On the Theory of Phthalocyanine Monomerization in Aqueous Surfactant Solutions

A. I. Rusanov*

Mendeleev Center, St. Petersburg State University, St. Petersburg, 199034 Russia
***e-mail: rusanov32@list.ru**
Received October 28, 2020; revised November 3, 2020; accepted November 6, 2020

Abstract—A thermodynamic theory has been formulated to substantiate a number of new phenomena experimentally revealed in the colloid science of surfactants. A description has been given for the formation of particular micelles via surfactant adsorption on their cores, the role of which is played by monomers and dimers of phthalocyanines. This gives rise to the formation of surfactant micelles and *protomicelles* containing solubilized monomers and dimers. The gradual formation of the (proto)micelles (coverage of the core surface with surfactant molecules or ions) upon the addition of a surfactant to a system is completed before the critical micelle concentration of the surfactant is reached. In terms of the chemical potentials and concentrations, equations have been derived to describe the influence of surfactants on the state of the monomers and dimers of phthalocyanines in aqueous solutions. It has been found that the concentrations of both particles grow with surfactant concentration. Alterations in the distribution of dimers over their structural forms with variations in surfactant concentration have been analyzed. It has been shown that, as surfactant content in a solution increases, the distribution of dimers shifts toward labile structures with the inevitable disintegration of phthalocyanine dimers into monomers. An equation has been derived to determine a new physical parameter, *monomerization concentration*, which corresponds to the passage from the dimeric state (inherent in phthalocyanines in pure water or dilute surfactant solutions) to the monomeric state in surfactant solutions. Equations have been presented for the chemical potentials of micelles (containing solubilized phthalocyanine monomers) and protomicelles (containing solubilized dimers). The latter actually disappear when the surfactant concentration rises approaching the critical micelle concentration.

INTRODUCTION

Being widely used in the industry and medicine, phthalocyanines are of great interest from the chemical standpoint. A phthalocyanine molecule is 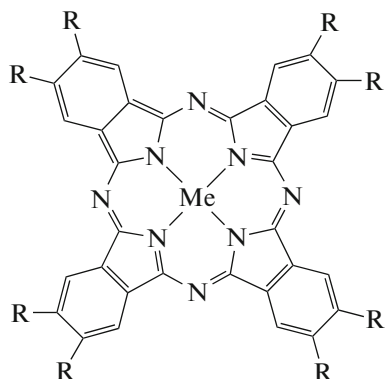based on a planar macrocycle (Fig. 1), to which diverse functional groups may be attached. Similarly to surfactants, there are cationic and anionic phthalocyanines, and their joint study together with surfactant just asks to be performed. Such works began to be carried out as early as in the past century. These studies involved even micellar systems [1–3]; however, they had a purely chemical character mainly concerning photochemistry and micellar catalysis. The interest in their physical and colloidal properties arose only on the doorstep of the 21th century [4, 5], when it became clear that surfactants can serve as efficient agents of phthalocyanine monomerization. The monomerization of phthalocyanines is a great problem, and we will clarify it.

It is known that there are no insoluble substances. When they write in a chemical handbook "water-insoluble," this means that a substance is very poorly soluble in water. The majority of phthalocyanines are such substances (their solubility in water is expressed in μM). The reason for this situation is the same as that for the low solubility of hydrocarbons, i.e., the hydrophobic effect. The incorporation of a nonpolar particle with a hydrophobic surface into water bulk

Fig. 1. Structural formula of metal (Me) phthalocyanine molecule (R denotes functional groups).

destroys the structure of the latter and requires a great work. The larger the particle (macrocycle diameter is 3 nm) and the area of the hydrophobic contact, the stronger this factor. However, if two macrocycles are aggregated, the aforementioned work (calculated per one molecule) is almost halved. This explains the fact that phthalocyanines dissolved in water occur predominantly in the dimeric form (the formation of molecular aggregates of higher orders is actually excluded at such low concentrations). At the same time the dimerization has a negative effect on the functional (chromophoric) properties of phthalocyanines: the quantum yield of fluorescence, the lifetime of the excited state, etc., decrease. That is why the practically important problem of phthalocyanine monomerization has arisen.

Note that the dimerization of phthalocyaninates is not a consequence of their low solubility, but rather it results from the large hydrophobic surface of the macrocycle. Therefore, the attachment of functional groups that increase phthalocyanine solubility to the macrocycle will change nothing. This was evidently shown in [4], where experiments were carried out with phthalocyanine having dendrite branches actually studded with sodium ions, which transformed the phthalocyanine into an anionic polyelectrolyte. Similarly to ants, the collective efforts of the polyanions pulled phthalocyanine molecules into water; then.... Then the macrocycles aggregated into dimers! The authors of [4], who dealt with the anionic phthalocyanine, used a cationic surfactant (hexadecyltrimethylammonium bromide) to suppress the dimerization. Its addition gradually decreased the content of dimers, while increasing the concentration of monomers. Unfortunately, the data interpretation in [4] was based on interionic electrostatic interaction alone, although the role of the hydrophobic effect is much more important, as follows even from the fact that it so easily overcomes the mutual repulsion of similarly charged ions during the formation of normal micelles of ionic surfactants. This oversight was corrected in [5], where the role of the hydrophobic effect in the aggregation processes was taken into account. In addition, the feasibility of using reverse micelles for phthalocyanine monomerization was shown in [5].

