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QUANTITATIVE ANALYSIS OF MICELLAR EFFECT ON THE REACTION RATE OF ALKALINE FADING OF PHENOLPHTHALEIN

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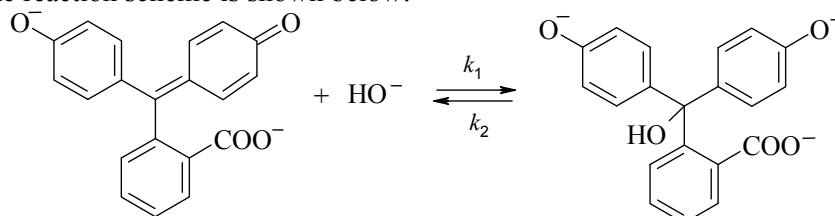
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Quantitative treatment of the kinetic data of the reaction between phenolphthalein dianion and hydroxide ion in aqueous solutions containing variable concentration of various surfactants is presented. Following surfactants are used: Brij-35 (nonionic), sodium *n*-dodecyl sulfate (anionic), cetyltrimethylammonium bromide (cationic) and 3-(dimethyl-*n*-dodecylammonio)-propanesulfonate (zwitterionic). The quantitative treatment is carried out basing of Piszkiwicz's, Berezin's, and Pseudophase Ion-Exchange (PIE) models. It is revealed that the Berezin's model is a more applicable one for describing the effect of nonionic, anionic, and zwitterionic micellar systems. The values of the corresponding kinetic parameters are discussed. The effect of cetyltrimethylammonium hydroxide on the reaction is also examined and quantitatively described by the PIE model. The research of systems based on a cationic surfactant shows previously unknown effect called by us as "diverting influence".

Keywords: Phenolphthalein Fading, Surfactant, Micellar Rate Effect, Piszkiwicz's Model, Berezin's Model, Pseudophase Ion-Exchange Model.

Introduction

This paper is a continuation of our previous studies [1-3] and is devoted to the quantitative treatment of the experimental data of the rate constants of the reaction between phenolphthalein, PP^{2-} , and hydroxide ion in solutions of surfactants of various types: non-ionic (Brij-35), anionic (sodium *n*-dodecylsulfate, SDS), cationic (cetyltrimethylammonium bromide, CTAB and (cetyltrimethylammonium hydroxide, CTAOH), and zwitterionic (3-(dimethyl-*n*-dodecylammonio)-propanesulfonate, DMDAPS). The reaction scheme is shown below:



Here k_1 is the rate constant of the carbinol ROH^{3-} formation; k_2 is the rate constant of the reverse reaction. As a qualitative conclusion of the previous observations it can be stated that the addition of any surfactant, the rate of the direct reaction decreases [1-3].

The quantitative treatment is carried out basing on most popular models [4-10]. Namely, the Piszkiwicz's model [11-13], which uses the mass action law model of micelle formation, and the Berezin's [14] and Pseudophase Ion-Exchange (PIE) [4] models, which are based on the pseudophase model of micelle formation, are considered.

It is important to gain insight into the mechanism of the above mentioned influence of the surfactants on the rate constant and to test the applicability of the models to similar systems.

Experimental part

Materials, preparation of solution and the experimental procedure were as described previously [1-3]. The NaOH solution was carbonate-free.

Apparatus. Spectrophotometer Hitachi U-2000 UV-visible and photocolormeter KFK-2M were used for kinetic measurements at 25 and 35 °C. The KFK-2M device was equipped with cuvette holder through which thermostated water was continuously circulated. Zetasizer Nano ZS Malvern was used for the study of the colloidal particles size via dynamic light scattering (DLS) at 25 °C.

Procedure of the rate constants determination. The rate constants of the reaction were determined spectrophotometrically under pseudo-first order conditions at 35 °C for SDS, CTAB, Brij-35, and DMDAPS systems, and at 25 °C for CTAOH. The hydrophobic PP was initially dissolved in 96 % aqueous ethanol, therefore in all working solutions the alcohol content was 1.2 vol %. In all systems under study, the PP and NaOH concentrations were 1.8×10^{-5} and 0.041 M, respectively. Under these conditions the reaction between PP^{2-} and HO^- is reversible. The neutral and monoanionic forms of phenolphthalein are practically absent at this concentration of the alkali, judging by the thermodynamic values of the indices of thermodynamic dissociation constants of PP at 25 °C, $pK_{a1} = 8.97$ and $pK_{a2} = 9.73$ [15].

The second-order rate constants, k_1 , were calculated by Eq. (1) [1-3].

$$k_1 = \frac{k'_1 + k_2}{[HO^-] + K^{-1}} \quad (1)$$

Here $k'_1 = k_1[HO^-]$ is pseudo-first order rate constants; K is the equilibrium constant given by (2).

$$K = \frac{k_1}{k_2} = \frac{A_0 - A_\infty}{A_\infty[HO^-]} \quad (2)$$

Here A_0 , and A_∞ are the absorbance at time zero, and equilibrium, respectively.

