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CHEMICAL KINETICS AND CATALYSIS

The Influence of the Nature of Surfactants and Dispersion Medium on the Catalytic Effect of Reverse Micellar Systems

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Abstract—The catalytic effect of reverse micellar systems in alkaline hydrolysis of phosphonic acid esters is to a considerable extent determined by the structure of the substrate and surfactant and the nature of the oil phase but weakly depends on the surface potential of the aggregates. AOT–butanol–decane–water, sodium dodecyl sulfate–butanol–decane–water, and cetyltrimethylammonium bromide–butanol–decane–water micro-emulsions exhibit specific catalytic properties rather than catalytic properties intermediate between those of the surfactant–alkane–water and surfactant–alkanol–water three-component systems.

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INTRODUCTION

Reverse micellar systems (micelles and water/oil microemulsions) are extensively used as media for chemical reactions [1, 2]. Like other supramolecular catalytic ensembles, they are intermediate between homogeneous and heterogeneous catalysts. Oil (volume) and water microregions are distinguished between in reverse micellar systems. These regions are separated by a monomolecular layer of a surfactant, which allows them to be treated as microheterogeneous solutions. This feature is responsible for the high solubilizing ability of microemulsions with respect to substances of various natures and provides the possibility to widely vary the concentrations of reagents and their microenvironments.

In [3, 4], we studied the kinetics of hydrolysis of four-coordinate phosphorus acid esters in systems based on sodium *bis*(2-ethylhexyl)sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS). In SDSalkanol-water and AOT-alkane-water systems, acceleration and deceleration, respectively, of the alkaline hydrolysis of phosphorus acid esters are predominantly observed. We therefore studied the catalytic effect of reverse micelles and microemulsions under the conditions of the transition from three- to four-component systems with varying the $\sigma = [co-surfactant]/[surfac$ tant] molar ratio for various types of surfactants and substrates. The structure of substrates was selected taking into consideration the electrophilic properties of the phosphorus atom and hydrophobic properties of compounds. For this reason, we studied the kinetics of alkaline hydrolysis of three phosphonates,

$$\begin{array}{c} R \\ R'O \\ R'O \\ \end{array} \xrightarrow{P-O} - NO_2 + 2^{-}OH \longrightarrow \begin{array}{c} R \\ R'O \\ \end{array} \xrightarrow{P-O^{-} + ^{-}O} - NO_2 + H_2O \\ R = ClCH_2, \quad R' = C_2H_5 (1), \quad R = ClCH_2, \quad R' = C_6H_{13} (2), \quad R = R' = C_2H_5 (3). \end{array}$$

The rate constants for second-order reactions in water were $k_{2,w} = 4.0, 3.0, \text{ and } 0.155 \text{ M}^{-1} \text{ s}^{-1}$ for **1**, **2**, and **3**, respectively, under identical conditions (alkali and surfactant concentrations and the $W = [\text{H}_2\text{O}]/[\text{surfactant}]$ molar ratio), which ensured commensurate reactivities of all the phosphonates.

EXPERIMENTAL

Commercial AOT, SDS, cetyltrimethylammonium bromide (CTAB) from Aldrich and Sigma were used without additional purification, and phosphonates 1-3 were synthesized as recommended in [5]. Butanol and decane were purified according to [6]. All solutions

System	$k_{\rm obs} \times 10^3$, s ⁻¹	$k_{\rm obs}/k_{\rm w}$	$k_{\rm obs} \times 10^3$, s ⁻¹	$k_{\rm obs}/k_{\rm w}$	$k_{\rm obs} \times 10^3$, s ⁻¹	$k_{\rm obs}/k_{\rm w}$
	Subst	Substrate 1 Substrate 2		rate 2	Substrate 3	
SDS-butanol-water	0.634	0.016	8.75	0.30	3.11	2.0
AOT-decane-water	23	0.575	22.3	0.743	1.35	0.87
AOT-butanol-water	135	4.4	121	4.0	8.3	5.4

Table 1. Kinetic data on alkaline hydrolysis of phosphonates 1-3 in three-component reverse micellar systems on the basis of anionic surfactants (0.01 M NaOH, 0.25 M surfactant, W = 13)

were prepared using doubly distilled water. Reverse micellar systems were obtained by mixing the components and shaking the mixtures until transparent solutions were formed.