Ten years later, such studies were continued in Russia and have become an independent scientific field, which is developed at present [6−19]. The colloido-chemical aspect of the data interpretation has also been enhanced, and the term "solubilization" has been used. The simplest approach to the interpretation is as follows. Phthalocyanines are monomerized via solubilization of their monomers in surfactant micelles. Therefore, below the critical micelle concentration (CMC), only dimers of phthalocyanines are present in a solution, while only their monomers exist above the CMC. However, it has been shown [17−19] that the surfactant-induced monomerization of phthalocyanines begins long before the CMC is reached. As a matter of fact, this was shown as early as in [4]. However, there is one nuance here. When we say "below CMC" or "above CMC," we mean the CMC that a surfactant had in the absence of a solubilizate. It is known from the solubilization theory (see, e.g., [20−23]) that the presence of a solubilizate always reduces the real CMC. However, this reduction is commonly not so large. Its experimental evaluation [17−19] has confirmed that surfactant-induced phthalocyanine monomerization develops much below this changed CMC as well.

As compared with [4], one more interesting fact was observed in [17−19]. In [4], it was stated that, as a surfactant is added, the number of phthalocyanine dimers continuously decreases while the content of monomers increases. However, the spectrophotometric data of [17−19] have shown that, at low surfactant concentrations (when the content of dimers is still high and can easily be monitored), the addition of a surfactant somewhat increases the concentration of the dimers. Hence, surfactants enhance the solubility of phthalocyanines independently of their aggregative form (were the dimers more stable, the solubility of phthalocyanines would increase all the same).

The presented Introduction opens a number of questions that require the theoretical interpretation. A great deal of information has been accumulated on phthalocyanines, and it is high time to pass from hypotheses and speculative explanations to mathematical relations. Seemingly, it is most simple to use the developed apparatus of surfactant physical chemistry for this purpose [20−22]. However, it is mainly based on the mass action law, while the latter becomes invalid in our complex case of surfactants combined with phthalocyanines (the constant of the law of mass action becomes changeable). It is obvious that we should proceed from more general relations, and this circumstance makes us to turn to the main parameter of chemical thermodynamics, i.e., the chemical potential.

CHEMICAL POTENTIALS OF PHTHALOCYANINES, SURFACTANTS, AND MICELLES

Statistical mechanics gives the following expression for chemical potential μ_i of an ith component of a multicomponent liquid medium (as calculated per one molecule):

$$\mu_i = \mu_i^v + w_i + kT \ln(c_i f_i \Lambda_i^3), \qquad (1)$$

where μ_i^v is the chemical potential of a molecule with a resting center of mass in vacuum; w_i is the work of molecule transfer from a fixed position in vacuum to a fixed position in a pure solvent; c_i is the concentration (the number of i-type molecules in unit volume); and f_i and Λ_i are the activity coefficient and the de Broglie

wavelength (depends on temperature alone) of an individual i-type molecule, respectively [24]. This value is related to the partition function of the translational motion of molecules and is specified by equation

$$\Lambda_i \equiv \frac{h}{(2\pi m_i k T)^{1/2}}, \qquad (2)$$

where h is the Planck constant and m_i is the mass of the i-type molecule.

In the thermodynamics of solutions, activity coefficient f_i reflects only the interaction between solute molecules (does not take into account the interaction with a solvent). Upon the infinite dilution, this interaction is absent, and the solution becomes ideal at $f_i = 1$. The concentrations inherent in aqueous phthalocyanine solutions are so low that interactions are seemingly absent in them. So, how are dimers formed? Indeed, were the hydrophobic effect absent, dimers would be formed only as a result of the mutual attraction between monomers. However, we have another case. Nonpolar particles interact with each other by featureless dispersion forces; however, they interact with water in the same way; hence, no efficient attraction can take place between them. They do not mutually attract each other, but rather water "presses" them against each other by the hydrophobic effect force to yield dimers. The magnitude of this force is impressive, if we remember the aforementioned example from [4], where the adhesion force between two phthalocyanine macrocycles overcame the mutual electrostatic repulsion between two multiply charged polyanions. Taking into account all of the aforementioned, we may now take $f_i \approx 1$ and exclude activity coefficient f_i from expression (1). Then, it acquires the form of

$$\mu_i = \mu_i^v + w_i + kT \ln(c_i \Lambda_i^3), \qquad (3)$$

where all factors that are explicitly related to the hydrophobic effect are included into work w_i.

