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QUANTITATIVE ANALYSIS OF MICELLAR EFFECT ON THE REACTION RATE OF CATIONIC TRIPHENYLMETHINE DYES WITH WATER ACCORDING TO BEREZIN`S MODEL

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Several approaches quantitatively describe the effect of surfactant micellar solution on the reaction rate. The most used among them are Piszkiewicz's, Berezin's, and Pseudophase Ion-Exchange (PIE) models. The last-named was developed by Bunton and Romsted.

Piszkiewicz's model is based on representations of the micellization according to the mass action law with the formation of a catalytic micelle, which consists of some surfactant molecules and a substrate. In our previously paper, this model was used to explain the kinetic micellar effect on the reaction of cationic triphenylmethine dyes with water once again showed the main disadvantages of this approach.

Berezin's model is based on another model of micelle formation viz. the pseudophase model, and the binding of reagents by micelles is considered as the distribution of a substance between two phases. In this work, we aim to consider the applicability of Berezin's approach for the interaction of malachite green and brilliant green cations with water molecule as a nucleophile in aqueous systems of nonionic, anionic, cationic, and zwitterionic surfactants. On the whole, Berezin's model performed well when applied to the description of the micellar effect on the reaction of similar dye with the hydroxide ion. However, it was revealed that this model does not take into account the change in the local concentration of the HO^- ions due to a compression of the double electric layer upon addition of reacting ions to the system, as well as the constant of association of the HO^- ions with cationic head groups of surfactant. In this case, when water is used as a nucleophile, the question of the degree of nucleophile binding can be solved differently.

The PIE model is also based on a pseudophase model of micellization, but a substrate binding by micelles is considered as an association in a stoichiometric ratio of 1:1, and a nucleophile concentration is expressed in a local concentration based on the neutralization degree of micelles. Given the latter, its approach cannot be applied to the kinetic micellar influence on the reaction of cationic triphenylmethine dyes with water.

Keywords: Berezin's model, malachite green, brilliant green, micellar rate effect, surfactant.

Introduction

The models of the kinetic micellar effect are usually tested using the reactions of nucleophilic addition of hydroxide ions or alkaline hydrolysis [1-6]. In a previous paper, we began to consider the applicability of Piszkiewicz's kinetic micellar model on the reaction between an ion and a neutral molecule. As an example of this reaction type, we used the fading of cationic triphenylmethine dyes in an acidic medium due to the interaction with water molecule as a nucleophile [7].

Earlier it was established that ratio of the observed second-order rate constant and the corresponding constant in water, $k_{\text{obs}}/k_{\text{w}}$, increases with increasing the $c_{\text{surfactant}}$, with a plateau in the micellar region [7]. In the case of sodium dodecylsulfate, SDS, the constancy of the k_{obs} value is achieved already in the premicellar region. The premicellar surfactants effect was explained by the high affinity of the dye and surfactant monomers, which leads to micelle formation before its critical micelle concentration, CMC, value, or by the dye interaction with premicellar surfactant aggregates.

According to the pseudophase Berezin's model, the kinetic micellar influence is considered based on: (i) the binding of reagents by micelles is a distribution between two phases and (ii) micellar pseudophase and the aqueous phase are considered as separate media in which chemical reactions take place simultaneously [8,9]:

$$v = k_{obs}[Dye^+]_t[\mathrm{H_2O}]_t = k_w[Dye^+]_w[\mathrm{H_2O}]_w(1-CV) + k_m[Dye^+]_m[\mathrm{H_2O}]_m CV \,. \tag{1}$$

Here k_m is the second-order rate constant in the micellar pseudophase; $[Dye^+]$ and $[\mathrm{H_2O}]$ are the concentrations of the reagents in each phase. The indices m and w refer to the micellar and aqueous phases, respectively, and the suffix t corresponds to the total concentrations; V is the molar volume of the surfactant; C is the concentration of the micellized surfactant. The factors CV and $1 - CV$ are the fractions of micellar pseudophase and aqueous phase volume, respectively.

