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Water content in micelles and the Laplace formula

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In this Brief Report, a formula to estimate the water content of micelles is proposed. It is based on the Laplace equation and it gives a plausible explanation of the various globular shapes the micelles take at different amphiphile concentrations. The formula is applied to an aqueous solution of Triton X-100. The estimated water content, 11 water molecules per monomer, is lower than a previous reported value obtained from geometric arguments by other authors [R. J. Robson and E. A. Dennis, J. Phys. Chem. **81**, 1075 (1977)].

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INTRODUCTION

Micelles are the most evident manifestation of amphiphilic molecules in aqueous solvents. In particular, when amphiphilic molecules are surface active agents (surfactants), the resultant systems of micelles have a wide range of practical applications. Detergency, drug microencapsulation in the pharmaceutical industry, and the ternary oil recovery processes in the petroleum industry are a few examples of processes that involve the formation of aggregates of amphiphilic molecules.

In view of these important applications, the behavior of aqueous solutions of amphiphiles has been widely studied. Nowadays it is known that amphiphilic molecules form different kinds of aggregates giving a very rich phase diagram that includes regions in which the system behaves as a true micellar solution, or as a liquid crystal (lamellar phase), or even as a solid crystal [1,2]. In this Brief Report we discuss, from a theoretical point of view, the micelle formation in the solution phase. In particular attention is focused on its water content [3]. While most of the previous analyses on this particular aspect of micellization are mainly supported on geometrical arguments [4,5], we explore here a route based on the Laplace equation instead. Our approach gives a simple formula that relates the micelles water content with its size and surface tension.

WATER CONTENT, SHAPE, AND SIZE OF MICELLES

When a small quantity of soluble amphiphile is added to water, part of it is dissolved into the bulk and part forms a monolayer at the air-water interface. The amphiphile monomers in the monolayer are in equilibrium with those in the bulk solution. At the interphase the polar heads, of the amphiphile molecules, are in contact with the water and the tails point to the air. In the bulk, the molecules undergo a hydrophilic hydration near the polar heads an a hydrophobic hydration around the tails. Thus a new order of the water molecules surrounding the amphipolar monomer is established. When the monomer's concentration reaches a critical value, the added amphiphile begins to associate to form micelles.

Micelle formation is a cooperative phenomena usually studied from a thermodynamic point of view [6]. It results as a balance [7] between the hydrophobic effect and the self-association of amphiphilic molecules. The "driving force" of this mutual association is the tendency of hydrophobic tails to "escape" from water [8]. The free amphiphile concentration in equilibrium with micelles changes only slowly with the concentration of micelles [7].

From a mechanical point of view, the equilibrium of micelles in solution is guaranteed by the Laplace formula. In general, for ellipsoidal micelles, it reads

$$\Delta p = \left[\frac{1}{r_1} + \frac{1}{r_2} \right] \sigma \ , \tag{1}$$

where σ is the surface tension, r_1 and r_2 are the semiaxis of the micelle, and Δp is the pressure difference between the interior and exterior of the micelle.

It is well accepted that micelles are composed by ordered amphiphilic molecules and water molecules associated with them. This water is the residual one which remains tied to the amphipolar molecules after the micellation process. Micelles are in fact an ordered assembly of amphipolar molecules and water. We postulate that the interface between these units (the micelles) and the bulk water acts as a membrane that separates two aqueous solutions of different amphiphile concentration. Then, in first approximation, the pressure difference across these membranes is [9]

$$\Delta p = \frac{kT}{v} \Delta c \ , \tag{2}$$

where v is the molecular volume of the pure solvent (water) and Δc is the concentration difference of surfactant in the micelle and in the bulk, respectively. Since the mono-

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mer concentration in the bulk is much smaller than in the micelles, we can then approximate $\Delta c \simeq N_A / N_W$. In this expression N_A is the aggregation number and N_W is the number of water molecules bound to the micelle. Then Eq. (2) and (1) yield

$$N_W = \left[\frac{1}{r_1} + \frac{1}{r_2} \right]^{-1} \frac{kT}{\sigma v} N_A \ . \qquad (3)$$

Physically it is possible to admit that the water content per monomer must be nearly constant. The increase of the aggregation number results in a proportional increase of the bound water. Formula (3) says that, if the water content per monomer N_W / N_A is kept constant, all globular shapes for which $(1/r_1 + 1/r_2)$ remains unaltered are allowed.

Let us apply this expression to estimate the water content for a micelle of Triton X-100. The micelles are assumed to be spherical with a radius $r \simeq 48$ Å ($r = r_1 = r_2$) as given by Helenius and Simons [10]. The temperature is $T = 298.15$ K and the aggregation number $N_A = 134$ [10]. The surface tension is $\sigma \simeq 29$ dyn/cm [11]. From these data, Eq. (3) gives a water content per micelle $N_W = 1495$ molecules; that is 11 molecules per monomer. The present numerical analysis also could be done for any globular shape.

It should be remarked that Robson and Dennis [4], by geometrical considerations, found $N_W = 5400$ molecules. This number was obtained by assuming that all the empty space left by the amphiphilic molecules is filled by water molecules. Since they consider $N_A = 143$, this result corresponds to 38 water molecules per monomer.

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