The values of the sum $k'_1 + k_2$ were obtained as the slopes of the dependences of $\ln(A_t - A_\infty)$ versus time, Eq. 3 [1-3].

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - (k'_1 + k_2)t \quad (3)$$

Here A_t is the absorbance at time t .

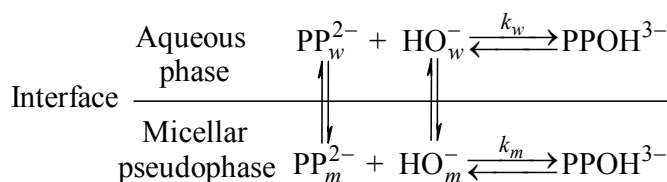
In water, the following values were obtained: $k_1 = 2.25 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$, $k_2 = 6.50 \times 10^{-4} \text{ s}^{-1}$, $K = 34.6$ (ionic strength $I = 0.041 \text{ M}$, 1.2 vol % ethanol, at 35 °C). Using the above K value and the thermodynamic value of the ionic product of water at 35 °C, 2.089×10^{-14} [18], and calculating the activity coefficients by the Debye–Huckel equation (second approach), a thermodynamic value of $pK_{a3} = 12.37$ for the reaction $R^{2-} = ROH^{3-} + H^+$ may be estimated. A value $pK_{a3} = 11.73$ was determined spectrophotometrically under equilibrium conditions at $I = 0.2 \text{ M}$ (KCl), at 25 °C, using the pH values in the activity scale [15]. Re-calculation to the thermodynamic value by estimating the activity coefficients via the Davies equation leads to $pK_{a3} = 12.42$.

Results and Discussion

Figure 1 shows the dependences of rate constants of the interaction of PP^{2-} with hydroxide ion on concentrations of surfactants: Brij-35, CTAB, DMDAPS and SDS, taken from previous papers [1-3]; some experimental data in the micellar region were added within the course of the present study.

Observed rate constants indicate that an increase in surfactants concentration leads to a decreasing in the rate constant reaching a plateau, where the further addition of the surfactant practically does not influence the rate constant. The ratio of the rate constants corresponding to plateau and water (k_{plateau}/k_w) equals 0.81, 0.57, 0.075, and 0.74 for SDS, CTAB, DMDAPS, and Brij-35, respectively. The surfactants show influence from concentrations: 8×10^{-5} , 3×10^{-3} , 1×10^{-5} , $8 \times 10^{-5} \text{ M}$ for CTAB, DMDAPS, Brij-35, and SDS, respectively.

As shown in our previous paper, the hydrophobic poorly water-soluble phenolphthalein is to high extend bound in molecular form by surfactant micelles [2]. Under such conditions, the reaction will proceed in both phases according to Scheme 1.



Scheme 1. Proceeding of the reaction in the presence of micelles.

Here k_m and k_w are the rate constants referring to the micellar and aqueous phases, respectively. The subscripts w and m indicate the aqueous phase and the micellar pseudophase, respectively.

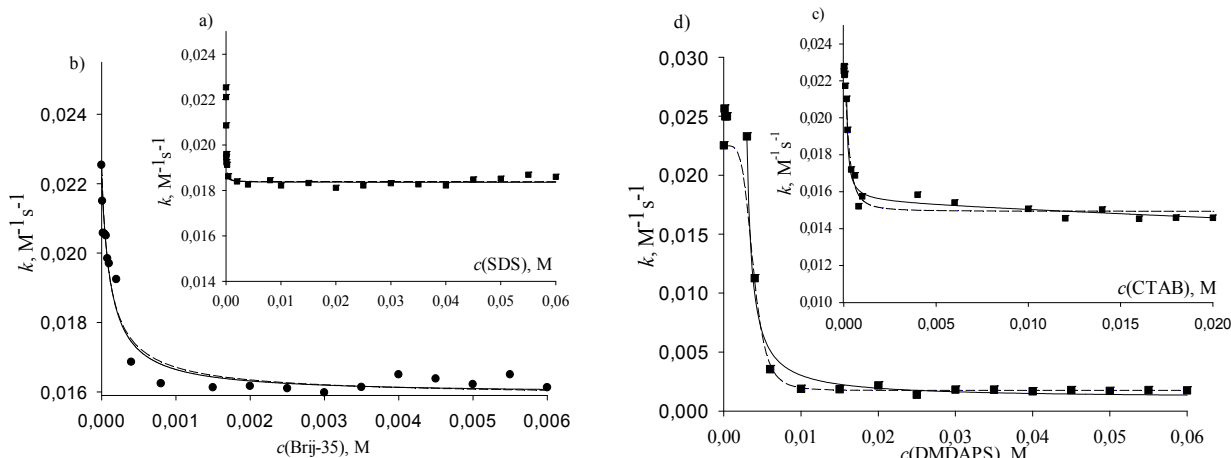


Figure 1. Dependence of the rate constants of the reaction $\text{PP}^{2-} + \text{HO}^-$ on surfactant concentration: SDS (a), Brij-35 (b), CTAB (c), DMDAPS (d); 1.2% vol. ethanol; pH = 12.30, 35 °C. Broken line is drawn using values calculated according to Eq. (5), solid line (for $c(\text{surfactants}) > \text{kinetic CMC}$) is drawn using results of calculations according to Eq. (9) with $\Psi = +59$ mV (see below).