According to the traditions of surfactant physical chemistry [20–22], we attribute numerals $i = 1$ and 2 to a surfactant as a potential solubilizer and phthalocyanine as a potential solubilizate, respectively. Taking into account that phthalocyanine monomers and dimers may be simultaneously present in a solution, let us write two versions of expression (3) for phthalocyanine:

$$\mu_{21} = \mu_{21}^v + w_{21} + kT \ln(c_{21} \Lambda_{21}^3), \qquad (4)$$

$$\mu_{22} = \mu_{22}^v + w_{22} + kT \ln(c_{22} \Lambda_{22}^3), \qquad (5)$$

where additional subscripts 1 and 2 indicate that a value refers to the monomer and dimer, respectively. It is known from micellization theory [20–22] that, in aggregative systems, the chemical potential is determined with respect to monomers. Therefore, it may be

stated that Eq. (4) characterizes the chemical potential of phthalocyanine as a whole (μ_{21} in the left-hand side may be replaced by μ_2). Expression (5) is devoid of this property.

The aforementioned equations are sufficient for solving a number of problems concerning the monomerization of phthalocyanines under the action of surfactants. As a first problem, let us consider the relation between the quantitative characteristics of a surfactant and the concentration of phthalocyanine monomers in a solution.

Influence of a Surfactant on the Concentration of Phthalocyanine Monomers

Let us place a phthalocyanine crystal into pure water, with the crystal being sufficiently large to remain in contact with the solution after equilibrium concentration c_2^0 is established (this concentration is referred to as solubility). At equilibrium, the chemical potentials of phthalocyanine in the solid and liquid phases are equal, while the potential in the solid phase depends only on temperature and pressure. Hence, at constant temperature and pressure, the chemical potential of phthalocyanine in the solution will be maintained constant independently of any chemical processes and variations in the chemical composition of the solution. Now, let us imagine that a surfactant is added to the saturated phthalocyanine solution (the experiments were carried out in this way in [17–19]). Then, surfactant concentration in the solution will grow; however, the chemical potential of phthalocyanine will remain unchanged as well as the chemical potential of the monomers in Eq. (4) ($\mu_2 = \mu_{21}$). At a constant temperature, all values in the right-hand side of Eq. (4), with the exception of w_{21} and c_{21}, are constant, and we may write

$$w_{21} + kT \ln(c_{21} \Lambda_{21}^3) = C_1, \qquad (6)$$

where C_1 is some constant (constant term Λ_{21}^3 temporarily remains in the left hand side of Eq. (6), because only dimensionless values may be placed under the sign of logarithm).

Now, let us turn to term w_{21}, which represents the work of the transfer of one phthalocyanine molecule from vacuum to a fixed point in a pure solvent. Term "pure" implies the absolute absence of other phthalocyanine molecules in the solvent. In the absence of a surfactant, the "pure solvent" is water; in the presence of a surfactant, it is an aqueous surfactant solution. In the former case, the incorporation of a phthalocyanine molecule into water requires a great work (we denote it as w_{21}^0), while, in the latter case, the work is decreased owing to the adhesion of the hydrocarbon tails of surfactant molecules or ions to the hydrophobic surface of the phthalocyanine molecule. If the advantage in

the work is u (the work of surfactant molecule detachment from the phthalocyanine surface is positive), the following relation is valid:

$$w_{21} = w_{21}^0 - un, \qquad (7)$$

where n is the number of surfactant molecules attached to one phthalocyanine molecule. The substitution of Eq. (7) into Eq. (6) yields

$$c_{21}\Lambda_{21}^3 = \exp\left(\frac{C_1 - w_{21}^0 + un}{kT}\right). \qquad (8)$$

At $n = 0$ (i.e., in the absence of a surfactant), Eq. (8) takes the following form:

$$c_{21}^0\Lambda_{21}^3 = \exp\left(\frac{C_1 - w_{21}^0}{kT}\right), \qquad (9)$$

where c_{21}^0 is the equilibrium concentration of phthalocyanine monomers in the absence of surfactants. Now, by comparing Eqs. (8) and (9), we obtain our first result as

$$c_{21} = c_{21}^0 \exp\left(\frac{un}{kT}\right) = c_{21}^0 \exp(\tilde{u}n), \qquad (10)$$

where $\tilde{u}$ is the dimensionless (in the kT units) work of detachment of one surfactant molecule from the hydrophobic phthalocyanine surface. Equation (10) shows that the concentration of phthalocyanine monomers rapidly (exponentially) grows with the number of surfactant molecules attached to a phthalocyanine molecule.

It is obvious that number n is related to surfactant concentration c_1 in a solution and that both values vary symbatically. If we consider the adhesion of surfactant molecules to phthalocyanine monomer as the onset of the formation of a micelle containing the solubilized monomer, number n may be referred to as the aggregation number. But, the aggregation number is often (e.g., in the mass action law) supposed to be a constant value (in the micellization theory, this is referred to as the quasi-chemical approximation). However, this is true only for completely formed micelles. At present, a general theory is developed that implies variable aggregation numbers [25, 26]. It comprises a concentration range within which the aggregation number is, naturally, variable. The difference is that, for ordinary micelles, this range is narrow and hardly visible, while, in our case of a micelle containing solubilized monomer, it is extended and easier to study. In [25], an analogy was noted between the aggregation number in a micelle and the Langmuir adsorption of a surfactant monolayer (any micelle is a closed surfactant monolayer, which is curved). In our case, this analogy unambiguously takes place and is much more pronounced. First, we have finished particles of "adsorbents" (phthalocyanine monomers and dimers), with the numbers of the adsorption sites for surfactant molecules on them being limited (for the monomer, this is

