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SHORT COMMUNICATION

N. Vila Romeu
G. Taddei

Aggregation energies of nonionic micelles calculated via pair potentials

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N. Vila Romeu[1] · G. Taddei (✉)
Department of Chemistry
University of Florence
via G. Capponi 9, I-50121 Florence, Italy
e-mail: taddei@dada.it

[1] *Present address*: Department of Physical Chemistry and Organic Chemistry
Faculty of Sciences of Orense
University of Vigo
Orense, Spain

Abstract The aggregation energies of two different forms of nonionic isolated micelles belonging to a binary oil-in-water system were calculated by using pairwise central potentials. One of the micelles is an elongated form (the spherocylinder); the other one is a flat form (the square tablet). The spherocylinder and the square tablet degenerate into the same spherical micelle at low aggregation numbers, whereas they form elongated cylinders and lamellae, respectively, at very high aggregation numbers. Both forms are of particular importance in some nematic systems involving a phase transition. The interaction energy among the polar heads of the amphiphilic molecules was calculated using a central Lennard-Jones potential. The interaction energy among the hydrocarbon chains in the micelle bulk was calculated via a phenomenological potential model. The calculations were performed considering a wide range of values of the parameters involved (i.e. polar head diameter, chain length). The entropic contribution to the aggregation free energy is similar for both micelles, and so their relative stability depends principally on the aggregation energy. The micelle aggregation energy depends strongly on the aggregation number and other geometrical parameters for both forms. The present results are consistent with those obtained using the surfactant parameter model, which permits the evaluation of the elastic bending energy of the micelle membrane for both forms.

Key words Colloids · Amphiphilic aggregates · Micelles · Aggregation energy

Introduction

The calculation of the aggregation energy among amphiphilic molecules in colloidal aggregates is a difficult task. The amphiphilic molecules contain many atoms, their hydrocarbon chains are not rigid, and so a rigorous calculation of the aggregation energy in terms of intramolecular and intermolecular interactions appears difficult. A variety of computer simulation treatments have been developed. All of them present peculiar advantages and limits (see the discussion in Ref. [1]). These simulations – which require very fast computers – contain several parameters to be fixed and these parameters must be handled with care in the computations. The difficulties involved in these statistical simulations can be surprisingly great even for the simplest amphiphilic aggregates, i.e. the micelles. There are many statistical studies on micelle aggregation and equilibrium stability [2–7]. In general the calculated micelles do not present an ordered structure in their bulk. The simulations emphasize too much the liquidlike packing of amphiphiles in micelles. Even if the micelles are dynamical aggregates, evidence for a fencelike close packing of the hydrocarbon chains in the micelle membrane is certain [8, 9]. Micelles can assume distinct equilibrium forms and a change of form can trigger a phase transition in the micellar system [10].

It seems useful to resort to models which are easy to handle and which are physically sound for calculating the stability of the possible distinct equilibrium forms of micelles. A semiempirical model – not statistical in nature – which has recently been presented [11] adopts central pairwise potentials which are well known in calculations of many properties of gases, liquids and solids where the interactions among the molecules are of the van der Waals type [12, 13].

The close packing of the amphiphilic molecules in micelles simplifies the application of this model since

1. The fencelike close-packed structure of hydrocarbon chains of the micelle bulk (with a minimum overlap among the chains and/or voids) favors easily predictable equilibrium forms of the micelle, such as spheres (S), spherocylinders (SC), rectangular tablets (RT) and circular tablets (CT), tori, and others [14].
2. The theoretical treatments are the easiest, because the micelle form can be assumed a priori as an equilibrium form and no minimization of the calculated free aggregation energy is required [14].

In contrast, different amphiphilic aggregates – such as vesicles – do not have forms which are predictable a priori on the basis of the molecular packing requirements, and so the calculated aggregation energy has to be minimized by using elaborate mathematical treatments [15, 16].

When elongated (rodlike) or flat (disklike) micelles are to be considered, the most reliable forms are not prolate and oblate ellipsoids but SC and RT, respectively. It was shown [14] that, despite the great success of the ellipsoidal forms in colloid chemistry [8], the prolate and oblate ellipsoids are physically unsound when they have high eccentricities, since distinct zones of their membrane have very different curvatures. It is physically meaningless that the same amphiphilic molecules self-assemble spontaneously in those kinds of micelles.