The kinetics of hydrolysis was studied spectrophotometrically on a Specord M-400 instrument by monitoring changes in the absorption of the *p*-nitrophenolate anion at 400 nm. The observed rate constants (k_{obs}) were determined from the $\ln(A_{\infty} - A) = -k_{obs}t + \text{const}$ dependences, where A and A_{∞} are the optical densities of solutions at time t and after reaction completion, respectively. The rate constants were calculated using the method of weighted least squares; the final result was obtained as the arithmetic mean of three measurements which differed by no more than 5%.

RESULTS AND DISCUSSION

The reactivity of compounds in reverse microemulsions is determined by several factors such as the structure of the reagents, their distribution between various microregions, and the nature of their microenvironment. In water in the absence of surfactants, the reactivities of substrates 1-3 are to a great extent determined by the influence of the substituent at phosphorus (its electrophilic properties) and decrease in the series $1 > 2 \ge 3$. A determining factor in microemulsions is probably the distribution of reagents and the properties of the microenvironment in the reaction zone. Generally, the kinetic scheme of bimolecular reactions between reagents S (substrates) and Nu (nucleophiles) in microemulsions presupposes their distributions over all pseudophases and the contributions to the observed rate constants from all microregions [7]. A simpler scheme can be suggested for the alkaline hydrolysis of phosphorus acid esters. We must then take into account the distribution of the substrate between the oil phase and surface layer and the distribution of the nucleophile (hydroxide ion) between the aqueous nucleus and surface layer. The reaction zone is limited to the surface layer, and the process is characterized by the rate constant k_i and distribution constants $K_{\rm S}$ and $K_{\rm OH}$,



Here, the indices "o," "w," and "i" denote oil, water, and the interphase layer.

The localization of the reagents in the surface layer of microemulsions based on AOT and SDS shown in the scheme was proved in [3, 4]. In addition, we showed that the reaction zone shifted when the composition of microemulsions [3] and temperature [8] were varied. These shifts substantially influenced the reactivities of the compounds. In discussing the rate of reactions in microemulsions, the localization of the reagents and the microscopic properties of the medium in the reaction zone are therefore put to the fore.

The kinetic data on three-component systems are presented in Table 1. In water in the absence of surfactants, the reactivity of the substrates decreases in the series $1 > 2 \gg 3$. Approximately the same tendency is observed in the AOT-decane-water and AOT-butanolwater systems (Table 1). In the SDS-butanol-water three-component system under experimental conditions, the reactivity series is rearranged, and k_{obs} and the catalytic effect (k_{obs}/k_w) , where k_w is the pseudo-first-order rate constant in water) decrease in the series 2 > 3 > 1. Catalysis is only observed for phosphonate 3, whereas the rate of the reaction decreases for substrates 1 and 2. It was at the same time shown [9] that the process was accelerated for substrates 1 and 2 in the SDS-hexanol-water system at 0.002 M NaOH, and the series of phosphorus acid ester activities correlated with the electronic and steric substituent effects as in aqueous solutions; the k_{obs} value was higher for substrate 1.

This leads us to conclude that the inversion of the order of substrate 1 and 2 reactivities in going from the SDS–*n*-hexanol–water and AOT–decane–water systems to surfactant–*n*-butanol–water mixtures can be related to changes in the localization of substrates when

the oil phase becomes more hydrophobic; that is, the transition from butanol to hexanol and then to decane evens out differences in the hydrophobic properties of substrates and results in their localization in the same microregion. A determining reactivity factor then becomes the electrophilic properties of the reaction center.