For a complete interpretation of the micellar effect, it is necessary to determine the reaction rate constants in the micellar pseudophase and to evaluate the binding of the reagents to the micelles. Berezin's, Piszkiwicz's, and Pseudophase Ion-Exchange models were used for this purpose.

Application of the Piszkiwicz's model

Piszkiwicz proposed a simple model for describing the effect of micellar surfactant on the rate constant, based on the idea of a so-called catalytic micelle [11-13]. The advantage of this model is that it is capable of describing the effect of pre-micellar region surfactant. According to this model, the second-order rate constant at low surfactant concentrations is given by Eq. (4).

$$k_{obs} = \frac{k_w K_D + k_m [D]^n}{K_D + [D]^n} \quad (4)$$

Here k_w is the reaction rate constant in the absence of surfactant; n is a number of surfactant molecules, which aggregate to form a catalytic micelle; K_D is the dissociation constant of this micelle back to its free components; k_m is the reaction rate constant in the catalytic micelle.

Parameters of Piszkiwicz's model obtained by fitting the experimental data via Eq. (4) are presented in Table 1. Such treatment of experimental points is characterized by high values of the determination coefficients (r^2). However, the standard errors exceed K_D value, which indicates a statistical insignificance of the influence of this parameter on the reaction rate. The calculated k_m values are lower than the corresponding k_w value.

The obtained non-integer values of the n parameter reflect the usual result when using Eq. (4). According to Piszkiwicz [11-13], the non-integer values imply multiple equilibria in the formation of a catalytic micelle. This raises doubts about the validity of the formalism used in the derivation of the equation.

Table 1. Parameters of Eq. (4)^a

Surfactant	r^2	$k_m \times 10^2, \text{M}^{-1}\text{s}^{-1}$	K_D	n
Brij-35	0.967	1.58 ± 0.03	$(3 \pm 4) \times 10^{-4}$	0.9 ± 0.1
DMDAPS	0.985	0.18 ± 0.05	$(1 \pm 77) \times 10^{-11}$	4.7 ± 0.1
CTAB	0.987	1.49 ± 0.01	$(5 \pm 7) \times 10^{-7}$	1.7 ± 0.2
SDS	0.959	1.84 ± 0.01	$(3 \pm 5) \times 10^{-6}$	1.2 ± 0.2

^a Standard errors of the parameters are given. $k_w = (2.25 \pm 0.01) \times 10^2 \text{M}^{-1}\text{s}^{-1}$ at 35 °C.

Application of the Berezin's model

The general equation of Berezin's theory for a bimolecular reaction is normally simplified, with respect to the values of partition coefficient of the reagents between water phase and micellar pseudophase, P [12]. The partition coefficient of the dye, $P_{pp^{2-}}$, should be much higher than unity due to the (probable) hydrophobic interaction. The value of the partition coefficient of hydroxide ion, P_{HO^-} , may be estimated by Eq. (5) [6, 12].

$$P_{HO^-} = \exp(F\Psi / (RT)) \quad (5)$$

Here P_{HO^-} is the partition coefficient of hydroxide ion; F is the Faraday constant; Ψ stands for the difference between the electrical potentials of the phases; T is the absolute temperature; and R is the gas constant.

Values of P_{HO^-} , calculated using the literature Ψ values, are presented in Table 2. According to these P_{HO^-} values, for SDS, DMDAPS, and Brij-35, Eq. (6) is applicable.

$$k_{obs} = \frac{k_m P_{pp^{2-}} [D_n] V + k_w}{1 + P_{pp^{2-}} [D_n] V} \quad (6)$$

For CTAB system, $P_{HO^-} > 1$, therefore:

$$k_{obs} = \frac{k_m K_{pp^{2-}} K_{HO^-} [D_n] / V + k_w}{\{1 + K_{pp^{2-}} [D_n]\} \{1 + K_{HO^-} [D_n]\}} \quad (7)$$

Here k_{obs} is the observed second-order rate constant; k_m and k_w are the corresponding constant in the micellar pseudophase and in surfactant-free system, respectively; V is the molar volume of the surfactant, which equals to 1.064 M^{-1} for Brij-35 [17], 0.314 M^{-1} for DMDAPS [18], 0.364 M^{-1} for CTAB [19], and 0.246 M^{-1} for SDS [17]; $[D_n]$ is the concentration of the micellized surfactant, which equals the total surfactant concentration from which CMC is subtracted; $K_{pp^{2-}}$ and K_{HO^-} are the binding constants of the reagents, expressed in framework of Berezin's model [14] in the following way

$$K_{pp^{2-}} = (P_{pp^{2-}} - 1)V \text{ and } K_{HO^-} = (P_{HO^-} - 1)V, \quad (8)$$

though another way of derivation of the relation between K and P leads to $K = PV$.