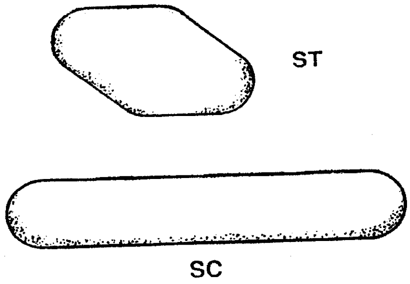

Fig. 1 The micelle forms considered: square tablet (*ST*), and spherocylinder (*SC*). Both forms have smooth surfaces without cusps. Their shorter diameter is assumed to be 2*a*, where *a* is the hydrocarbon chain length of the amphiphile molecule

SC and RT (Fig. 1) have interesting features.

1. They can grow in size without any elastic stress. No curvature changes of the micelle membrane occur during the micelle growth. In contrast, curvature changes and elastic stresses occur in ellipsoids and other forms [14].
2. S and SC are the limiting cases of the RT or square tablet (ST), respectively, when the diameter of the SC is equal to the thickness of the RT for a given amphiphile (Fig. 1).
3. A continuous change in the form of the RT to the form of the SC (or vice versa) is easily obtainable when one geometrical parameter is modified. This change in form could assume a relevant physical role in some micellar systems which show phase transitions (see Conclusions).
4. SC and RT of very large sizes correspond, respectively, to the aggregates found in hexagonal phases and wormlike micelles [17] and to the lamellae (which are tablets of extremely large extension).

The results of calculations of the aggregation energies of isolated micelles belonging to an oil-in-water binary system are presented here. The assumed micelle forms are SC, ST and S. (The reasons for choosing ST instead of RT are given in Appendix 1). The energies were calculated for different aggregation numbers. The main goal of this paper is to evaluate the relative stability of the SC and the ST forms containing the same number of amphiphilic molecules. It would be necessary to calculate the aggregation free energies of both forms, i.e. to evaluate the aggregation entropies in addition to the aggregation energies; however, in Appendix 2 it is shown that the entropic contributions to the aggregation free energies are very close for both SC and ST forms, so the relative stabilities of these micelles depend principally on their aggregation energies.

The calculations were performed considering wide ranges of the values of the parameters involved. The results show that the SC is in general more stable than the ST for aggregation numbers up to about 900, and for chain lengths of the amphiphile ranging between 16 and 25 Å. These results are consistent with the calculations performed on SC and ST using the surfactant parameter model proposed by Hyde and coworkers [18, 19], which permits the evaluation of the elastic bending energies of the membranes of the aggregate.

Calculations and discussion

The interaction energy among the polar heads and the hydrocarbon chains of the amphiphilic molecules constituting both SC and ST micelles is calculated using the equation

$$E = -KA_s/A + u_0/2 \sum\left\{(r_0/r_{lk})^{12} - 2(r_0/r_{lk})^6\right\} \ , \quad (1)$$

where A_s and A are the surface areas of the spherical micelle and of the SC (or the ST), respectively, u_0 and r_0 are the coordinates of the minimum of the Lennard-Jones potential function, r_0 is the diameter of the polar head, r_{lk} is the distance between the lth and the kth polar heads. The sum is extended over the whole micelle surface with l and k ranging from 1 to N, where N is the micelle aggregation number.

In Eq. (1) $K = \sqrt{2aNu_0}/2r_0$, where a is the chain length of the amphiphilic molecule. The SC and S diameters and the ST thickness are assumed to be $2a$.