ultimate aggregation number n_∞). Second, in the studied region of micellization, the process of surfactant aggregation has not yet been developed, and concentration c_{11} of surfactant monomers can be supposed to coincide with total surfactant concentration c_1. Then, the Langmuir equation takes the following form:

$$n = n_\infty \frac{bc_1}{1 + bc_1}. \qquad (11)$$

The substitution of Eq. (11) into Eg. (10) leads to the second result of this section

$$c_{21} = c_{21}^0 \exp\left(\tilde{u}n_\infty \frac{bc_1}{1 + bc_1}\right), \qquad (12)$$

which directly relates the concentration of phthalocyanine monomers to the surfactant concentration. At low surfactant concentrations, we may take $bc_1 \ll 1$. Then, Eq. (12) is transformed into simple exponential dependence

$$c_{21} = c_{21}^0 \exp(\tilde{u}n_\infty bc_1). \qquad (13)$$

Phthalocyanine Dimers

As is known, a dimer is an associate of two monomers, and, although the forces (in our case, hydrophobic) bonding them are much weaker than chemical bonds (e.g., in H_2 or O_2), the dimer behaves as a single whole and may be considered to be a kind of a molecule (we already did this, when attributed a chemical potential to a dimer). If F and D($\equiv F_2$) are the chemical symbols of a monomer and a dimer, respectively, the equation of dimerization is written as

$$D = 2F. \qquad (14)$$

In the Gibbs chemical thermodynamics, the following rule is used to write the condition for the equilibrium of a chemical reaction: the symbols of substances must be replaced by their chemical potentials. Then, according to our denotations, the condition for the equilibrium of reaction (14) is

$$\mu_{22} = 2\mu_{21} = 2\mu_2, \qquad (15)$$

where we have used the aforementioned condition that the monomer chemical potential is identified with the chemical potential of the substance itself (remember that we have denoted phthalocyanine by numeral 2).

Equalities (14) and (15) reflect only the fact that a dimer consists of two molecules. For small spherical molecules, the manner in which they aggregate into dimers does not matter. However, for phthalocyanine macrocycles this is not an idle question. The rich statistical picture of microstructures in a solution comprises diverse types of contacts between phthalocyanine monomers; however, from the energetic point of view, it may be supposed that the cofacial adhesion of monomers, which results from the planar structure of the macrocycles, prevails. These adhesion contacts of

different extents are schematically represented in Fig. 2. Configuration *1* corresponds to the most compact form of a dimer with the minimal surface area. Gradually shifting the upper disc with respect to the lower one (configuration *2*), we, eventually, arrive at ultimate configuration *3*, in which the two monomers are ephemerally bonded to one another at the contact point. As a matter of fact, the dimer has already disintegrated into two monomers in configuration *3*. In this sequence, each dimer has its own probability of existence, while the picture as a whole may be characterized by an equilibrium distribution curve. It may be obtained from the condition of the equality between the chemical potentials of dimers of all types. In this case, Eq. (5) yields

$$c_{22} = \Lambda_{22}^{-3} \exp\frac{\mu_{22} - \mu_{22}^{v} - w_{22}}{kT}. \qquad (16)$$

At a preset temperature, Λ_{22}, μ_{22}, and kT values in Eq. (16) play the roles of constants, while μ_{22}^{v}, which refers the dimer in vacuum, is not a constant at all. In vacuum, the monomers attract each other by, at least, dispersion forces, and a work is always required to pass from one configuration to a next one in Fig. 2 (they are easy to imagine in Fig. 2). Chemical potential μ_{22}^{v} comprises this work. Having denoted the chemical potential of the compact dimer in vacuum as μ_{22}^{vc}, the chemical potential of any dimer in vacuum may be written as

$$\mu_{22}^{v} = \mu_{22}^{vc} + \Delta\mu_{22}^{v}, \qquad (17)$$

where the first term is constant, while the second one is variable (depends on the type of a dimer). Substituting Eq. (17) into Eq. (16), we obtain

$$c_{22} = \Lambda_{22}^{-3} \exp\frac{\mu_{22} - \mu_{22}^{vc} - \Delta\mu_{22}^{v} - w_{22}}{kT}. \qquad (18)$$

When a dimer is transferred from vacuum into water, additional (much greater) work w_{22} is required to overcome the hydrophobic effect. Similarly to Eq. (17), this work may be represented as

$$w_{22} = w_{22}^{c} + \Delta w_{22}, \qquad (19)$$

where w_{22}^{c} is the work required to immerse a compact dimer in water and Δw_{22} is the corresponding work increment (as a matter of fact, Eq. (19) is an identity as well as Eq. (17)). Now, using particular form of Eq. (18) for the compact dimer

$$c_{22}^{c} = \Lambda_{22}^{-3} \exp\frac{\mu_{22} - \mu_{22}^{vc} - w_{22}^{c}}{kT}, \qquad (20)$$

we write equilibrium distribution (16) as follows:

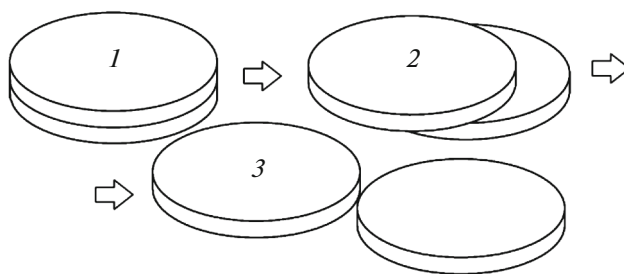$$c_{22} = c_{22}^{c} \exp\left(-\frac{\Delta\mu_{22}^{v} + \Delta w_{22}}{kT}\right). \qquad (21)$$

Fig. 2. Surfactant-induced variations in the degree of adhesion of dimer-composing macrocycles.

Work increment Δw_{22} has the positive sign as wells as $\Delta\mu_{22}^{v}$, and both these values grow with dimer surface area. Acting together, they promote a rapid decrease in the concentration (and, hence, the probability of existence and lifetime) of the dimer in pure water with an increase in its surface area. Therefore, the sharp peak of the probability corresponds to the compact dimer (Fig. 2, configuration *1*). Note that the prevalence of phthalocyanine dimers in solutions in pure water was long ago confirmed by spectrophotometric studies. Obviously, these dimers were compact.

The appearance of surfactant molecules in the solutions changes the situation, but, certainly, not at once. Surfactant molecules are attached to the hydrophobic phthalocyanine surface as if they were adsorbed. Since the chemical potential of the surfactant must be the same on the surfaces of dimers of all types, the density of the adsorption (surface concentration) and the degrees of surface coverage will also be equal for them. If, e.g., the free surface area of the dimers of all types decreases by 30%, it will, all the same, be larger for a dimer with the larger initial area. Distribution (16) will be qualitatively similar to that in pure water; however, the prevalence of the compact dimers will be less pronounced.

By analogy with Eq. (7), we may write

$$w_{22} = w_{22}^{0} - un, \qquad (22)$$

where w_{22}^{0} refers to surfactant-free water. Substituting Eq. (22) into Eq. (16), we obtain the following distribution of phthalocyanine dimers in an aqueous surfactant solution:

$$c_{22} = \Lambda_{22}^{-3} \exp\frac{\mu_{22} - \mu_{22}^{v} - w_{22}^{0} + un}{kT}. \qquad (23)$$

Here, μ_{22} is, as before, a constant, although its value differs from that in Eq. (20). Applying Eq. (23) to the most compact dimer (Fig. 1, configuration *1*, superscript "c"), we write

$$c_{22}^{c} = \Lambda_{22}^{-3} \exp\frac{\mu_{22} - \mu_{22}^{vc} - w_{22}^{0c} + un_{c}}{kT}. \qquad (24)$$

Now, having divided Eq. (23) by (24), we represent the distribution of dimers in the presence of a surfactant as follows:

$$c_{22} = c_{22}^{c} \exp\left(-\frac{\Delta\mu_{22}^{v} + \Delta w_{22}^{0} - u\Delta n}{kT}\right), \qquad (25)$$

where $\Delta n \equiv n - n_c > 0$ (since the aggregation number is minimum for the compact dimer, difference Δn is always positive).

Now, let us see attentively at the exponent in Eq. (25). All three values in the numerator are proportional to the free surface area of a dimer. Therefore, when speaking about a specific dimer of the sequence in Fig. 2, we keep in mind the entire sequence. Among the aforementioned three values, the third one (relevant to the presence of a surfactant) has a sign different from that of the two others. This fact makes it possible that the presence of a surfactant may reverse the type of the distribution of dimers. Let us see how this can happen. If a surfactant is added in small amounts, both n and Δn values are small, and the sign of the exponent (minus) remains unchanged, i.e., the compact dimers prevail in the presence of the surfactant as well. (Note that the existence of phthalocyanine dimers in both pure water and low-concentrated surfactant solutions was experimentally revealed in [17–19].) In the other limiting case, when the dimer surface is completely covered with surfactant molecules or ions (according to Langmuir, we, here, replace n by n_∞), the sign is reversed, and we have

$$-\Delta\mu_{22}^{v} - \Delta w_{22}^{0} + u\Delta n_\infty > 0. \qquad (26)$$

Indeed, when the surface is entirely covered, work Δw_{22}^{0} of hydrophobic interactions is completely eliminated owing to the hydrocarbon tails of surfactant molecules. However, they have polar groups, the effect of which is typically much stronger than $\Delta\mu_{22}^{v}$ (some exotic cases are not considered here). As a result, condition (26) is met, and the distribution of dimers is reversed; i.e., the compact dimers almost disappear, while configuration *3* in Fig. 2 becomes most probable, thereby suggesting dimer disintegration and phthalocyanine monomerization.