The value of surfactant concentration at which the change in the rate constant begins was used as the CMC value, for calculate $[D_n]$ values. This assumption is quite firmly entrenched by introducing the concept of "kinetic CMC" [20, 21]. Indeed, the DLS data give evidence for the presence of colloidal species in the solution of $1 \times 10^{-5} \text{ M}$ PP and CTAB beginning from $c = 2 \times 10^{-4} \text{ M}$ of the surfactant (Figure 2). Accordingly, for SDS, the aggregates appear at $2 \times 10^{-3} \text{ M}$, as determined by the DLS method.

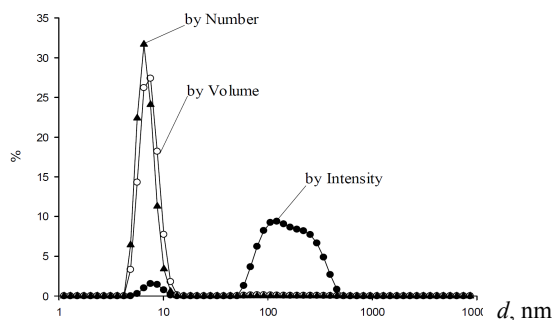


Figure 2. Size distribution by number, volume, and intensity in CTAB + PP solution; concentrations 2×10^{-4} and $1 \times 10^{-5} \text{ M}$, respectively, 0.041 M NaOH.

Parameters of Berezin's model obtained by fitting the data by Eqs. (6) and (7) are presented in Table 2. Treatment of experimental points by Eqs. (6, 7) is characterized by high values of the determination coefficients and satisfactory values of standard errors.

Since the Ψ values depend on the ionic strength of the aqueous phase and did not coincide as determined using different molecular probes, calculations using three P_{HO^-} values for CTAB solutions were carried out (Table 2) [22, 23]. The obtained values of r^2 show that for this system, a more appropriate value of Ψ is +59 mV, in comparison with the values of +118 and +124 mV.

Table 2. Parameters used to fit experimental data by Eqs. (5)–(8) ^a

Surfactant	Ψ , mV	P_{HO^-}	$K_{\text{HO}^-}^{\text{HO}^-}$, M^{-1}	r^2	$k_m \times 10^3$, $\text{M}^{-1}\text{s}^{-1}$	$P_{\text{pp}^{2-}} \times 10^{-4}$	$K_{\text{pp}^{2-}} \times 10^{-4}$, M^{-1}
Brij-35	–	–	–	0.944	16 ± 1	0.84 ± 0.01	0.89^{b}
DMDAPS	+37 [22]	4.0	1.1	0.986	1.1 ± 0.3	0.47 ± 0.06	0.15^{b}
CTAB	+59 [23]	9.2	3.0	0.965	1.87 ± 0.02	3.0^{b}	1.1 ± 0.2
	+118 [22]	84.8	30.5	0.574	0.221 ± 0.008	8^{b}	3 ± 4
	+124 [6]	109.4	39.5	0.332	0.177 ± 0.008	11^{b}	4 ± 9
SDS	–124 [23]	0.008	–	0.956	18 ± 1	14.0 ± 0.2	3.4^{b}

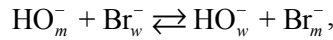
^a Standard errors of the parameters are given. $k_w = (2.25 \pm 0.01) \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ at 35 °C;

^b calculated according to Eq. (8).

The high values of $P_{\text{pp}^{2-}}$ indicate a strong binding of dye with surfactant micelles of different charge type, which is consistent with the concept of hydrophobicity of phenolphthalein. The values obtained for k_m are lower, than the value of the rate constant in surfactant-free system.

Application of the Pseudophase Ion-Exchange model by Bunton and Romsted

Among the surfactant systems considered, the PIE model is applicable only to the treatment of the influence of CTAB micelles. In terms of PIE model for such reactions, in the case of cationic micelles the counterions (Br^-) compete with reactive hydroxide ions in the Stern layer [4,5],



this equilibrium is described by the ion-exchange constant, $K_{\text{Br}^-}^{\text{HO}^-}$,

$$K_{\text{Br}^-}^{\text{HO}^-} = \frac{[\text{HO}_w^-][\text{Br}_m^-]}{([\text{HO}_m^-][\text{Br}_w^-])}. \quad (9)$$

Here $[\text{HO}_w^-]$ and $[\text{HO}_m^-]$ are the HO^- concentrations in aqueous phase and micellar phase, respectively; $[\text{Br}_w^-]$ and $[\text{Br}_m^-]$ are the Br^- concentrations in aqueous phase and micellar phase, respectively; $[\text{HO}_w^-] + [\text{HO}_m^-] = [\text{HO}^-]_{\text{total}}$, $[\text{Br}_w^-] + [\text{Br}_m^-] = [\text{Br}^-]_{\text{total}}$; $[\text{HO}^-]_{\text{total}}$ and $[\text{Br}^-]_{\text{total}}$ are total concentrations of HO^- and Br^- ions in the system.

