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Report

Experimental Confirmation of the Change of Water Structure in the Critical Range of Micelle Formation: A New Method of Critical Micelle Concentration (CMC) Determination

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The decrease in the water structure in the critical range of micelle formation, which had been deduced theoretically, was confirmed by means of a new determination method. The method was based upon the dependence of the gelatin helicity on the water structure and the correlation between the helix-coil equilibrium and the disintegration of gelatin microcapsules. The significant rise in the disintegration rate, indicating a decay of water structure, represents also a new method of critical micelle concentration (CMC) determination.

KEY WORDS: micelle formation; water structure; microcapsule disintegration; critical micelle concentration (CMC) determination.

INTRODUCTION

Thermodynamical measurements and considerations have shown that the occurrence of micelle formation is caused by a structural change in the environment and the involved entropy increase in the whole system (1,2). Micellization has proven to be an entropy-driven process adhering to the second law. Thus, the term "critical concentration of entropy change" is preferred to the common expression "critical concentration of micelle formation" (2).

In accordance with this conception the multimerization of the amphiphilic molecules is not primarily an ordering process of the surfactants, but a disordering process of the milieu water. The function of water therefore has to be considered as that of a reaction component in the reaction equation (2):

Up to now,

$$n \text{ (unimer)} \rightleftharpoons (\text{unimer})_n$$

Correctly,

$$(H_2O)_m + n \text{ (unimer)} \rightleftharpoons m\ (H_2O) + (\text{unimer})_n$$

To confirm this conclusion, the change of the water structure within the range of micelle formation had to be demonstrated. This determination was accomplished by a new indirect method (3,4). Since the change of the water structure was supposed to indicate the onset of micelle formation, the new method also represents a new procedure in the determination of critical micelle concentration (CMC).

METHODS

The investigations were based upon the following facts. The secondary structure of proteins is stabilized above all by the hydrophobic interactions and clusters (5,6). This means that the helicalization is made possible by the water structure. Proteins such as gelatin are therefore able to adapt their highly dynamical helical conformation within 10^{-7} to 10^3 sec to the medium (7,8). In this way the state of order in the solvent can inversely be deduced from the steric structure of a definite protein.

Among the important consequences of such a change in protein structure are the shift in solubility, capability of swelling, and strength (rigidity) (9,10). Using the correlation of these phenomena permits the so-called alloplastic effect to be quantified. If, as in the case of microcapsules, a large contact surface exists, protein preparations change their disintegration rate in close correlation with the water structure (3,4). By way of these indicator spheres, therefore, a new method of water structure determination was established, without disturbing the experimental system (4,11). To increase the sensitivity of the method, the experimental conditions had to agree with the range of easy helix-coil transformation. This transition region is given near 30°C (12–14). The measurements were directed to the disintegration time of the microcapsules at this temperature.

In the present experiments water was mixed with increasing amounts of different surfactants and tested. The surface-active agents were Tween 80 (Atlas-Goldschmidt GmbH, Essen/FRG), sodium dodecyl sulfate (Serva, Heidelberg/FRG) and cetylrimethylammonium bromide (BDH Chemicals Ltd., Poole/England). Thus, one nonionic and two ionic substances were chosen. As test particles dry vitamin palmitate AD_2 microcapsules (Danochemo/Denmark) were used. The observations of the disintegration times

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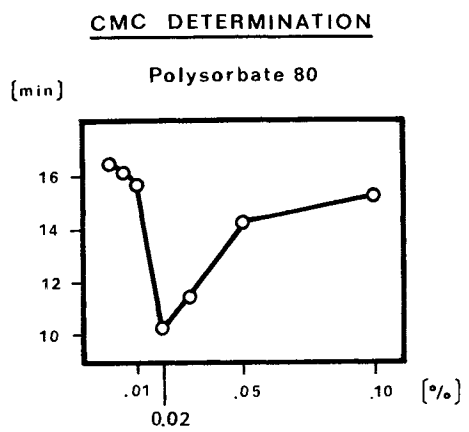

Fig. 1 Dependence of the disintegration time of microcapsules upon the concentration of a nonionic surfactant.

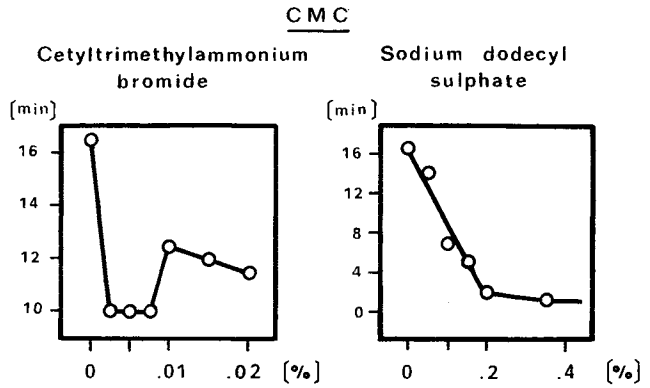

Fig. 2. Dependence of the disintegration time of microcapsules upon the concentration of ionic surfactants.

were performed with the aid of a hot-stage microscope (Mikroheiztisch Boetius, MLW VEB Analytik, Dresden/GDR) at a constant 30°C. After dispersing 3 mg of the microcapsules in 10 ml of the medium to be examined, the time was determined up to the point where all capsules had been disintegrated. The final point could be observed more precisely if the suspension was kept at room temperature (below the critical range of 30°C) for 10 min before it was brought to the hot plate.