The dependence of the rate constant on the surfactant concentration in Berezin`s model is described by equation (2) [8].

$$k_{obs} = \frac{k_m P_{Dye^+} P_{\mathrm{H_2O}} CV + k_w}{(1 + K_{Dye^+} C)(1 + K_{\mathrm{H_2O}} C)}, \tag{2}$$

Here $P_{Dye^+} = [Dye^+]_m / [Dye^+]_w$; $P_{\mathrm{H_2O}} = [\mathrm{H_2O}]_m / [\mathrm{H_2O}]_w$; K is the reagents binding constant, expressed in framework of Berezin’s model in the following way $K = (P - 1)V$ [9].

The results of quantitative analysis according to Berezin’s model and their discussion

Quantitative treatment was performed for previously published rate constants of the interaction of malachite green and brilliant green with water (Fig. 1) in aqueous surfactants systems: nonionic – Brij-35, anionic – SDS, cationic – cetyltrimethylammonium bromide (CTAB), and zwitterionic – 3-(dimethyldodecylammonio)-propanesulfonate (DMDAPS) [7].

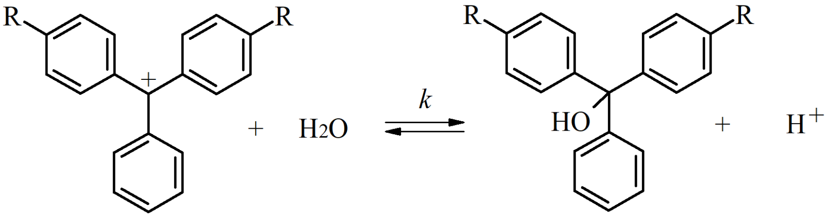

Figure 1. Interaction of malachite green, R = –N(CH$_3$)$_2$, and brilliant green, R = –N(C$_2$H$_5$)$_2$, with water.

The partition coefficient of the dye is much higher than unity because (i) the dyes binding by the micelles is confirmed by solvatochromic shift [7] and (ii) the binding is a consequence of hydrophobic interactions and electrostatic forces. The water distribution coefficient is close to unity. This follows from the MD modeling of the water volume fraction in the surface layer of micelles, obtained depending on its thickness: 59 vol% for 0.4 nm, 72 vol% for 0.6 nm, 83 vol% for 0.8 nm, 88 vol% for 1.0 nm, and 90 vol% for 1.1 nm [10]. Therefore, simplified equation (3) of Berezin's model can be used [8,9].

$$k_{obs} = \frac{k_m P_{Dye^+} CV + k_w}{1 + P_{Dye^+} CV} \tag{3}$$

Molar volumes of surfactants used in the calculations were 1.064 M^{-1} for Brij-35 [11], 0.314 M^{-1} for DMDAPS [12], 0.364 M^{-1} for CTAB [13], 0.246 M^{-1} for SDS [11].

The C value equals the total surfactant concentration from which CMC is subtracted [8,9]. However, a calculation using the CMC value, which corresponds to a dye-free system, showed a discrepancy between theory and experiment for systems, in which the change in the rate constant began in the pre-micellar concentration range; the obtained R^2 values were less than 0.8. Therefore, for these systems, the "kinetic CMC" value, that is the surfactant concentration at which changes in the rate constant begin to occur, was used as the CMC value. For systems in which the change in the rate constant occurs immediately, the concentration of the micellized surfactant was taken to be the surfactant monomers concentration. It should be noted that this approach is quite applied [14,15]. Its validity is to some extent confirmed based on particle size data obtained by the dynamic light scattering, where it was found that at the presence of the triphenylmethine dye the micelle formation occurs earlier than in a dye-free system [1,2].

The application of equation (3) to reactions with H_2O as a nucleophile in Brij-35, DMDAPS, CTAB, and SDS systems shows a satisfactory correspondence between the experimental points and the points calculated by equation (3), except anionic surfactant solutions near CMC from 0.002 to 0.015 M (see Fig. 2). Probably, this discrepancy is due to the possibility of H^+ ions concentrating in the Stern layer of anionic surfactant micelles due to electrostatic attraction at low micelles concentrations. This also accelerates the interaction of the dye with water, because the rate constant of this reaction increases with decreasing pH [16,17]. The H^+ ions concentrating in micelles decreases with increasing SDS concentration, which reduces this effect on the observed rate constant. However, this effect was not taken into account in equation (3). The obtained parameters according to Berezin's model are given in Table 1.