The $K_{\text{Br}^-}^{\text{HO}^-}$ value is equal to 15, as determined in our recent paper [24], has been used in calculations.

Equation (10) of the dependence of the observed pseudo-first order rate constant of bimolecular reaction on surfactant concentration is written in terms of the local concentration of micellar-bound HO^- $[\text{HO}^-]_m = [\text{HO}_m^-] / (V[D_n])$ [5].

$$k'_{\text{obs}} = \frac{k_w[\text{HO}_w^-] + k_m K_{\text{pp}^{2-}}^m [\text{HO}^-]_m [D_n]}{1 + K_{\text{pp}^{2-}}^m [D_n]} \quad (10)$$

Here $K_{\text{pp}^{2-}}^m$ is the constant of the binding of the dye anion by the micellar aggregate; V is the molar volume of Stern layer ($V = 0.14 \text{ M}^{-1}$ [25, 26]).

The molar ratio $m_{\text{HO}^-} = [\text{HO}_m^-] / [D_n]$ may be determined by the equation:

$$m_{\text{HO}^-}^2 + m_{\text{HO}^-} \left[\frac{[\text{HO}^-]_{\text{total}} + K_{\text{Br}^-}^{\text{HO}^-} [\text{Br}^-]_{\text{total}}}{(K_{\text{Br}^-}^{\text{HO}^-} - 1)[D_n]} - \beta \right] - \frac{\beta [\text{HO}^-]_{\text{total}}}{(K_{\text{Br}^-}^{\text{HO}^-} - 1)[D_n]} = 0. \quad (11)$$

Here β is the fraction of micellar surface charge that is neutralized by counterions (usually β is around 0.8 [4,27]).

The effect of CTAOH micelles was also investigated within the framework of the PIE model. It is of interest because this is a surfactant with reactive counterions. For such type of surfactant, the value of m_{HO^-} is equal to β . The dependence of the pseudo-first order rate constant of reaction between PP^{2-} and hydroxide ion on the concentration of CTAOH in the presence of 0.02 M NaOH is shown in Figure 3. The reaction practically does not proceed in this system without addition of sodium hydroxide. The increase in surfactant concentration leads to acceleration of the reaction reaching a plateau. Consequently, the dye binding by micelles shifts PP^{2-} to a medium with a higher concentration of HO^- ions. The value of local concentration of micellar-bound HO^- is estimated as β/V , i.e. ~ 5.7 M [5]. Considering this value, it is not clear how to explain in the framework of PIE model that the reaction does not occur in the system without added NaOH and why an increase in the total HO^- concentration causes the possibility of the reaction to proceed.

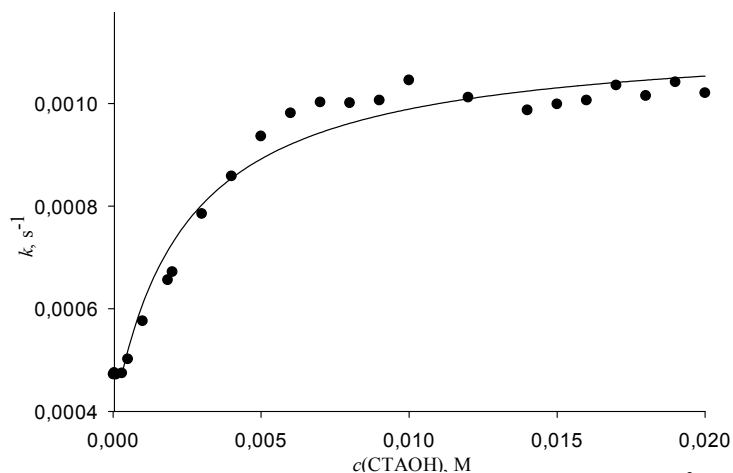


Figure 3. Dependence of the pseudofirst order rate constants of reaction between PP^{2-} and HO^- on the CTAOH concentration at 25 °C, 0.02 M NaOH. Solid line is drawn using values calculated according to Eq. (10).

