.

A distribution in association constants will always lead to a micellar weight distribution and both distributions are intimately connected.

At low association numbers the hydrocarbon chains in the micelles are only partly in contact with each other and an appreciable hydrocarbon-water contact remains. As the decrease in this hydrocarbon-water contact is the main driving force for micellization these small micelles will have relatively small stability constants.

Increasing the association number will result in cooperative effects on the change in free energy of micellization,

and k_i will increase. Addition of a monomer to an "incomplete" micelle will decrease the alkyl chain - water contact area of all the molecules already present in the associate. At a certain micellar size with association number i = n the most efficient packing of the molecules will occur. For the sake of simplicity one could visualize such a micelle as a sphere with radius equal to the length of the hydrocarbon tail of the molecule.

If the micelle grows beyond this size, its shape will have to change and prolate or oblate ellipsoids, cylinders or discs will be formed. For these large micelles the change in free energy of association becomes independent of the association number. This common association constant will be denoted by K. In Fig.2 (solid line) we give the expected general shape of the dependence of k_i on i.

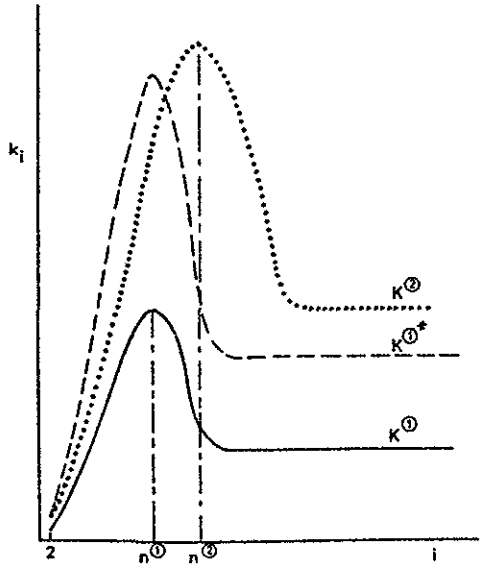

Fig.2. A schematic picture of the dependence of the association constant k_i on the association number i. The full line represents the dependence for homologue 1 in salt-free solutions. After addition of a salting-out agent the broken line is obtained. The dotted line represents the dependence in salt-free solutions for a higher homologue.

The concentration of micelles with i = n is given by

$$\frac{C_n}{C_1} = \Pi_2^n k_i (C_1)^{n-1} \equiv (K_1 C_1)^{n-1} \qquad [4]$$

in which we define K_1 as the geometrical average of all associ-

ation constants between 2 and n. At or above the critical micelle concentration the product K_1C_1 is quite near unity.

We now introduce two simplifications:

(i) Since the concentrations of micelles with $i < n$ will be much smaller than C_n, we ignore them.

(ii) We assume the association constant K to apply to all micelles with $i > n$.

These assumptions give rise to a sharp transition between stability constants of "small" and "large" micelles and to a distribution as depicted in Fig.3.

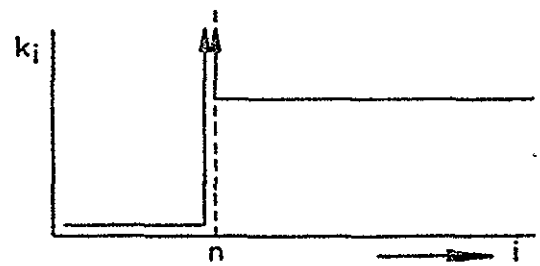

Fig.3. A simplified picture of the dependence of k_i on i.

The equivalent micellar concentration ($E_m = E_t - C_1$), expressed in amount monomer per unit volume, can now be calculated as a function of K_1, K, n and C_1, and with straightforward algebra we find:

$$E_t - C_1 = C_n \left(\frac{n}{1-X} + \frac{X}{(1-X)^2}\right) \qquad [5]$$

with $X \equiv kC_1$. Likewise we find for the weight average micellar association number:

$$N_w \cong \frac{\Sigma\, i\, C_i}{\Sigma\, C_i} = n + \frac{X}{1-X} + \frac{X}{(1-X)^2\left(n + \frac{X}{1-X}\right)} \qquad [6]$$

For the micellar sizes to remain finite X must be smaller than unity.