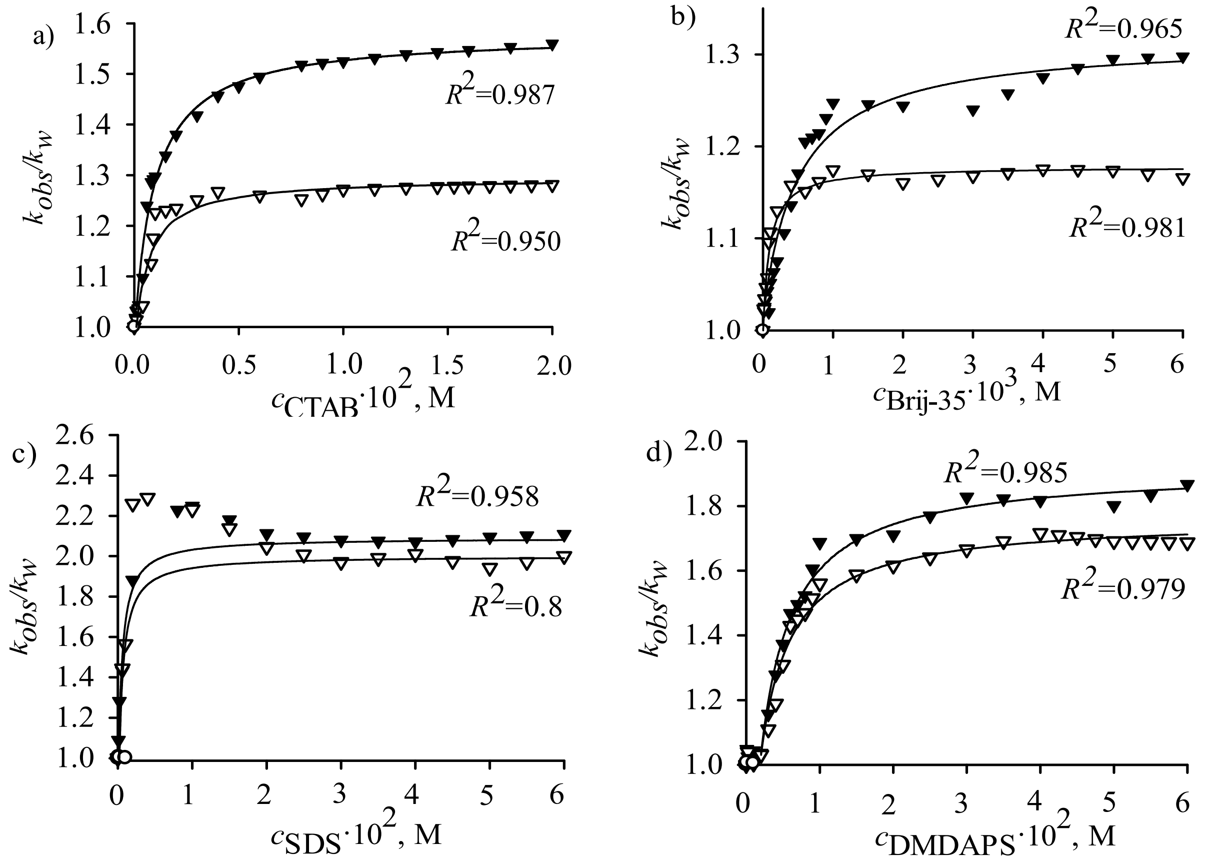

Figure 2. Dependence of k_{obs}/k_w reactions of MG^+ (▼) and BG^+ (Δ) with H_2O on the $c_{surfactants}$: (a) CTAB, (b) Brij-35, (c) SDS, and (d) DMDAPS. The lines are drawn according to Berezin's model.