A comparison of the catalytic activities of threecomponent systems for substrate 3 shows that their effect increases in the series AOT-decane-water < SDS-butanol-water < AOT-butanol-water. This tendency is disturbed for substrates 1 and 2 because of changes in their localization, see above. According to Table 1, both the nature of the oil phase and the structure of the surfactant influence the catalytic effect. The replacement of decane with butanol (the transition from the AOT-decane-water to AOT-butanol-water system) increases k_{obs} approximately sixfold for all the three substrates, and reaction inhibition changes for catalysis. The replacement of SDS with AOT (the transition from the SDS-butanol-water to AOT-butanol-water system) increases k_{obs} by a factor of 2.7 for 3. For 2, k_{obs} increases 13.8 times, and with 1, the effect reaches two orders of magnitude, which is likely to a greater extent related to changes in the localization of the reagents than to the replacement of the surfactant.

The kinetic data on the SDS-butanol-decane-water AOT-butanol-decane-water four-component and microemulsions are shown in the figure. These data were obtained at various σ values, which characterize the content of butanol in the systems. The kinetics of hydrolysis of phosphonate 1 only slightly depends on the composition of the oil phase. The reactivities of substrates 2 and 3 change differently depending on the structure of the surfactant. On the whole, the tendencies characteristic of three-component solutions are retained for substrate 3, and the k_{obs} value is somewhat higher in the system based on AOT over the whole range of σ variations; this value increases as the fraction of butanol grows larger. The k_{obs} value approaches the value of the rate constant in the AOT-butanol-water system as σ increases in microemulsions based on AOT.

The reactivity of compound **2** in four-component microemulsions is higher in systems based on SDS than in systems based on AOT. In passing from the SDS–butanol–water three-component system to the SDS–butanol–decane–water four-component mixture, the reactivity of phosphonate **2** changes qualitatively. The addition of decane (30 vol %) sharply increases the observed rate constant for the alkaline hydrolysis of **2** compared with the three-component system (from 0.008 to ~0.06 s⁻¹), and k_{obs} increases as the fraction of the alcohol grows larger. It follows that the distribution of the reagents and the ratio between the factors that determine the catalytic effect change for phosphonate **2** in passing from the three- to four-component micro-emulsion based on SDS.



Dependences of the observed rate constant for alkaline hydrolysis of phosphonates (1) **1**, (2, 2') **2**, and (3, 3') **3** in surfactant–butanol–decane–water four-component microemulsions on the σ = [butanol]/[surfactant] molar ratio; 0.01 M NaOH, 0.25 M surfactant, W = 13; surfactants: (1–3) AOT and (2', 3') SDS.

Similar reasoning is valid with reference to the kinetic behavior of substrate **2** in microemulsions based on AOT. At a large content of decane (90 vol %), the observed rate constant is close to its value in the AOT–decane–water system. The k_{obs} value, however, decreases as the fraction of the alcohol in the oil phase increases. At the highest σ value corresponding to 70 vol % butanol in the oil phase, $k_{obs} = 0.005 \text{ s}^{-1}$, which is much lower than k_{obs} in the AOT–butanol–water system (0.121 s⁻¹).

We measured the surface potential of reverse microemulsions based on AOT and SDS. For this purpose, we studied the acid-base properties of *p*-nitrophenol in these systems at various pH values and calculated pK_a by the Henderson–Hesselbach equation,

$$pK_{a, obs} = pH$$
+ log[*p*-nitrophenol]/[*p*-nitrophenolate]. (1)

The potential was calculated by the equation

$$pK_{a, obs} = pK_{a, 0} - F\Psi/2.303RT,$$
(2)

where $pK_{a,0}$ is the nonelectrostatic component of the shift of pK_a , F = 96486 C/mol is the Faraday constant, and R = 8.314 J/(mol K) is the gas constant.