For the dependence of N_w on C_t two important rather extreme situations can be distinguished:

(i) $1/n < 1 - X < 1$. This condition leads to micellar systems with narrow size distributions and $N_w \approx n$.

(ii) $1 - X < 1/n \ll 1$. In this case wide size distributions are obtained and N_w can be approximated by

$$N_w = 2\,(K/K_1)^{\frac{n-1}{2}}\,(c_m/c_1)^{\frac{1}{2}} \qquad [7]$$

The concentrations are now expressed in mass per unit volume. c_m is the micellar and c_1 the monomer concentration ($\approx$ CMC). Wide distributions can only occur if K is somewhat larger than K_1; otherwise K_1C_1 approaches unity faster than KC_1 and C_n will strongly dominate all other micellar concentrations.

A. Effect of Addition of Electrolytes

Electrolytes exert an influence on the critical micelle concentrations. For nonionic or zwitterionic surfactants these phenomena are often described with the general terms of salting-out or salting-in effects on the activity of the free monomer molecules. On the basis of this theory Mukerjee (4) derived eq.[1].

Salt effects on uncharged micelles with result in a change in free energy of micellization per molecule independent of the micellar size, so that we expect all constants k_i in eq.[2] to change by the same factor. This means that K and K_1 will both change and that their ratio will remain approximately constant. As the value of n for these types of surfactants will mainly be determined by the geometry of the molecules, we furthermore expect n to be independent of the electrolyte content. The expected change in the dependence of k_i on i on addition of a salting-out agent is shown in Fig.2. As a consequence, the plot of N_w versus c_m/c_1 (see eq.[7]) will not be affected by the addition of salt. At constant micellar concentration, c_m, however, large effects on average micellar weights can occur due to changes in c_1.

B. Effect of Chain Length

Geometrical factors will undoubtedly lead to an increase in n with increasing chain lengths. K and K_1 will also increase. The change in the ratio K/K_1, however, is more difficult to predict.

The area per molecule at the surface of the hydrocarbon core of densely packed spherical micelles with diameters 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. The packing of the parts of the hydrocarbon chain close to the surface of the hydrocarbon core will be more constrained (smaller number of possible

configurations) for large micelles than for small ones. On elongation of the carbon chains, this effect will become relatively less important, leading to an increase in K/K_1 (see dotted curve in Fig.2).

If repulsive forces between the polar groups, which extend away from the hydrocarbon core, are considerable, as in the case of ionic surfactants or strongly hydrated nonionics, another mechanism is also operating. The area per head group measured at some fixed distance outside the core of small densely packed spherical micelles decreases with elongation of the hydrocarbon chain. The repulsive forces will therefore increase with the chain length. The area per head group in strongly elongated micelles, however, will be less dependent on the chain length, and an increase in K/K_1 can be expected. For zwitterionic micelles the situation is more complicated, since depending on the orientation of the dipoles attractive or repulsive forces exist. The change in area per molecule will change the electrostatic interactions and the number of possible configurations of the polar groups.

The combined increase of n and K/K_1 will result in a strong increase in N_w as a function of c_m/c_1. The effect of N_w at fixed c_m will, of course, be even much greater, due to the decrease in the CMC with increasing chain length.

C. Ionic Micelles

In principle, the association model outlined above is also applicable to ionic micelles, but the long range repulsive forces between the polar groups will strongly oppose the formation of larger micelles. Beyond $i = n$, k_i will therefore strongly decrease before approaching the constant value K and the micelles will be rather isodisperse. An increase of the salt content or of the surfactant concentration will be accompanied by a decrease in the electrostatic interactions. An increase in k_i and in polydispersity are expected.

III. MICELLAR WEIGHT DETERMINATION OF Di-C_6 AND Di-C_7

A. Method of Evaluation

Micelle formation of the synthetic lecithins di-C_6 and di-C_7 was studied with light scattering and ultracentrifugation. Details of the experiments and the procedures for calculating the micellar weights are described extensively in ref.2b. Here we will only briefly discuss the general approach.