Table 1. The parameters obtained according to Berezin's model for the reactions of dyes with water in Brij-35, DMDAPS, CTAB, and SDS micellar systems

Surfactant	R^2	k_m, $M^{-1}s^{-1}$	P_{dye}
The reaction of MG^+ with H_2O $k_w = 4.44\times10^{-6}$ $M^{-1}s^{-1}$ at pH = 3, t = 25 °C, $I = 1\times10^{-3}$ M			
Brij-35	0.965	$(5.88 \pm 0.04)\times10^{-6}$	$(2.1 \pm 0.2)\times10^3$
DMDAPS	0.985	$(8.52 \pm 0.08)\times10^{-6}$	$(7.2 \pm 0.6)\times10^2$
CTAB	0.987	$(7.02 \pm 0.04)\times10^{-6}$	$(2.6 \pm 0.2)\times10^3$
SDS	0.958	$(9.6 \pm 0.1)\times10^{-6}$	$(4.1 \pm 0.9)\times10^3$
The reaction of BG^+ with H_2O $k_w = 6.21\times10^{-6}$ $M^{-1}s^{-1}$ at pH = 3, t = 25 °C, $I = 1\times10^{-3}$ M			
Brij-35	0.981	$(7.32 \pm 0.02)\times10^{-6}$	$(1.03 \pm 0.09)\times10^4$
DMDAPS	0.979	$(1.09 \pm 0.08)\times10^{-5}$	$(7.6 \pm 0.7)\times10^2$
CTAB	0.950	$(8.04 \pm 0.05)\times10^{-6}$	$(3.8 \pm 0.6)\times10^3$
SDS	0.8	$(1.24 \pm 0.01)\times10^{-5}$	$(6.5 \pm 0.9)\times10^3$

The ratios of the observed rate constant corresponding to the plateau and the second-order rate constant in water, $k_{plateau}/k_w$, are 1.17, 1.28, 1.69, and 2.00 for Brij-35, CTAB, DMDAPS, and SDS, respectively for BG and 1.30, 1.56, 1.87, and 2.11 for Brij-35, CTAB, DMDAPS, and SDS, respectively for MG [7]. Based on the data presented in Table 1, a conclusion can be made that the observed change of the rate constant is a consequence of (i) the dyes concentrating in the micellar pseudophase, (ii) an almost equivalent water concentration in the bulk phase and micellar pseudophase, (iii) a weak increase in the rate constant of reaction in micellar medium as compared with water.

An analogy should be drawn with the difference between $k_{\text{plateau}}/k_{\text{w}}$ and $k_{\text{m}}/k_{\text{w}}$ values for the Dye^+ + HO^- interaction, where $k_{\text{plateau}}/k_{\text{w}}$ = 1.33, 1.42, and 14.69, and $k_{\text{m}}/k_{\text{w}}$ = 1.33, 1.52, and 2.10 in the micellar solutions of DMDAPS, Brij-35, and CTAB, respectively [2]. Hence the values of $k_{\text{plateau}}/k_{\text{w}}$ and $k_{\text{m}}/k_{\text{w}}$ are substantially differ only for CTAB system due to the enhanced concentration of the HO^- ions on the surface of cationic micelles (see equation (2)), which was confirmed by the high value of the distribution coefficient of HO^- in this system.

However, in the absence of concentrating of a nucleophile the $k_{\text{m}}/k_{\text{w}}$ values are quite close to $k_{\text{plateau}}/k_{\text{w}}$ viz. the high P_{dye} value does not have the same strong accelerating effect to the nucleophile concentrating. This can be explained by estimating the ratio between the amount of dye and surfactant monomer in 1 liter of micellar pseudophase, for example, for BG and CTAB. The dye concentration in the micellar phase is $P_{dye} \times [Dye]_{\text{t}} = P_{dye} \times 1 \cdot 10^{-5} = 0.038$ M. The surfactant concentration per 1 L of the micellar phase estimates based on the surfactant molar volume is 3.18 mol. For one dye in the micellar phase, there are 84 surfactant molecules, which is commensurate with the micelles aggregation number. That is, despite the dye concentrating in the micellar pseudophase, there is 1 dye per 1 micelle. High $[\text{Dye}]_m/[\text{Dye}]_w$ value at working dye concentration determines only that at a certain micelles concentration the reaction in the micellar pseudophase is the rate-determining step (see equation (1)).