The boundary state is determined by the following condition:

$$-\Delta\mu_{22}^{v} - \Delta w_{22}^{0} + u\Delta n(c_1^*) = 0. \qquad (27)$$

Surfactant concentration c_1^*, which corresponds to the solution of Eq. (27) at a preset $\Delta n(c_1^*)$ function, may be referred to as the *monomerization concentration* of phthalocyanine. In particular, when employing the Langmuir equation

$$\Delta n(c_1) = \Delta n_\infty \frac{bc_1}{1 + bc_1}, \qquad (28)$$

relation (27), which is used to find c_1^*, acquires the form of

$$-\Delta\mu_{22}^{v} - \Delta w_{22}^{0} + u\Delta n_\infty \frac{bc_1^*}{1 + bc_1^*} = 0. \qquad (29)$$

The existence of the monomerization concentration was assumed as early as in [17–19]. Now, the rigorous theoretical substantiation has been given to this notion.

Effect of Surfactant on the Concentration of Phthalocyanine Dimers

Above, we have analyzed the distribution of dimers of different types. Now, we shall consider a dimer in its average (most probable) configuration. Taking into account the equality of the first and third terms in Eq. (15), it may be stated that the fixation of the chemical potential of phthalocyanine under the conditions of the aggregation equilibrium means also the constancy of dimer chemical potential μ_{22}. Then, proceeding from Eq. (5), we, by analogy with Eq. (6), have

$$w_{22} + kT\ln(c_{22}\Lambda_{22}^3) = C_2. \qquad (30)$$

When a dimer is transferred from vacuum into a surfactant solution, its surface, similarly to the surface of a monomer, is, to some extent, covered with surfactant molecules or ions. Therefore, by analogy with Eq. (7), we may write

$$w_{22} = w_{22}^0 - un, \qquad (31)$$

where n is the number of adhered surfactant molecules (aggregation number). It is obvious that works u of detachment of a surfactant molecule in Eqs. (7) and (31) are identical. Substitution of Eq. (31) into Eq. (30) yields

$$c_{22}\Lambda_{22}^3 = \exp\left(\frac{C_2 - w_{22}^0 + un}{kT}\right). \qquad (32)$$

At $n = 0$ (i.e., in the absence of a surfactant), Eq. (32) acquires the form of

$$c_{22}^0\Lambda_{22}^3 = \exp\left(\frac{C_2 - w_{22}^0}{kT}\right), \qquad (33)$$

while the comparison between Eqs. (32) and (33) shows that

$$c_{22} = c_{22}^0 \exp\left(\frac{un}{kT}\right) = c_{22}^0 \exp(\tilde{u}n), \qquad (34)$$

where $\tilde{u}$ is, as that in Eq. (10), the dimensionless (in kT units) work of one surfactant molecule detachment from the hydrophobic phthalocyanine surface.

Now, the attempt to pass from the aggregation number to the surfactant concentration (with the help of Langmuir equation (11), as before) encounters a

number of complications in the case of dimers. As has been shown above, the structure and free surface area of an average dimer depend on surfactant concentration. When using the approach based on the adsorption theory, where dissolved phthalocyanine plays the role of an adsorbent with respect to a surfactant, we have a unique case: while dimers exist, the real surface area of the adsorbent and the number of the sites for the adsorbate (surfactant) depend on surfactant concentration in a solution. Under such conditions, the Langmuir equation is, naturally, invalid, and it is necessary to formulate a new theory with account of the aforementioned functional dependence. It has not yet been available, and we have only to consider the region of a strongly diluted surfactant solution, in which configuration *1* (Fig. 2) is realized. Then, taking $bc_1 \ll 1$ in the Langmuir equation, we, by analogy with Eq. (13), arrive at the following relation:

$$c_{22} = c_{22}^0 \exp\left(\tilde{u} n_\infty b c_1\right), \qquad (35)$$

where c_{22}^0 is the concentration of phthalocyanine dimers in pure water. It follows from relation (35) that, in a dilute surfactant solution occurring at equilibrium with the solid phase of phthalocyanine, the concentration of its dimers grows exponentially with surfactant content in the solution. The fact of this growth has already been revealed experimentally [17−19].

Surfactant Micelles and Protomicelles Involved in Phthalocyanine Solubilization

When surfactant molecules or ions cover the entire surface of a phthalocyanine molecule, this structure as a whole resembles a normal surfactant micelle containing one solubilized phthalocyanine molecule. According to the classical colloid science, the addition of a surfactant is accompanied by micellization followed solubilization (e.g., the cleaning action of detergents is realized in this way). In our case, we have the opposite order of the events. Initially, a phthalocyanine particle (monomer or dimer) is present in a solution. This particle serves as a sight of micellization and, being covered with surfactant molecules or ions, it is transformed into a solubilizate-containing micelle. This process is in no way relevant to the common micellization (in the absence of a solubilizate), and, as has been noted in [17−19], may occur at concentrations below the CMC of a given surfactant.