Average total molecular weights, thus including monomer contributions, were calculated from equations for multicomponent systems (2b, 5, 6, 7):

$$\frac{K^1 c_t}{R_{90}} = \frac{1}{\sum_i f_i M_i n_i^2} + c_t \frac{\sum\sum_{ij} f_i f_j n_i n_j A_{ij}}{(\sum_i f_i M_i n_i^2)^2} \qquad [8]$$

and

$$\left(\frac{RT}{\omega^2 r c_t}\frac{dc_t}{dr}\right)^{-1} = \frac{1}{\sum_i f_i M_i \rho_i} + c_t \frac{\sum\sum_{ij} f_i f_j \rho_j A_{ij}}{(\sum_i f_i M_i \rho_i)^2} \qquad [9]$$

$K^1 = 2\pi n_o^2 \lambda_v^{-4} N_o^{-1}$, n_o = refractive index of solvent, λ_v = wavelength in vacuum, N_o = Avogadro's constant, R_{90} = excess Rayleigh ratio perpendicular to incident beam, c_t = total concentration in mass per unit volume, f_i = weight fraction of micellar species with association number i, n_i $(=\partial n/\partial c_i)$ = refractive index increment, R = gas constant, T = absolute temperature, ω = angular velocity, r = distance from centre of rotation and ρ_i $(=\partial\rho/\partial c_i)$ = density increment.

Experimentally, it was found that both the refractive and the density increments are smaller for micelles than for free monomers. We assumed the increments to be independent of the micellar size ($i \geq 2$).

The interaction parameter A_{ij} is related to the change of the activity coefficient γ_i of component i with the molar concentration of component j at constant solvent chemical potential, temperature and molar concentration of the other solutes.

$$A_{ij} = (\partial \ln \gamma_i / \partial C_j)_{\mu_o, T, C'} \qquad [10]$$

To assess the weight average micellar weights we will have to subtract the contributions of the free monomers. Generally, light scattering data from micellar solutions have been interpreted by using the Debye approximation, in which the monomer activity ($\approx$ CMC) is taken constant. Using this method, however, some details are lost, especially in the case of rather small micelles and at micellar concentrations comparable with the monomer concentrations. We therefore used an association model in which the change of the monomer activity with the micellar concentration is allowed for. A procedure to do this has been extensively discussed by Adams and Filmer (8). Their theory is based on association equilibria where the chemical potential of each species participating in the association reaction can be described by eq.[3]. The monomer weight fraction

(f_1) can then be obtained from the dependence of the weight average total molecular weight $\langle M \rangle_w$ on the surfactant concentration. This association model also gives the possibility of calculating the number average molecular weights $\langle M \rangle_n$. Estimates of the weight average total molecular weights can be obtained when eqs.[8] and [9] are multiplied by the z-average increments $\langle (\partial n/\partial c)^2 \rangle_z$ and $\langle \partial \rho/\partial c \rangle_z$, respectively.

To calculate the second terms on the right-hand sides of eqs.[8] and [9] we further need the weight fractions of the different micellar species. The specific micellar distribution function used has only a small influence on the calculated second virial coefficient and we assumed the Schulz distribution (7) to apply. This two-parameter function is easy to integrate and one of these parameters can be expressed as $\langle M \rangle_w / \langle M \rangle_n$, which in turn can be assessed from the experiments with the method of Adams. From the experiments we found $\langle M \rangle_w / \langle M \rangle_n$ for di-C_7 micelles to be around 2 and for di-C_6 around 1.05 to 1.1.

The last problem in the calculation of the micellar weights is the estimation of the interaction parameter A_{ij}. As electrostatic dipole intermicellar interactions are probably quite small, one could visualize the micelles as rigid particles, which only interact because of their finite sizes. A_{ij} is related to the pair correlation function (5) and can be obtained from the mutual pair excluded volume. Isihara and Hayashida (9) solved this problem for particles of arbitrary size and shape and arrived at

$$A_{ij} = N_o \, (v_i + v_j + (1/4\pi)(x_i s_j + x_j s_i)) \qquad [11]$$

where v_i stands for the volume of molecule i with surface s_i. x_i equals 4π times the average distance of the centre of particle j to the tangent plane with particle i. We assumed the free monomer to be spherical and the micelles to be spherical or spherocylindrical. Several spherocylindrical micellar structures with different packing densities have been used in these calculations.