The obtained P_{dye} values agree with the theoretical ideas about dyes binding degree according to hydrophobic interactions. The values of the distribution coefficient of the cationic triphenylmethine dyes obtained by equation (3) can be placed in the following order: $P_{\text{BG}}(10300) > P_{\text{MG}}(2100) > P_{\text{methyl violet}}$ (870 [2]) for the Brij-35 micellar system, i.e. in the absence of electrostatic interactions between the dye and the micelles. This order correlates, $R^2 = 0.996$, with decreasing order of log of octanol-water partition coefficient of dyes, log*P*: 2.3 [18] (2.77) for BG > 0.62 [19] (0.80) for MG > 0.5 [20] (0.43) for methyl violet (in brackets the log*P* value calculated in the program KowWin (Syracuse Research Corporation)). This shows that the P_{dye} values obtained by Berezin's model correspond to the fact that less hydrophilic dyes have a greater affinity to the weakly polar micellar pseudophase. The absence of a correlation between the P_{dye} value and the micelles surface potential indicates that BG and MG binding is rather due to hydrophobic interactions than electrostatic interactions. Probably, such predominance of hydrophobic interactions is expressed for weakly hydrophilic substrates.

The obtained k_{m} values (Table 1) are higher than the k_{w} value. Considering that for the reaction of an ion with a neutral molecule, the influence of the primary salt effect due to the high ionic strength of ionic micelles may be absent. Such a result can be explained by the low polarity of the micellar medium according to Amis's equation (4) and the Hughes-Ingold rules [21-23]. However, some effect of the difference in the hydrogen cation concentration in the aqueous and micellar phases is also not excluded, as these reactions are pH-dependent in an acidic environment, but this effect should not be significant (in acidic surfactant-free system *d*lg*k*/*d*pH equals 0.46 for $\text{MG}^+ + \text{H}_2\text{O}$ reaction and 0.6 for $\text{BG}^+ + \text{H}_2\text{O}$ reaction [24]).

Using the obtained k_{m} values, the values of the effective relative dielectric constant, ε_r^{eff} (Table 2) were calculated by Amis's equation (4). Taking the approach distance for the two particles to react, r_{AB}, is equal to 2 Å based on the values of the sum of the van der Waals radii of carbon and oxygen equals 3.1 Å [25], i bond length C–O equals 1.4 Å [26],

$$\ln k = \ln k_{\infty} + \frac{1}{4\pi\varepsilon_0}\left(\frac{z_A e \mu_B}{k_B T \varepsilon_r r_{AB}^2}\right). \tag{4}$$

Here k_{∞} is the rate constant in a medium with relative permittivity of infinite magnitude; μ_B is the dipole moment of the reacting molecule; z_i is the reacting ion charge; e is the elementary charge; r_i is the ion radius; k_B is the Boltzmann constant; ε_0 is the vacuum permittivity; ε_{r} is the relative dielectric constant of the solvent.

Table 2. The effective relative dielectric constant of the Brij-35, DMDAPS, SDS, and CTAB micellar microenvironment of the reagents

The reagents	ε_r^{eff}			
	Brij-35	DMDAPS	SDS	CTAB
MG^+ and H_2O	56	41	37	47
BG^+ and H_2O	63	43	39	57

The ε_r^{eff} value shows what the relative dielectric constant value of the solvent is equivalent to the micellar microenvironment as an indicator of the medium polarity. The Stern layer of ionic micelles and the surface layer of non-ionic micelles are probably the dye cation location in the micellar pseudophase and the obtained ε_r^{eff} values belong to the dye microenvironment in them. These values differ from the corresponding values estimated using other probes [27]. For example, in the paper [28] using $E_T(30)$ molecule, the values of $\varepsilon_r^{eff}=28$ for CTAB and $\varepsilon_r^{eff}=27$ for Brij-35 were obtained. This may be due to the slightly different microenvironment of the probes and the studied triphenylmethine dyes in the Stern layer. Since, as shown in the paper [10], the decisive factor that determines the polarity of the microenvironment is the water amount around the probe. The Stern layer is equally hydrated for micelles of different charge types [10]. Dye cations, which are electrostatically attracted to the main anionic groups of surfactants, are somewhat shielded from water; therefore, their microenvironment in DMDAPS and SDS micelles is weakly polar. Also, the probe hydration will be determined by the available substituents.