W	σ	pK _{a, obs}	p <i>K</i> _{a, 0}	-Ψ, mV				
SDS-butanol-decane-water								
13	4	9.03	8.68	21				
13	15	8.56	8.4	9				
13	27	8.54	8.41	7.8				
AOT-butanol-water								
20	_	9.31	8.68	38				
AOT-butanol-decane-water								
20	0.5	9.1	8.68	25				
13	4	8.93	8.68	14.9				
13	15	8.5	8.41	5.2				
13	26	8.5	8.41	5.2				

Table 2. Calculated surface potentials of reverse micellar system on the basis of SDS and AOT

Table 3. Kinetic data on alkaline hydrolysis of phosphonates 1–3 in reverse micellar systems based on CTAB, W = 13

Substrate	[Surfac- tant], M	σ	$k \times 10^3$, s ⁻¹	$k_{\rm obs}/k_{\rm w}$				
CTAB-butanol-water								
1	0.25	_	0.44	0.05				
2	0.25	-	0.25	0.04				
3*	0.25	_	23.1	14.9				
CTAB-butanol-decane-water								
1	0.24	4	1.57	0.20				
1	0.24	10	3.09	0.39				
1	0.24	27	77.3	9.7				
2	0.24	4	0.038	0.006				
2	0.24	10	0.13	0.02				
2	0.24	27	2.87	0.48				
3*	0.24	10	9.45	6.1				
3*	0.24	27	18.8	12.1				

* 0.01 (in other cases, 0.002) M NaOH was added.

An analysis of the data listed in Table 2 leads us to draw two important conclusions. First, the surface potential is somewhat higher in microemulsions based on SDS than in systems with AOT. This can be related not only to the nature of the head groups of the surfactants but also to the nature of the surface layer as a whole. The cone-shaped geometry of the AOT molecule presupposes a larger distance between its head groups and creates the possibility of the penetration of oil phase hydrocarbons and co-surfactants into the interphase zone, which decreases the surface potential. For the linear SDS surfactant, the geometric factor requires a close packing of molecules, which presupposes a higher surface potential. Secondly, in going from three- to four-component solutions and as the content of the alcohol (the σ parameter) increases, the potential drops fairly sharply. This effect is probably caused by an increase in the distance between charged head groups as a result of the insertion of co-surfactant molecules. Note that there is no well-defined correlation between changes in the surface potential and phosphonate hydrolysis rate constants. A decrease in the potential as σ increases causes sometimes an increase and sometimes a decrease in reactivity.

The results obtained (Table 2) are of independent interest, because they characterize the properties of reverse aggregates and the dynamics of their changes in going from ternary reverse micelles to water/oil microemulsions. The corresponding information is still not easily accessible. In addition, these data are of importance for using reverse systems as nanoreactors.

For comparison, we studied three- and four-component catalytic systems on the basis of CTAB, which is a cationic surfactant (Table 3). The rate of alkaline hydrolvsis of substrates 1 and 2 decreases 20 and 25 times, respectively, in the CTAB-butanol-water system; for substrate 3, the rate of hydrolysis increases. According to [3], the reason for this is probably the displacement of the reaction zone as the concentration of alkali changes. The kinetics of hydrolysis of less reactive substrate 3 was studied at higher pH values.

A strong influence of the composition (of the butanol/decane ratio) of the dispersion medium on the catalytic effect is observed in four-component microemulsions on the basis of CTAB. The rate constants of the reactions with all substrates increased as the fraction of butanol grew. With phosphonate 1, the transition from reaction inhibition to catalysis occurred at $\sigma = 27$. As distinct from direct micelles, the surface potential of reverse micelles does not have a determining influence on the sign of the catalytic effect in ion-molecular reactions. The inhibition/catalysis transition is caused by the inversion of the interphase surface potential to a lesser extent than by the nature of the microenvironment of reagents, which is determined by the structure of surfactants and the composition of the oil phase.

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