Although in general the excluded volume model with eqs.[10] and [11] is in conflict with the use of eq.[3] , the assumption that this last equation is valid and that the method of Adams can be used to calculate the monomer concentrations does not lead to significant errors in micellar systems.

B. Results

Some of our results (2b) on di-C_6-lecithin are shown in Fig.4.

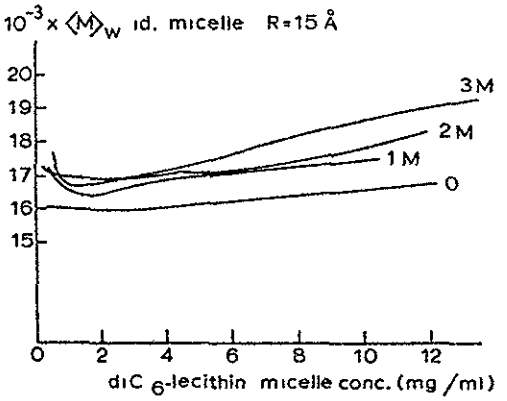

Fig.4. Weight average micellar weights, from light scattering, as a function of the di-C_6-lecithin micellar concentration, in aqueous solutions containing various NaCl concentrations. The micellar weights are corrected for non-ideality using the spherocylinder model with a radius of 15 Å.

The average micellar weights in the absence of added NaCl is around 16 000, which could correspond to spherical micelles with radii of 18 Å. This value is not unrealistic in view of the length of the whole monomer molecule. However, in this "compact" structure there is a substantial contact of the hydrocarbon part with the polar interface and elongated micelles are perhaps more probable.

One could also visualize the micelles in an alternative model, where the contact between the hydrocarbon part and the water and the polar groups is avoided (10). In this case we chose for a spherocylinder of which the radius of the hydrocarbon core is given by the length of the alkyl chains (≈ 7.8 Å). A sphere with this radius can only accommodate 6.2 monomers, where in fact an association number of around 35 was found. To accommodate the polar groups we assumed the outer radius of the cylinder to equal 15 Å. The results shown in Fig.4 were based on this last model. If the compact spherical structure is used in the evaluation of A_{ij} the calculated micellar weights increase somewhat less with the lecithin concentration (2b).

The average micellar weights of di-C_7-lecithin are shown in Fig.5. The different lines in this figure originate from different assumed micellar structures in the calculation of A_{ij}.

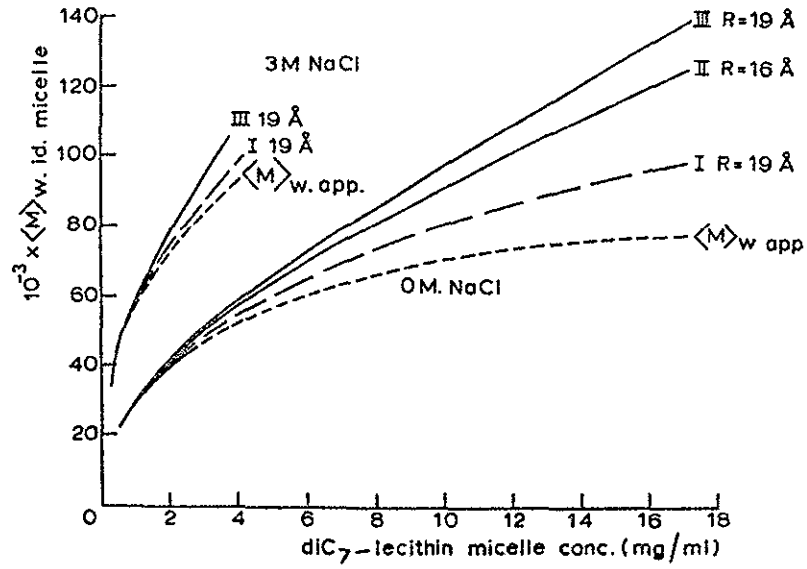

Fig.5. Weight average micellar weights of di-C_7-lecithin as a function of the micellar concentration in 0 M and 3 M NaCl (upper set of curves). The dotted lines represent the apparent weights. The broken lines I were obtained from the compact micelle model and the full lines II and III were derived from the spherocylinder model with outer radii of 16 Å and 19 Å respectively and with as little hydrocarbon-water contact as possible.