The first term in Eq. (1) refers to chain–chain interactions in the micelle bulk. K is obtained from the equations of the dispersion energy between two closely packed cylinders [20] (the hydrocarbon chains), when the polarizability integrals of the chain and polar head are approximately equal. The latter term in Eq. (1) simulates the van der Waals interactions between the polar heads at the micelle interface. The polar heads are assumed to be spherical and without ionic charges. The polar heads are close-packed and the distance between one head and the nearest neighbor heads is equal to r_0 . The packing of the polar heads in the spherical segments of the SC and the ST is not so regular as in the parallelopipedal segment of the ST or in cylindrical segments of the SC and the ST. In these spherical segments the head packing can leave some unavoidable holes or voids; however, the spherical segments of the SC and the ST have the same total area (for a given amphiphilic molecule), and so these holes do not affect the relative aggregation energies of the SC and the ST. A short discussion on the mathematical treatment used in the calculations is given in Appendix 1.

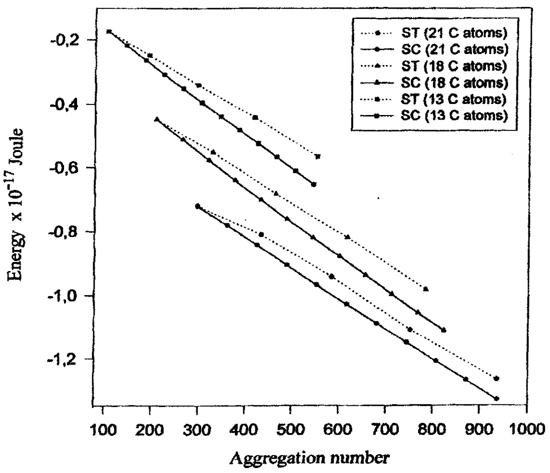

Fig. 2 Aggregation energy of the SC and the ST against the aggregation number. Spherical micelles correspond to the *points* at the *extreme left* of the curves. The calculations are made using a value of 5.5 Å for the polar head diameter and different hydrocarbon chain lengths. $u_0 = 4.8 \times 10^{-21}$ J. The numbers of carbon atoms of the (single) chains were calculated via the Tanford formulae [21]

The aggregation energies of the SC and the ST are shown against the aggregation number in Figs. 2–4. Several calculations are performed using different polar head diameters and different chain lengths. The range of values considered here for r_0 is derived from the literature values [12, 13]. The same for the value of u_0 in Eq. (1). The range of values of the chain length a is consistent with the data reported by Tanford [21].

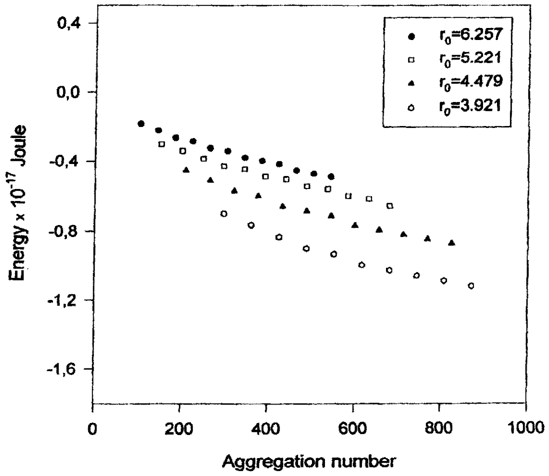

Fig. 3 Aggregation energy of the SC against the aggregation number, calculated using a constant chain length of 20 Å and different polar head diameters (see the text and Fig. 2)

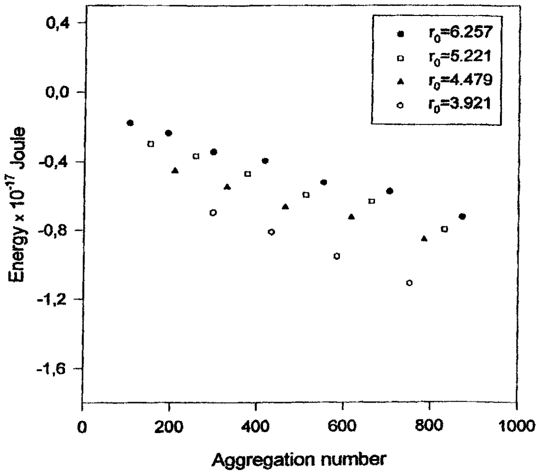

Fig. 4 Aggregation energy of the ST against the aggregation number, calculated using a constant chain length of 20 Å and different polar head diameters (see the text and Figs. 2, 3)

The number of carbon atoms (for a single chain) is calculated by the Tanford formulae.