Conclusions

The application of Berezin's model gives satisfactory results for describing the effect of nonionic, anionic, cationic, and zwitterionic micelles in the case of interaction of the dyes with water as a nucleophile:

i. shows a satisfactory correspondence between the experimental points and the points calculated by Berezin's model equation, which is characterized by a high R^2 value;

ii. the correlation between the obtained P_{dye} values by Berezin's model equation and the dyes log*P* values corresponds to the fact that the less hydrophilic substrates have a greater affinity to the weakly polar micellar pseudophase.

iii. the obtained k_m values by Berezin's model equation correspond to the concept of the effect of weakly polar micellar pseudophase according to the Hughes-Ingold rules.

However, the model has some problems in the case of the reaction involving hydroxide ions in cationic micelles. Where for reliable calculations of the partition coefficient of HO^- ion by electrostatic approach it is necessary to take into account the change in the local concentration of the HO^- ions due to a compression of the double electric layer upon addition of reacting ions to the system. Moreover, Berezin's model, like the pseudophase ion-exchange model, does not take into account the "diverting" effect of cationic head-groups owing to their electrostatic attraction of the HO^- ions [1-3].

According to Berezin's model, the dependences of the observed rate constant of BG^+ or MG^+ and H_2O reaction on the surfactants concentration can be explained by the following quantitative parameters:

– «BG – Brij-35»: $[BG]_m/[BG]_w = 1.03\times10^4$, $k_m/k_w = 1.18$;
– «BG – DMDAPS»: $[BG]_m/[BG]_w = 7.6\times10^2$, $k_m/k_w = 1.76$;
– «BG – SDS»: $[BG]_m/[BG]_w = 7.8\times10^3$, $k_m/k_w = 2.00$;
– «BG – CTAB»: $[BG]_m/[BG]_w = 3.8\times10^3$, $k_m/k_w = 1.29$;
– «MG – Brij-35»: $[MG]_m/[MG]_w = 2.1\times10^3$, $k_m/k_w = 1.32$;
– «MG – DMDAPS»: $[MG]_m/[MG]_w = 7.2\times10^2$, $k_m/k_w = 1.92$;
– «MG – SDS»: $[MG]_m/[MG]_w = 4.1\times10^3$, $k_m/k_w = 2.16$;
– «MG – CTAB»: $[MG]_m/[MG]_w = 2.6\times10^3$, $k_m/k_w = 1.58$;

– based on the MD modeling data of the water volume fraction in the surface layer of micelles [10], the water distribution coefficient is close to unity; $P_{H_2O} \approx 0.6–0.9$. The surface layer of micelles is sufficiently hydrated regardless of the main surfactant groups charge [10];

– the change in the observed rate constant due to (i) the distribution of reagents between the water phase and the micellar pseudophase and (ii) a corresponding k_m/k_w value. Stern layer of ionic micelles and surface layer of non-ionic micelles is usually the location of triphenylmethine dyes.

– the obtained $k_\mathrm{m}/k_\mathrm{w} > 1$ can be explained by the lower polarity of the reagent location in the micellar pseudophase than in the water following the Hughes-Ingold rules and Amis's equation. The obtained k_m value corresponds to the microenvironment with the following values of relative dielectric constant as an indicator of the medium polarity: 56–63, 41–43, 37–39, and 47–57 for Brij-35, DMDAPS, SDS, and CTAB micelles, respectively. The weakly-polar microenvironment in DMDAPS and SDS micelles is a consequence of the proximity of the dye cation to the negatively charged head group, which makes them shielded from water.

– at working dye concentration equal to 1×10^{-5} M, the high P_{dye} corresponds to ~1 dye per 1 micelle, does not have the strong increasing k_obs effect, and determines that at a certain micelles concentration the reaction in the micellar pseudophase is the rate-determining step. The correlation between the P_{dye} value and the $\log P_{dye}$ value and the uncorrelation between the P_{dye} value and the micelles surface potential value indicated that BG and MG binding is predominantly due to hydrophobic interactions than electrostatic interactions. However, the main surfactant groups charge affects the location and microenvironment of the dye in nonionic, anionic, cationic, and zwitterionic micelles.

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А.М. Лагута. Кількісний аналіз міцелярного впливу на швидкість реакції катіонних трифенілметинових барвників з водою за моделлю Березіна.

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Існує ряд моделей, що кількісно описують вплив міцел ПАР на швидкість реакції. Серед них найчастіше використовуються моделі: Пішкевича, Березіна і Псевдофазна іонообмінна (ПІО) Бантона та Ромстеда.