In case I we assumed micelles with weights below 20 000 to have compact spherical structures. Larger micelles then again have spherocylindrical shapes. In cases II and III we used the model in which the hydrocarbon-water contact was avoided and a thickness of 7 or 10 Å respectively was allowed for the polar groups.

From these experiments we conclude that:

(1) The micelles of di-C_6-lecithin have rather narrow size distributions. The weight average micellar weight, in the absence of added salt, is around 16 000 to 18 000 (association numbers ≈ 35) and increases only slightly with concentration. Addition of NaCl leads to a very limited increase of the average micellar weight and to a decrease in the CMC.

(2) Di-C_7-lecithin associates into micelles with a broad size distribution with average micellar weights between 20 000 and around 100 000. Accurate assessments of the micellar weights at high lipid concentrations are complicated by the relatively strong influence of the second virial coefficient. The specific assumptions concerning the micellar structure

do have an influence on the details of the results, but the overall conclusions remain unaltered. The ratio $\langle M \rangle_w / \langle M \rangle_n$ for the micelles is close to 2.

Addition of 3 M NaCl leads to a strong increase in the micellar weight at fixed micellar concentrations, accompanied by a decrease in the CMC by a factor of 4. Within our experimental accuracy NaCl has, however, no effect on the dependence of N_w on $(c_m/c_1)^{\frac{1}{2}}$, as is shown in Fig.6.

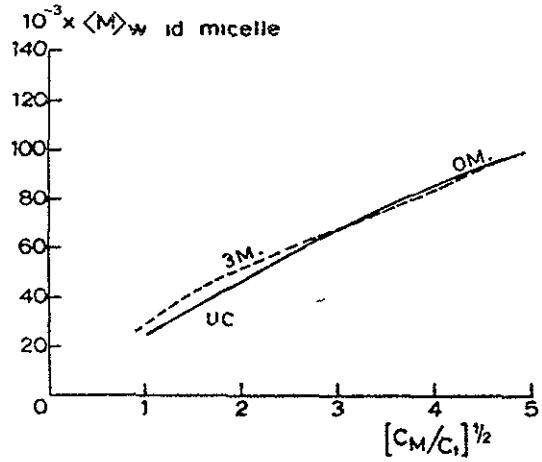

Fig.6. Ideal weight average micellar weights of di-C_7-lecithin as a function of the root of the ratio of micellar and monomer concentration. The molecular weights are idealized using the compact micelle model.
(——) = 0 M and (----) = 3 M NaCl.

In this graph the results from the "compact" micellar model are plotted Use of the micellar structure with little hydrocarbon-water contact (especially curve III in Fig.5) lead to a slight upward curvature when N_w is plotted versus $(c_m/c_1)^{\frac{1}{2}}$. In this case the thermodynamic non-ideality was probably somewhat overestimated.

IV. ASSOCIATION PHENOMENA OF Di-C_8-LECITHIN

Analysis of micelle formation of this lipid in electrolyte-free solutions is hampered by the appearance of a phase separation at concentrations slightly above the CMC. This demixing is sensitive to addition of electrolyte, and salting-out and salting-in phenomena can be observed at high salt concentrations. At lower concentrations (< 0.5 M) probably other electrostatic effects also play a role. In Fig.7 we have plotted the phase separation diagrams.