Treatment by the PIE model is characterized by high values of the determination coefficient only for CTAOH system. Parameters of the PIE model obtained by fitting the data for CTAOH system by Eqs. (9) and (10) are presented in Table 3. The high values of $K_{\text{pp}^{2-}}^m$ indicate a strong binding of the dye by CTAOH micelles. The values obtained for k_m are lower, than the value of the rate constant in water. The observed acceleration in the CTAOH system according to the PIE model is a consequence of the excess of the contribution of the change in the HO^- concentration, which increases 275-fold, over the change in the rate constant (decreased by 60-fold). The same result was obtained by Bunton et al. for the reaction of malachite green, MG^+ , with HO^- [28], but the PIE model does not give a clear explanation of the reason for the change in the rate constant. As shown in our previous article, the factors influencing the value of the rate constant in cationic micelles are high ionic strength and low polarity. The sign and the magnitude of the salt effect and the polarity effect are determined by the signs of the charge of the reacting ions. Therefore, they are not suitable for explaining the decrease in the rate constants of both reactions: MG^+ and PP^{2-} with HO^- .

Table 3. Results of the fitting experimental data to Eqs. (10) and (11)^a

Surfactant	r^2	$k_m, \text{M}^{-1}\text{s}^{-1}$	$K_{\text{pp}^{2-}}^m, \text{M}^{-1}$
CTAOH	0.961	$(1.99 \pm 0.04) \times 10^{-4}$	$(3.7 \pm 0.6) \times 10^2$

^a Standard errors of the parameters are given. $k_w = (1.20 \pm 0.01) \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C.

Probably, the reason of the decrease in the rate constant of the second order reaction on going from the aqueous phase to the micelle is a difference between the reactivity of the hydroxide ion in the aqueous phase and the Stern layer. As a possible reason, we expect a “diverting” effect of cationic head groups: counterions, including the reactive ones, are closely electrostatically associated with the head groups of micelle. An association constant of this process can allow determining the concentration of HO^- ions capable of reacting with the dye. Added NaOH to CTAOH system leads to the com-

pression of the diffuse part of the double electrical layer around the CTAOH micelle and thus the increase in the local HO^- concentration. This is a possible reason for the fact that the reaction with PP in the CTAOH system proceeds only on addition of 0.02 M NaOH. This effect, however, is not presumed in the common PIE model.

The dependence of the pseudo-first order rate constants of reaction between PP^{2-} and HO^- on the concentration of CTAB in the presence of 0.041 M NaOH was treated by Eqs. (10) and (11) using $K_{\text{Br}^-}^{\text{HO}^-} = 15$ and two unknown parameters k_m and $K_{\text{pp}^{2-}}^m$. The obtained r^2 value is very low ($r^2 = 0.2$), that shows the discrepancy between the experimental points and theoretically calculated by Eqs. (10) and (11).

Summary

Comparison of Piszkwicz's and Berezin's models has shown that in the general case the Berezin's model gives a more satisfactory treatment of the experimental data. The high values of partition coefficient of the dye indicate a strong binding of dye with different charge type micelles, which is consistent with the concept of hydrophobicity of phenolphthalein. The values obtained for k_m are lower, than the value of the rate constant in surfactant-free system. This indicates that binding of the dye by micelles leads to a decrease in the observed rate constant due to the low value of k_m . Taking into account the fact that molecules containing hydrophilic and hydrophobic groups are located in the surface layer of the micelle, the decrease in the rate constant upon the transfer of reagents from water to the micellar pseudophase is a consequence of a decrease in the polarity of the microenvironment of the reagents accompanying it, according to the Hughes–Ingold rule.

However, a special case is the system of cationic micelles. For CTAB system, the Berezin's model also gives a more satisfactory description of the experimental data than the PIE model. However, the use of the PIE model has shown what its problem is. This model does not take into account the change in the local concentration of 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 HO^- ions with cationic head groups of surfactant. However, the Berezin's model also does not take into account these changes, hence the question of quantitative processing for such systems remains open.