It is obvious that not only monomers, but also dimers of phthalocyanine present in a solution will be covered with surfactant molecules or ions to form micelles of larger sizes. Since dimers precede monomers, such micelles could also precede micelles with phthalocyanine monomers; therefore, they may be referred to as *protomicelles* [17]. However, we have known that, as surfactant concentration increases, dimers of type *3* (Fig. 2) increasingly prevail in the distribution of the dimers. They are within a hairbreadth

of being disintegrated into monomers, and their lifetime is very short; therefore, protomicelles are ephemeral aggregated structures. However, they occupy their modest niche in the equilibrium distributions, and thermodynamic regularities are quite applicable to them.

The processes of the formation of a micelle or a protomicelle (chemical symbols are M and P, respectively) of a surfactant (chemical symbol of its molecule or ion is S) in a phthalocyanine solution may be written as follows:

$$M = F + n_F S, \qquad (36)$$

$$P = D + n_D S, \qquad (37)$$

where (remember) F is phthalocyanine, D is dimer, and n is surfactant aggregation number (naturally, with different values denoted by subscripts F and D in Eqs. (36) and (37), respectively). In accordance with the aforementioned rule, the equilibrium conditions for these reactions are

$$\mu_M = \mu_{21} + n_F \mu_{11}, \qquad (38)$$

$$\mu_P = \mu_{22} + n_D \mu_{11}. \qquad (39)$$

Remember that, in micellar systems, the chemical potential of a surfactant coincides that of the monomers: $\mu_{11} \equiv \mu_1$ [20−22], while, for phthalocyanines, $\mu_{21} \equiv \mu_2$. If phthalocyanine chemical potential μ_2 is fixed (in [17−19], the experiments were performed under these conditions), not only μ_{21}, but also μ_{22} are constant according to Eq. (15). Then we, from Eqs. (38) and (39), obtain

$$\frac{d\mu_M}{d\mu_1} = n_F + \mu_1 \frac{dn_F}{d\mu_1}, \qquad (40)$$

$$\frac{d\mu_P}{d\mu_1} = n_D + \mu_1 \frac{dn_D}{d\mu_1}. \qquad (41)$$

In surfactant solutions each monomer and each dimer of phthalocyanine is coated with surfactant particles; therefore, the concentration of monomers is the same as the concentration of micelles, while the concentration of dimers is the same as the concentration of protomicelles. If dimers disintegrate, the protomicelles also disappear. In the previous sections, we have considered variations in the concentrations of the monomers and dimers (and, hence, the micelles and protomicelles) within the surfactant concentration range below the CMC and the monomerization concentration by Eq. (29). In this range, micelles and protomicelles are formed via the coverage of the monomer and dimer surfaces with surfactant particles. This process ends at higher concentrations (but, nevertheless, below the CMC), and the aggregation numbers acquire almost limiting values $n_F = n_{F\infty}$ and $n_D = n_{D\infty}$. Therewith, the distribution of dimers is reconstructed in favor of configuration *3* in Fig. 2, for which it is obvious that

$$n_{D\infty} = 2n_{F\infty}. \qquad (42)$$

Substituting this equality into (38) and (39) and taking into account Eq. (15), we find

$$\mu_P = 2\mu_M. \qquad (43)$$

Now, turning to relations (40) and (41), we see that conditions (42) and (43) make these relations to be identical. In other words, relation (41) for dimers is transformed into relation (40) for monomers. Taking into account the constancy of $n_{F\infty}$, the latter relation acquires the following form:

$$\frac{d\mu_M}{d\mu_1} = n_{F\infty}. \qquad (44)$$

It is obvious that condition (42) corresponds to the disintegration of dimers into monomers and the disappearance of protomicelles upon increasing the concentration (and, hence, the chemical potential) of a surfactant. At the same time, ordinary micelles containing solubilized phthalocyanine monomers remain preserved, and their chemical potential continues to grow with surfactant concentration according to Eq. (44).

CONCLUSIONS

The monomerization of phthalocyanines in surfactant solutions is so interesting for colloid science that undoubtedly deserves the development of a special theory. This has been done in this communication. The theory substantiates a number of new phenomena that have been revealed experimentally [17−19]. This is, primarily, the formation of particular micelles via surfactant adsorption on cores, the role of which is played by monomers and dimers of phthalocyanines. As a result, surfactant micelles and protomicelles are formed with solubilized monomers and dimers. Accordingly, surfactant micelles and protomicelles arise containing monomers and dimers solubilized in them. Their gradual formation (coverage of core surfaces with surfactant molecules or ions) in the course of adding a surfactant to a system is completed before the CMC of this surfactant is reached. The driving force of this process is the hydrophobic effect, and, during the process, the concentration of protomicelles decreases to negligible values, and this is the essence of phthalocyanine monomerization (in the form of solubilisate-containing micelles, with each of them containing only one phthalocyanine molecule).

When discussing the experimental data on phthalocyanines in surfactant solutions [17−19], it has been assumed that there is a monomerization concentration (by analogy with the CMC), i.e., a surfactant concentration at which the passage from dimers (in the form of which phthalocyanine exist in pure water and very dilute surfactant solutions) to the monomeric form of phthalocyanines occurs. The theory shows that this physical parameter does take place and is determined by a special condition (Eq. (27)), with its existence per se being of principal importance. While the methods are being developed for the mathematical solution of the equation, the experimental studies encounter their own challenge, i.e., the search for a reliable method for the direct experimental determination of this value.