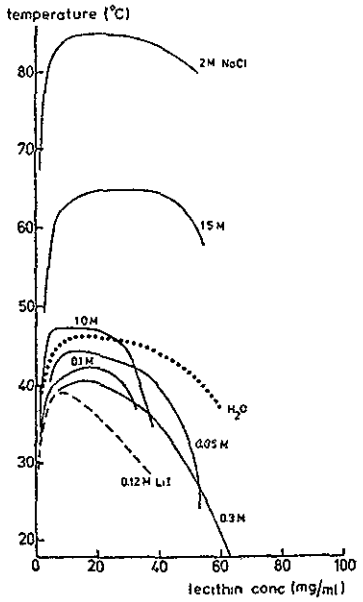

Fig.7. Phase separation diagrams of dioctanoyllecithin in aqueous solutions. The dotted line was obtained in electrolyte-free solutions. The full lines and the broken line refer to solutions containing NaCl and LiI, respectively.

The dependence of the critical temperatures on NaCl concentration is shown in Fig.8. LiI can suppress the demixing. Even in the presence of high concentrations of NaCl, addition of LiI leads to a decrease of the critical temperatures.

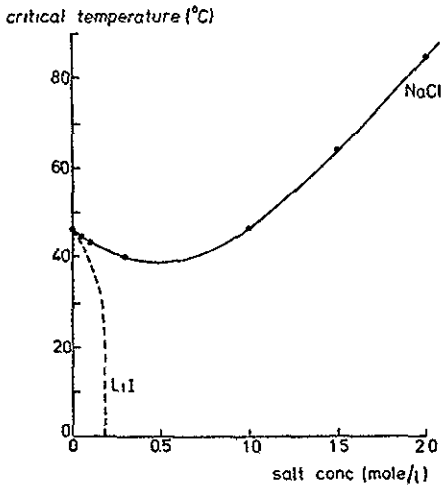

Fig.8. Critical temperatures of the phase separations as a function of the salt concentrations.

Micellar weight determinations were performed at room temperature after suppressing the phase separation with 0.2 M LiI. The micellar solutions, however, still show strong thermodynamic non-ideality, which hampers detailed analyses. The light scattering diagram (Zimm-plot) is shown in Fig.9.

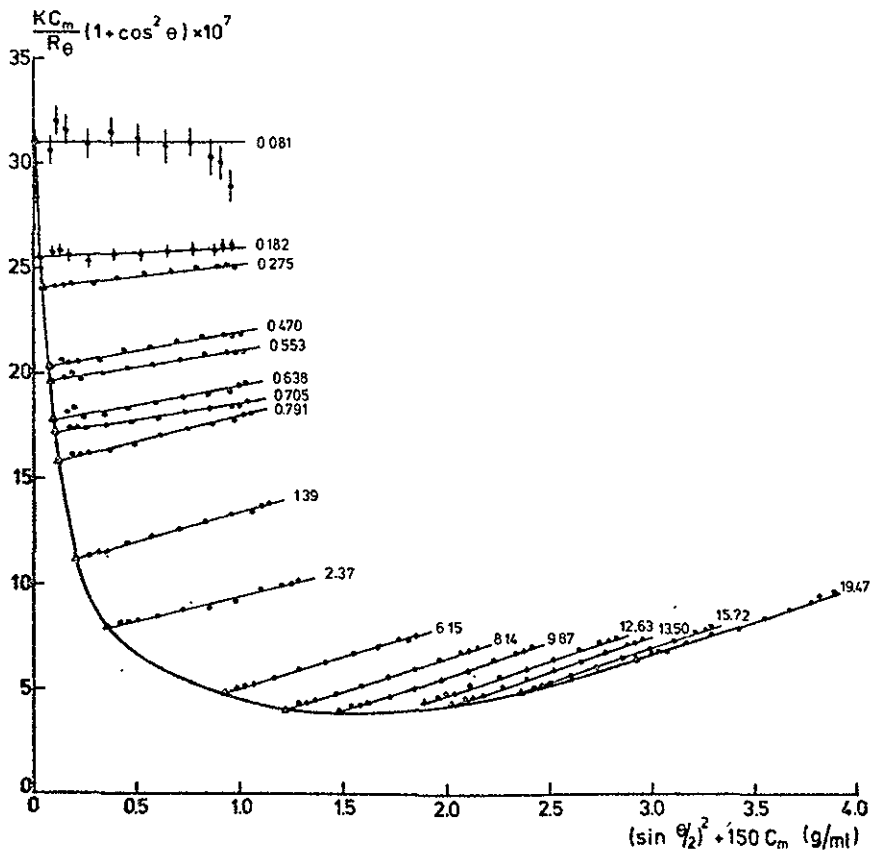

Fig.9. "Zimm plot" of dioctanoyllecithin at 25.0 °C, 0.2 M LiI and λ_v = 546 nm. The numbers to the right of the lines refer to micellar concentrations in mg/ml.