References

1. Roshchina E.V., Eltsov S.V. Micellar effects in the kinetics of reaction between phenolphthalein and hydroxide ion. (1) The effect of nonionic and anionic surfactants // *Visn. Hark. nac. univ.* 2013. №1085. Ser. Him. Issue 22 (45). P.119–126. (In Russian)
2. Laguta A.N., Eltsov S.V. Micellar effects in the kinetics of reaction between phenolphthalein and hydroxide ion. (2) The effect of cationic and zwitterionic surfactants // *Visn. Hark. nac. univ.* 2013. №1085. Ser. Him. Issue 22 (45). P.127–135. (In Russian)
3. Laguta A.N., Eltsov S.V. Micellar and salt effects in kinetics of the reaction between phenolphthalein and hydroxyl ion // *Visn. Hark. nac. univ.* 2014. №1136. Ser. Him. Issue 24 (47). P.19–30. (In Russian)
4. Bunton C. A., Savelli G. Organic Reactivity in Aqueous Micelles and Similar Assemblies. // *Adv. Phys. Org. Chem.* 1986. Vol. 22. P. 213–309.
5. Romsted L. S. Introduction to Surfactant Self Assembly. // in *Supramolecular Chemistry: From Molecules to Nanomaterials*, Wiley. 2012. P. 1–23.
6. Zakharova L., Valeeva F., Zakharov A., Ibragimova, A., Kudryavtseva L., Harlampidi H. J. Micellization and catalytic activity of the cetyltrimethylammonium bromide–Brij 97–water mixed micellar system. // *Coll. Int. Sci.* 2003. Vol. 263. P. 597–605.
7. Martinek K., Yatsimirski A. K., Osipov A.P., Berezin I. V. Micellar effects on kinetics and equilibrium of synthesis and hydrolysis of benzylideneaniline: A general kinetic conception of micellar catalysis. // *Tetrahedron* 1973. Vol. 29. P. 963–969.
8. Cheong M.-Y., Ariffin A., Khan M. N. A Comparative Analysis of Pseudophase Ion-Exchange (PIE) Model and Berezin Pseudophase (BPP) Model: Analysis of Kinetic Data for Ionic Micellar-mediated Semi-ionic Bimolecular Reaction. // *Bull. Korean. Chem. Soc.* 2007. Vol. 7. P. 1135–1140.

9. Garcia-Rio L., Leis J. R., Mejuto J. C., Navarro-Vazquez A., Perez-Juste J., Rodriguez-Dafonte P. Basic Hydrolysis of Crystal Violet in β -Cyclodextrin/Surfactant Mixed Systems. // *Langmuir* 2004. Vol. 20. P. 606–613.
10. Samiey B., Cheng C.-H., Wu J. Effects of Surfactants on the Rate of Chemical Reactions. *J. Chem.* 2014. Vol. 2014. P. 1–14.
11. Piszkiwicz D. Micelle catalyzed reactions are models of enzyme catalyzed reactions which show positive homotropic interactions. // *J. Am. Chem. Soc.* 1976. Vol. 98. No. 10. P. 3053–3055.
12. Piszkiwicz D. Positive cooperativity in micelle-catalyzed reactions. // *J. Am. Chem. Soc.* 1977. Vol. 99. No. 23. P. 1550–1557.
13. Piszkiwicz D. Cooperativity in bimolecular micelle-catalyzed reactions. Inhibition of catalysis by high concentrations of detergent. // *J. Am. Chem. Soc.* 1977. Vol. 99. No. 5. P. 7695–7697.
14. Berezin I. V., Martinek K., Yatsimirski A. K. Physicochemical foundations of micellar catalysis. // *Russ. Chem. Rev. (Usp. Khim.)* 1973. Vol. 42. P. 787–802.
15. Mchedlov-Petrosyan N. O., Romanenko A. V., Nikishina L. E. Acid–base equilibria of phenolphthalein in aqueous solutions. // *Zhurn. Anal. Khim.* 1984. Vol. 39. No. 8. P. 1395–1403.
16. Mishchenko K.P., Ravdel A.A. *Kratkiy spravochnik fiziko-khimicheskikh velichin.* Leningrad: Khimiya, 1974, 200 p. (In Russian)
17. Berthod A., Garcia-Alvares-Coque C. *Micellar liquid chromatography.* Dekker, N. Y., 2000, 603 p.
18. Sesta B. Physicochemical properties of decyldimethylammonium propanesulfonate and its homologous compounds in aqueous medium. // *J. Phys. Chem.* 1989. Vol. 93. P. 7677–7680.
19. Mittal K. L., Lindman B. Eds., *Surfactants in Solution,* Plenum: N. Y., 1984, 2.
20. Bunton C.A., Robinson L., Micellar effects upon the reaction of P-nitrophenyl diphenyl phosphate with hydroxide and fluoride ions. // *J. Org. Chem.* 1969. Vol. 4. P. 773–780.
21. Bunton C.A., Moffatt J. R. Ionic competition in micellar reactions: a quantitative treatment. // *J. Phys. Chem.* 1986. Vol. 90. No. 4. P. 538–541.
22. Mchedlov-Petrosyan N. O., Vodolazkaya N. A., Yakubovskaya A. G., Grigorovich A. V., Alekseeva V. I., Savvina L. P. A novel probe for determination of electrical surface potential of surfactant micelles: N,N'-di-n-octadecylrhodamine. // *J. Phys. Org. Chem.* 2007. Vol. 20. P. 332–344.
23. Eltsov S. V., Barsova Z. V. Ionization of long-chain fatty acids in micellar solutions of surfactants // *Kharkov University Bull.* 2008, № 820, Chem. Series. Issue 16 (39) P. 292–298 (In Russian).
24. Laguta A.N., Eltsov S.V., Mchedlov-Petrosyan N.O., Kinetics of alkaline fading of methyl violet in micellar solution of surfactants: Comparing Piszkiwicz's, Berezin's, and Pseudophase Ion-exchange models, *Int. J. Chem. Kin.*, in press.
25. Bunton C. A., Gan L.-H., Moffatt J. R., Romsted L. S., Savelli G. Reactions in micelles of cetyltrimethylammonium hydroxide. Test of the pseudophase model for kinetics. // *J. Phys. Org. Chem.* 1981. Vol. 85. P. 4118–4125.
26. Bunton C. A., Mhala M. M., Moffatt J. R. Nucleophilic reactions in zwitterionic micelles of amine oxide or betaine sulfonate surfactants. // *J. Phys. Org. Chem.* 1989. Vol. 93. P. 854–858.
27. Bunton C. A. Reactions in micelles and similar self-organized aggregates. // in *New Comprehensive Biochemistry.* 1984. Vol. 6. P. 461–504.
28. Bunton C.A., Carrasco N., Huang S.K., Paik C.H., Romsted L.S., Reagent distribution and micellar catalysis of carbocation reactions. // *J. Am. Chem. Soc.* 1978. Vol. 100. P. 5420–5425.