Figure 2 shows that the aggregation energies of the SC and the ST strongly decrease with increasing micelle aggregation number. Large micelles of the same amphiphile are more stable than smaller ones; this is a well-known effect. The relative stability of the SC and the ST is affected by the length of the hydrocarbon chain. As the chain length increases the stability of both micelle forms increases. This pattern suggests that the chain–chain interactions in the micelle bulk play an important role in increasing the micelle stability (the hydrophobic effect). The calculations giving rise to Fig. 2 were performed with $r_0 = 5.5$ Å and $u_0 = 4.8 \times 10^{-21}$ J. It appears that the SC is more stable than the ST. (A constant value of u_0 was used in all calculations since – as shown in Eq. (1) – a change in u_0 affects only the absolute values of the energies.)

Calculations performed using different values of the polar diameter r_0 show similar patterns. Figures 3 and 4 show the aggregation energy of the SC and the ST against the aggregation number when the chain length of the amphiphile is constant and equal to 20 Å, whereas the polar head diameter ranges between about 4 and 6 Å. The values of r_0 used in Figs. 3 and 4 are not integers since – according to Eq. (2) – r_0, a and n are not independent parameters. In addition, the values of n must be multiples of 4 (see Appendix 1).

Figures 3 and 4 show that as the head diameter increases the micelle stability decreases (for the same aggregation number). The surface area of the SC and the ST – for constant aggregation number and chain length – actually increases with the polar head diameter, and so that hydrophobic effect is lowered.

The results shown in Figs. 2–4 are consistent with the results obtained for the SC and the ST on the basis of a completely different model. Reference [14] gives the results of calculations of the stability of several micelle forms (including SC and ST) obtained via the surfactant parameter model [18, 19], a semiempirical model which permits the evaluation of the elastic bending energy of membranes belonging to various amphiphilic aggregates (micelles, vesicles, lamellae, etc.). The assumptions involved in the surfactant parameter model are different from the assumptions adopted in the present calculations.

Figures 2–4 of Ref. [14] show that values of the characteristic surfactant parameter p_0 which are close to 0.5 favor the stability of rodlike micelles (SC is more stable than ST), whereas values of p_0 close to unity favor flat micelles (ST is more stable than SC). p_0 depends on the geometry of the amphiphilic molecule in the absence of bending stresses. A quantitative evaluation of p_0 – on the basis of its definition and using the available molecular data – could be possible in principle; however, some parameters appearing in p_0 (e.g., the "effective" chain length, the polar head area) are defined in so vague a manner that it is difficult to assign quantitative values to them. Note that a little change in the numerical value of p_0 has serious consequences for the evaluation of the bending energy. These facts limit the reliability of the surfactant parameter model.

Conclusions

The model presented here has some advantages over other semiempirical models such as the surfactant parameter model. It works in terms of van der Waals interactions among molecules and uses reliable pair potentials which have been well known for many years in calculations of properties of many molecular systems [12, 13].

The model contains many assumptions.

1. No micelle–micelle and micelle–solvent interactions are included.
2. The entropic contributions and, in general, thermal effects are neglected.

Assumption 1 arises from the nonstatistical nature of the model. The statistical treatments which have been proposed until now distinguish only rodlike and disklike shapes among the possible micelle forms. For assumption 2 we note that the entropic contributions to the aggregation free energies of the SC and the ST are very close to each other, and so the relative stability of SC and the ST (for constant aggregation number) depends essentially on the aggregation energy term (see Appendix 2).

The choice of the SC and the ST forms is shown to be reliable. Some of the reasons are discussed in the Introduction. According to Ref. [10] the SC and the ST could play an important role in some nematic(cylindrical) – nematic(discotic) phase transitions observed in three amphiphile/decanol/water micellar systems. These phase transitions could be triggered by a change in the micelle form involving the ST and the SC; however, the data in Ref. [10] refer to ternary systems. The form transition between SC and ST has not been found in our calculations, which consider only binary systems.