Since the CMC is low and association numbers are high, no appreciable errors are introduced by subtracting a constant monomer contribution instead of a variable concentration derived from association equilibrium equations. We attempted to interpret these data with the help of eqs.[12] and [13] (2c,11).

$$\frac{K c_m (1+\cos^2\theta)}{R_\theta} = \frac{1}{\langle M\rangle_{w.app.}} + \frac{16\pi^2 n_o^2}{\lambda_o^2} \cdot \frac{\langle r_g^2\rangle_z}{\langle M\rangle_w} \cdot \sin^2(\theta/2) \quad [12]$$

$$\frac{1}{\langle M\rangle_{w.app.}} = \frac{1}{\langle M\rangle_w} + A_2 c_m \quad [13]$$

K equals K^1 from eq.[8] and multiplied by $(dn/dc)^2_{micelle}$. $\langle r_g^2\rangle_z$ stands for the z-average radius of gyration squared and is defined by:

$$\langle r_g^2\rangle_z = \langle M\rangle_w^{-1} \int_o^\infty M\, f(M) r_g^2\, dM \quad [14]$$

where f(M) is the weight distribution function.

The results, extrapolated to $\theta = 0$, are shown in Fig.10.

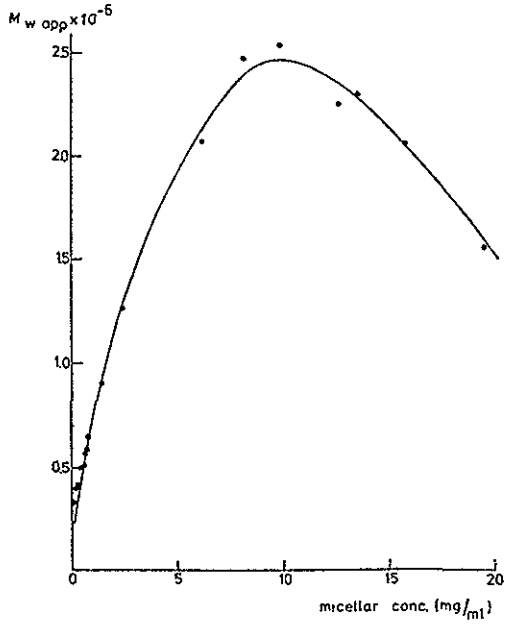

Fig.10. Apparent weight average micellar weights as a function of micellar concentrations.

The molecules are so large that the application of the theory of the excluded volume of rigid particles cannot be used for the evaluation of A_2. At low concentrations we assume the contribution of the virial coefficient to be negligible and according to our association model we assume $\langle M\rangle_w$ to increase linearely with $\sqrt{c_m}$.

The angular dependence of the scattering contains information on the micellar shape. We found $[\langle r_g^2\rangle_z/\langle M\rangle_w]^{\frac{1}{2}}$ to be independent of concentration and equal 3.1×10^{-9} cm.mol$^{\frac{1}{2}}$.g$^{-\frac{1}{2}}$. Adoption of the open association model then implies that $\langle r_g^2\rangle_z/\langle M\rangle_w$ is also independent of the micellar weight. This phenomenon is compatible with disc- or random coil-like micelles, but not with straight rigid rods. However, on assuming a disc shape, we would obtain a disc thickness of 3.6 Å, and a molecular area of 440 Å^2, which clearly is not realistic. More sensible results can be obtained with a coil-like structure. At c = 10 g/l and $\langle M\rangle_w = 2.38 \times 10^6$ we for instance obtain an end to end distance of 1170 Å ($=\sqrt{6\langle r_g^2\rangle_z}$). This is not unreasonable comparing it with a flexible rod with the same molecular weight and a radius of 20 Å and contour length of 4260 Å. On the basis of these observations we assumed that the micelles of di-C_6 and di-C_7 also have spherocylindrical and not disc-like shapes.