Модель Пішкевича заснована на представленні процесу міцелоутворення відповідно до закону дії мас з утворенням каталітичної міцели, яка складається з декількох молекул ПАР і барвника. Раніше проведені розрахунки за цією моделлю з метою пояснення кінетичного міцелярного ефекту на реакцію катіонних трифенілметинових барвників з водою черговий раз показали основні недоліки цієї моделі.

Модель Березіна заснована на іншій моделі міцелоутворення, а саме псевдофазній моделі, при цьому зв'язування реагентів міцелами розглядається як розподіл речовини між двома фазами. У цій роботі ми ставимо за мету розглянути застосовність моделі Березіна для взаємодії катіонних барвників малахітового зеленого і брильянтового зеленого з водою як нуклеофілом у водних системах неіонної, аніонної, катіонної і цвітеріонної ПАР. У цілому модель Березіна непогано себе зарекомендувала раніше при застосуванні до опису впливу міцел на реакцію аналогічних барвників з гідроксид іоном. Однак було виявлено, що ця модель не враховує зміну локальної концентрації HO^{-} іонів за рахунок стиснення подвійного електричного шару при додаванні реагуючих іонів в систему, а також константу асоціації HO^{-} іонів з катіонними головними групами ПАР. У даному випадку при використанні води в якості нуклеофіла питання про ступінь зв'язування нуклеофіла може бути вирішене іншим шляхом.

Модель ПІО також заснована на псевдофазній моделі міцелоутворення, але зв'язування барвника міцелами розглядається як асоціація в стехіометричному співвідношенні 1:1, а концентрація нуклеофіла виражається через локальну концентрацію, виходячи зі ступеня нейтралізації міцел. З огляду на останнє, її не можна застосувати до досліджуваних систем.

Ключові слова: модель Березіна, малахітовий зелений, брильянтовий зелений, міцелярний ефект, поверхнево-активна речовина.

А.Н. Лагута. Количественный анализ мицеллярного влияния на скорость реакции катионных трифенилметиновых красителей с водой по модели Березина.

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Существует ряд подходов, количественно описывающих влияние мицелл ПАВ на скорость реакции. Среди них наиболее часто используются модели: Пишкевича, Березина и Псевдофазная ионнообменная (ПИО) Бантона и Ромстеда.

Модель Пишкевича основана на представлении процесса мицеллообразования в соответствии с законом действия масс с образованием каталитической мицеллы, которая состоит из нескольких молекул ПАВ и красителя. Ранее проведенные расчеты по этой модели с целью объяснения кинетического мицеллярного эффекта на реакцию катионных трифенилметиновых красителей с водой очередной раз показали основные недостатки этой модели.

Модель Березина основана на другой модели мицеллообразования, а именно псевдофазной модели, при этом связывание реагентов мицеллами рассматривается как распределение вещества между двумя фазами. В настоящей работе мы ставим цель рассмотреть применимость модели Березина к взаимодействию катионных красителей малахитового зелёного и бриллиантового зелёного с водой как нуклеофилом в водных системах неионогенного, анионного, катионного и цвиттерионного ПАВ. В целом модель Березина неплохо себя зарекомендовала ранее при применении к описанию влияния мицелл на реакцию аналогичных красителей с гидроксид ионом. Однако было выявлено, что эта модель не учитывает изменение локальной концентрации HO^{-} ионов из-за сжатия двойного электрического слоя при добавлении реагирующих ионов в систему, а также константу ассоциации HO^{-} ионов с катионными головными группами ПАВ. В данном случае при использовании воды в качестве нуклеофила, вопрос о степени связывания нуклеофила может быть решен иным путем.

Модель ПИО также основана на псевдофазной модели мицеллообразования, но связывание красителя мицеллами рассматривается как ассоциация в стехиометрическом соотношении 1:1, а концентрация нуклеофила выражается через локальную концентрацию, исходя из степени нейтрализации мицелл. Учитывая последнее, ее нельзя применить к исследуемым системам.

Ключевые слова: модель Березина, малахитовый зеленый, бриллиантовый зеленый, мицеллярный эффект, поверхностно-активное вещество.