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А. Н. Лагута, С. В. Ельцов, Н. О. Мчедлов-Петросян. Количественный анализ мицеллярных эффектов на константу скорости щелочного гидролиза фенолфталеина.

Приводится количественная обработка кинетических данных по реакции между дианионом фенолфталеина и гидроксид ионом в водных растворах, содержащих переменные концентрации поверхностно-активных веществ различного типа. Были использованы следующие поверхностно-активные вещества: Бридж-35 (неионное), додецилсульфат натрия (анионное), цетилтриметиламмоний бромид (катионное) и 3-(диметилдодециламмоний)-пропансульфонат (цвиттерионное). Количественная обработка проведена на основе моделей Пишкевича, Березина и Псевдофазной ионообменной (ПИО). Выявлено, что модель Березина более применима для описания влияния неионных, анионных и цвиттерионных мицеллярных систем. Обсуждаются значения соответствующих кинетических параметров. Влияние цетилтриметиламмония гидроксида на реакцию также изучено и количественно описано моделью ПИО. Исследование систем, основанных на катионном поверхностно-активном веществе, показывает ранее неизвестный эффект, названный нами «отвлекающий эффект».

Ключевые слова: обесцвечивание фенолфталеина, поверхностно-активное вещество, кинетические мицеллярные эффекты, модель Пишкевича, модель Березина, Псевдофазная ионообменная модель.

А. М. Лагута, С. В. Ельцов, М. О. Мчедлов-Петросян. Кількісний аналіз міцелярних ефектів на константу швидкості лужного гідролізу фенолфталеїну.

Наводиться кількісна обробка кінетичних даних по реакції між діаніоном фенолфталеїну та гідроксид іоном у водних розчинах, що містять змінні концентрації поверхнево-активних речовин різного зарядного типу. Були використані наступні поверхнево-активні речовини: Бридж-35 (неіонна), додецилсульфат натрію (аніонна), цетилтриметиламоній бромід (катіонна) і 3-(диметилдодециламоній)-пропансульфонат (цвітеріонна). Кількісна обробка проведена на основі кінетичних моделей Пішкевича, Березина і псевдофазній іонообмінній. Обговорюються значення відповідних кінетичних параметрів. Виявлено, що модель Березина більш застосовна для опису впливу міцелярних систем. Отримані високі значення коефіцієнта розподілу барвника вказують на сильне його зв'язування міцелами поверхнево-активних речовин, що узгоджується з концепцією гідрофобності фенолфталеїну. Отримані значення констант швидкості в міцелі нижчі, ніж у системі без доданої поверхнево-активної речовини, що пояснено зменшенням полярності мікрооточення реагентів у відповідності до правила Хьюза-Інгольда. Таким чином, спостережуване гальмування реакції у системах аніонної, неіонної та цвітеріонної поверхнево-активних речовин є наслідком зв'язування фенолфталеїну міцелами та обумовлено зменшенням константи швидкості, що відбувається при цьому.

Вплив цетилтриметиламоній гідроксиду на реакцію також вивчено і кількісно описано за рівнянням Псевдофазної іонообмінної моделі. Спостережуване прискорення в системі цетилтриметиламоній гідроксиду, відповідно отриманим значенням параметрів псевдофазної іонообмінної моделі, обумовлено переважанням впливу збільшення концентрації HO^- над зниженням константи швидкості, що відбувається при переході реагентів від водної фази до міцелярної псевдофази. Дослідження систем на основі катионних поверхнево-активних речовин, показало раніше невідомий ефект, названий нами «відволікаючий ефект»: зменшення реактивності гідроксид іонів, внаслідок їх електростатичної взаємодії з катионними головними групами поверхнево-активної речовини.

Ключові слова: знебарвлення фенолфталеїну, поверхнево-активна речовина, кінетичні міцелярні ефекти, модель Пішкевича, модель Березина, Псевдофазна іонообмінна модель.