V. COMPARISON OF EXPERIMENTS WITH ASSOCIATION MODEL

In Fig.11 we have plotted experimental results from di-C_6, di-C_7 and di-C_8 in one graph.

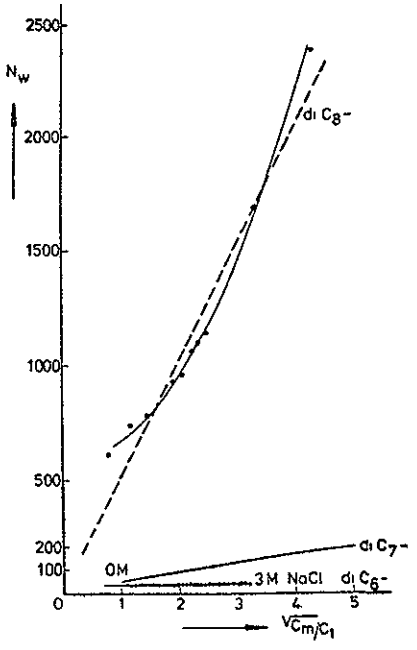

Fig.11. The weight average association number for three lecithin homologues as a function of the square root of the ratio of the micellar and monomer concentrations. The broken line for di-C_8 was calculated from $N_w = 2.38 \times 10^7 \times (526.5)^{-1} \times (c_m)^{\frac{1}{2}}$. The full line for di-$C_6$ refers to NaCl-free solutions while the dotted line refers to solutions containing 3 M NaCl.

We see that the association numbers strongly increase with chain length. The approximate values for the parameters K, K/K_1, n and $1-KC_1$ are given in Table 2, from which we see that the general trends are in agreement with the model discussed in chapter II.

TABLE 2
Parameters of the Association Model for three Lecithin Homologues

	K in $l.mol^{-1}$	K/K_1	n	$1-KC_1$
di-C_6	60	1.10	27	0.17
di-C_7	700	1.24	30	0.006
di-C_8	4050	(1.33)	(40)	0.002

In the case of di-C_8 it was impossible to calculate K/K_1 and n independently. Many different combinations can be used as long as $(K/K_1)^{\frac{n-1}{2}}$ is around 255. Separate estimations of n and K_1 can in this case, of course, only be obtained at concentrations low compared to the CMC where deviations from eq.[7] occur and eq.[6] has to be used.

The agreement with the theory concerning the effect of NaCl on micelle formation of di-C_7 has already been shown in Fig.6 where the rather straight line is virtually unaffected by the addition of NaCl. Taking the results for di-C_6 from Fig.4, we arrive at the same conclusions, although the effects are much smaller in that case.

VI. CONCLUSIONS

In this paper we have presented a simple theory for the dependence of the average micellar weight on the concentration of non-ionic surfactants. The theory predicts an increase in micellar polydispersity with increasing micellar concentrations, hydrocarbon chain length and concentration of a salting-out electrolyte.

Micellar weights of three short-chain lecithin homologues containing two equal fatty acid esters of 6, 7 and 8 carbon atoms were determined by light scattering and ultracentrifugation. The results were interpreted with the help of equations for an association equilibrium between monomers and micelles and thermodynamic non-ideality based on the excluded volume of rigid particles.

The micelles of di-C6 are rather monodisperse with micellar weights around 16 000 to 18 000. NaCl addition leads to a small increase in the average micellar weights. Di-C_7 gives polydisperse micelles ($\langle M\rangle_w/\langle M\rangle_n \approx 2$) and weight average weights ranging from 20 000 to 120 000. Addition of NaCl in this case leads to a very strong increase in the micellar weights at a fixed micellar concentration. The average micellar weight of di-C8-lecithin increases strongly with lipid concentration and average weights between 250 000 at low concentrations upto several millions at concentrations around 1 % have been obtained.

In general, the experimental results are in good agreement with the association theory.

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