The results obtained here are in good agreement with the results obtained [14] on the relative stability of many micelle shapes using the bending energy model. This model achieved great success for studying the structures of all kinds of amphiphilic aggregates (see the review in Ref. [22]).

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Appendix 1

A regular network of points (the centers of the polar heads) on the surface of the RT is created using appropriate systems of coordinates. Only one-eighth of the RT is considered because of the symmetry of this micelle form. The theory is formulated for the RT, even if the calculations are performed only for the ST. The growth in size of the ST (and the SC) depends on one geometrical parameter, whereas the growth of the RT depends on two independent parameters. The latter fact introduces useless arbitrary choices during the calculations. The mathematical formalism used for the SC and the S is derived from the general formalism made for the RT, since the S and the SC are limiting cases of the RT (see later).

In order to avoid holes or voids in the cylindrical segments, an integer number of polar heads on these segments is chosen as the input datum. The radius of the cylindrical segments (which is assumed to be equal to the hydrocarbon chain length) is given by the equation

$$a = r_0/2\sin(\pi/n) \ , \tag{A1}$$

where n is a multiple of 4. Equation (A1) assumes that the centers of the polar heads lie on the vertices of a regular polygon (of n sides of length r_0) inscribed in a cylinder of radius a. The centers lie on the cylindrical surface.

Equations (A2) and (A3) refer to one-eighth of a spherical segment of the RT.

The latitude u_m is given by

$$u_m = 2(m^* - 1)\sin^{-1}(r_0/2a) + \beta$$

with

$$m^* = 1, 2, \ldots, (n/4); \quad m = (t+1), (t+2), \ldots, (t+n/4)$$

$$\text{and} \quad \beta = \cos^{-1}\left(\frac{2a^2 - 3r_0^2/4}{2a\sqrt{[a^2 + (r_0/2)^2]}}\right) - \tan^{-1}(r_0/2a) \ . \tag{A2}$$

The longitude v_{mi} is given by

$$v_{mi} = 2(i^* - 1)\sin^{-1}(r_0/2r_m) + \beta_m$$

with

$$i^* = 1, 2, \ldots, n_m; \quad i = (s+1), (s+2), \ldots, (s+n_m)$$

$$\text{and} \quad r_m = a[1 - (h_m/a)^2]^{1/2}; \quad h_m = a\sin u_m \tag{A3}$$

$$n_m \subset \pi/4\sin^{-1}(r_0/2r_m)$$

(β_m is given by β where r_m replaces a) .

s and t are the numbers of the orthogonal layers of the parallelopipedal segment of the RT. When $s = t > 0$ the RT becomes a ST; when $s = 0$ and $t > 0$ (or vice versa) the RT becomes a SC; when $s = t = 0$ the RT becomes a S.

Appendix 2

The order of magnitude of the difference between the aggregation entropies of the SC and the ST can be estimated on the basis of the following equations.

$$\Delta S_{\mathrm{SC}} = S_{\mathrm{SC}} - Ns; \quad \Delta S_{\mathrm{ST}} = S_{\mathrm{ST}} - Ns \ , \tag{A4}$$

where s is the entropy of the monomer of the amphiphile in solution.

$$\Delta S_{\mathrm{SC}} - \Delta S_{\mathrm{ST}} = S_{\mathrm{SC}} - S_{\mathrm{ST}} \tag{A5}$$

Only the rotational contribution to S_{SC} and S_{ST} is considered. The SC and the ST differ from each other above all in their shape (i.e. in their moments of inertia) rather than in their molecular packing.

$$\Delta S_{\mathrm{SC}} - \Delta S_{\mathrm{ST}} \cong (k_B/2)\ \ln\{12a^2L^4/[D^2(a^2 + D^2)^2]\} \ , \tag{A6}$$

where L and D are related since the SC and the ST have equal N. Within the ranges of values of a and D considered in this paper, we have in absolute values

$$T(\Delta S_{\mathrm{SC}} - \Delta S_{\mathrm{ST}})/(E_{\mathrm{SC}} - E_{\mathrm{ST}}) \cong 10^{-1} - 10^{-2} \ . \tag{A7}$$

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