FUNDING

REFERENCES

1. Darwent, J.R., *J. Chem. Soc., Chem. Commun.,* 1980, p. 805.
2. Daraio, M.E., Aramendía, P.F., San Román, E.A., and Braslavsky, S.E., *Photochem. Photobiol.,* 1991, vol. 54, no. 3, p. 367.
3. Howe, L. and Zhang, J.Z., *Photochem. Photobiol.,* 1998, vol. 67, p. 90.
4. Li, X.Y., He, X., Ng, A.C.H., Wu, C., and Ng, D.K.P., *Macromolecules,* 2000, vol. 33, p. 2119.
5. Chen, Z.J., Li, X.Y., Ngai, T., Wu, C., and Ng, D.K.P., *Langmuir,* 2001, vol. 17, p. 7957.
6. Gol'dshleger, N.F., Kalashnikova, I.P., Baulin, V.E., and Tsivadze, A.Yu., *Prot. Met. Phys. Chem. Surf.,* 2011, vol. 47, p. 457.
7. Goldshleger, N.F., Chernyak, A.V., Kalashnikova, I.P., Baulin, V.E., and Tsivadze, A.Yu., *Russ. J. Gen. Chem.,* 2012, vol. 82, p. 927.
8. Gol'dshleger, N.F., Lobach, A.S., Gak, V.Yu., Kalashnikova, I.P., Baulin, V.E., and Tsivadze, A.Yu., *Prot. Met. Phys. Chem. Surf.,* 2014, vol. 50, p. 599.
9. Goldshleger, N.F., Chernyak, A.V., Lobach, A.S., Kalashnikova, I.P., Baulin, V.E., and Tsivadze, A.Yu., *Prot. Met. Phys. Chem. Surf.,* 2015, vol. 51, p. 212.
10. Goldshleger, N.F., Gak, V.Yu., Kalashnikova, I.P., Baulin, V.E., Ivanchikhina, A.V., Smirnov, V.A., Shiryaev, A.A., and Tsivadze, A.Yu., *Prot. Met. Phys. Chem. Surf.,* 2018, vol. 54, no. 174.
11. Goldshleger, N.F., Kalashnikova, I.P., Gorbunova, Yu.G., Martynov, A.G., Baulin, V.E., and Tsivadze, A.Yu., *Prot. Met. Phys. Chem. Surf.,* 2018, vol. 54, p. 33.
12. Goldshleger, N.F., Gak, V.Yu., Lapshina, M.A., Baulin, V.E., Shiryaev, A.A., and Tsivadze, A.Yu., *Russ. Chem. Bull.,* 2018, vol. 67, p. 2205.
13. Movchan, T.G., Averin, A.A., Baulin, D.V., Plotnikova, E.V., Baulin, V.E., and Tsivadze, A.Yu., *Colloid J.,* 2018, vol. 80, p. 501.
14. Movchan, T.G., Chernyad'ev, A.Yu., Plotnikova, E.V., Averin, A.A., Tsivadze, A.Yu., and Baulin, V.E., *Colloid J.,* 2018, vol. 80, p. 667.
15. Movchan, T.G., Chernyad'ev, A.Yu., Plotnikova, E.V., Tsivadze, A.Yu., and Baulin, V.E., *Colloid J.,* 2019, vol. 81, p. 711.
16. Movchan, T.G., Chernyad'ev, A.Yu., Plotnikova, E.V., Tsivadze, A.Yu., and Baulin, V.E., *Colloid J.,* 2020, vol. 82, p. 16.

17. Rusanov, A.I., Movchan, T.G., and Plotnikova, E.V., *Doklady Phys. Chem.* 2020, vol. 495, Part 2, p. 181.

18. Movchan, T.G., Rusanov, A.I., and Plotnikova, E.V., *Colloid J.,* 2021, vol. 83, p. 97.

19. Movchan, T.G., Rusanov, A.I., and Plotnikova, E.V., *Colloid J.,* 2021, vol. 83, p. 97.

20. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.

21. Rusanov, A.I., *Micellization in Surfactant Solutions. Chemistry Reviews,* Vol'pin, M.E., Ed., Reading: Harwood Acad. Publ., 1996, vol. 22, part 1. ISBN 90-5702-297-4.

22. Rusanov, A.I. and Shchekin, A.K., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Lan', 2016, 2nd ed.

23. Rusanov, A.I., *Colloid J.,* 2021, vol. 83, p. 127.

24. Kuni, F.M., *Statisticheskaya fizika i termodinamika* (Statistical Physics and Thermodynamics), Moscow: Nauka, 1981.

25. Rusanov, A.I., *Colloid J.,* 2017, vol. 79, p. 654.

26. Rusanov, A.I., *Colloid J.,* 2018, vol. 80, p. 81.

Translated by A. Kirilin