RESULTS AND DISCUSSION

The results showed that the disintegration time changed significantly as a function of the content of ionic as well as nonionic surfactants when the range of micelle formation was reached. As little as 0.005% of the surface-active agent was detectable (Figs. 1 and 2). When the surfactant concentration was increased, a minimum of the disintegration time was met, indicating a maximal disordering of the water structure. Above this limit concentration there was no further decrease in the disintegration time.

The behavior of the concentration–disintegration time curves proved to be different for all of three surface-active agents. Considering the mechanism and selectivity of the determination method, the effect is based essentially upon a change of the water structure. The intensity of this change (shift of the disintegration time of microcapsules) correlates with the surfactant structure. Within the range of CMC the minimal disintegration time or maximal disintegration rate is equal to the loss of structure (gain of entropy) in the medium. The minimum of the curves signals the CMC.

The CMC values determined are comparable to the results of other authors and other methods (Table I). In the case of ionic surfactants, however, the new method shows somewhat lower values than are described in the literature. Obviously, an interpretation of this deviation is true, which was once given for the comparison of methods in general (15): "CMC might be defined as the concentration at which the presence of micelles becomes perceptible. The value thus defined would depend on the sensitivity of the method of measurement and would inevitably become lower and lower as the sensitivity is improved." Consequently, the relatively low CMC values found by the microcapsule technique are likely to be caused by the high sensitivity of the method. The small increase in the temperature prevailing under the test conditions has no significant influence (16,17). Perhaps the interaction between gelatin and surfactants, especially surfactant anions, must be taken into consideration (18–20). It may slightly promote or impair the helix-coil transition. In the concentration range of 0.003 g microcapsules/10 ml, variations in the concentration of the microcapsules proved to be insignificant.

On the basis of these results the reduction of the water structure in the range of micelle formation was confirmed experimentally. The conclusion can be drawn that most of the other methods of CMC determination, such as the measurement of the osmotic pressure or vapor pressure (21), the surface tension (22), and the density (23), may likewise be procedures directed to the change of water structure. However, while these methods are generally based upon an instrumental manipulation influencing the structural state, the principle of microcapsule disintegration operates *in situ*. Independent of the method an increase in the measured values occurs above the CMC in most cases. This effect has been

Table I. Comparison of Observed and Described CMC Values

Surfactant	Observed value (g/100 ml)	Described value[a] (g/100 ml)	Described value[a] (mol/liter)
Polysorbate 80 (Tween 80)	0.01–0.02	0.010	$1 \cdot 10^{-5}$
Cetyltrimethylammonium bromide	0.025	0.034	$9.2 \cdot 10^{-4}$
Sodium dodecyl sulfate	0.200	0.234	$8.1 \cdot 10^{-3}$

[a] U. Pfüller, *Mizellen, Vesikel, Mikroemulsionen*, VEB Verlag Volk und Gesundheit, Berlin, 1986, p. 26

interpreted with respect to the fact that the composition of the micelles changes and tends to attain a thermodynamically optimal equilibrium when the tenside content of the whole system increases.

Since the decrease in the degree of order is identical to an increase in entropy, the thermodynamical parameters characterizing this process are involved. The change of the free enthalpy ΔG° and the entropy ΔS correlates with the CMC in the following manner:

$$\Delta G^\circ = RT \cdot \ln (\text{CMC}) = \Delta H^\circ - T\Delta S^\circ$$

Thus, the CMC can be calculated using the thermodynamic parameters (24,25). The entropy change influences the CMC and the free enthalpy of the micelle formation in a similar way as the temperature; entropy and enthalpy vary in linear dependence (25). Such relations reflect the correspondence between the shift of entropy and that of water structure (26), expressed by the intensity of microcapsule disintegration. The differences in the degree of structural order and entropy seem to be in agreement with the differences in the disintegration times. The absolute values of disintegration time, however, depend upon the quality of the microcapsules. But these deviations in quality are unimportant, since the determination method is based on a relative principle. Besides the nearly universal applicability, high sensitivity, and indifference, it is this relativity which is among the advantages of the procedure; it makes the method independent of a special type of gelatin microcapsules.

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