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Notes

Study of the Reaction 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane + OH⁻ in Nonionic Micellar Solutions

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Introduction

Our research has been focused on the study of micellar effects on electron transfer and on ligand substitution reactions. Most of the processes studied involved hydrophilic charged species, and changes in the reaction rates were not observed when the processes were studied in nonionic micellar systems since they take place in the aqueous phase of the micellar solutions. The reaction of dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-phenyl)-ethane, DDT, with hydroxide ions has a well-understood mechanism.[1−5] DDT is a neutral molecule sparingly soluble in water (solubility, 1.2 ppb[6]), and thus, the possibility of the reaction taking place in the aqueous phase of a micellar system is precluded, as previous studies in cationic micellar systems have shown.[2−5] On this basis, one could expect that changes in the surfactant concentration affect the reaction rate and, therefore, this process seems to be a good candidate in order to investigate kinetic micellar effects in nonionic micellar solutions. In this work the reaction DDT + OH⁻ was studied in aqueous micellar solutions of dodecyl tricosaoxyethylene glycol ether, Brij₃₅, and octylphenol(ethylene oxide)₉,₅ ether, Triton X-100. The influence of the changes in the surfactant concentration as well as in the sodium hydroxide concentration on the observed rate constant was studied. All the experiments were carried out at 298.2 K. The authors have tried to study the reaction in other aqueous nonionic micellar solutions (as various Tweens) but solubility problems precluded the experiments. To rationalize kinetic micellar effects, structural studies of the micellar reaction media are necessary since they can give information about the reaction media at a molecular level. To carry out these structural studies, tension surface measurements as well as fluorescence and light scattering measurements were performed.

Experimental Section

Materials. The 1,1,1-trichloro-2,2-bis(*p*-phenyl)ethane, DDT, was purchased from Aldrich. Aqueous solutions of sodium hydroxide (obtained from Merck) were prepared, and their concentration of hydroxide ions was determined by titration. Dodecyl tricosaoxyethylene glycol ether, Brij₃₅, and octylphenol-(ethylene oxide)₉,₅ ether, Triton X-100, were obtained from Aldrich and were used without further purification. Pyrene was obtained from Aldrich. The critical micelle concentrations, cmc, of the aqueous solutions of these two nonionic surfactants obtained by use of surface tension measurements were in good agreement with those in the literature (see below).

Surface Tension Measurements. Surface tensions were measured using a platinum plate attached to a Krüss Digital tensiometer K10 (Krüss Gmbh, Hamburg, Germany), as described elsewhere.[7] The cmc values were calculated from the points showing discontinuity in the plots of the surface tension against surfactant concentration profiles.

Fluorescence Measurements. Fluorescence measurements were made by using a Perkin-Elmer LS5 spectrofluorometer. Emission espectra of solutions of pyrene (1×10^{-6} mol dm⁻³) in aqueous Triton X-100 and Brij₃₅ solutions, in the absence and presence of sodium hydroxide, were recorded. Before spectra were obtained, oxygen was removed by purging with pure nitrogen for 10−15 min. The excitation wavelength was 352 nm, and excitation and emission slits were each 10 nm. In these spectra fluorescence intensities were measured at 373 nm (band I) and 384 nm (band III). The intensity ratio of the vibronic bands (I/III) is called the pyrene I:III ratio. The pyrene I/III ratio method[8,9] to determine cmc values is based on the sensitivity to the microenvironment nature of the pyrene vibrational structure. Below the cmc, there are no micelles present and the pyrene fluorescence spectrum corresponds to a polar environment. When the micelles are formed, at surfactant concentrations above the cmc, pyrene is solubilized inside the micelles, and consequently, the polarity of its microenvironment decreases sharply, and also does the value of pyrene ratio I/III.

Light-Scattering Measurements. Photon correlation spectroscopy was performed with a Malvern apparatus in aqueous micellar nonionic solutions in the presence of various surfactant concentrations and at five different scattering angles between 30° and 140°, using the green line ($\lambda = 514.5$ nm) of an argon ion laser (Coherent I300). The dynamic light scattering experiments were performed with a Malvern K7032 correlator equipped with 256 channels.

All our experiments show biexponential functions, and the data were analyzed by using a REPES algorithm.[10] This behavior was previously found by other authors for aqueous Brij₃₅ and Triton X-100 micellar solutions.[11,12] The two decays show a diffusive behavior, that is, $\Gamma = D_m q^2$, Γ being the decay constant, where D_m is the apparent diffusion coefficient and q is the

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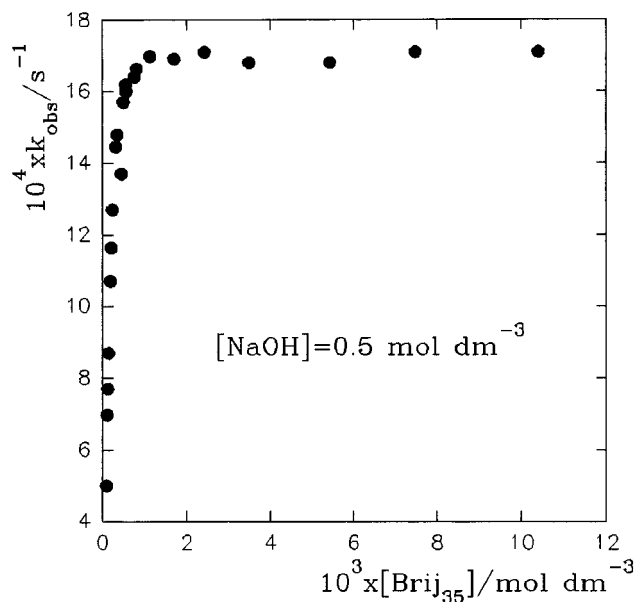
Figure 1. Plot of the observed rate constant, k_{obs}/s^{-1}, against the surfactant concentration for the reaction DDT + OH$^-$ in aqueous Brij$_{35}$ micellar solutions. $T = 298.2$ K.

Figure 2. Plot of the observed rate constant, k_{obs}/s^{-1}, against the surfactant concentration for the reaction DDT + OH$^-$ in aqueous Triton X-100 micellar solutions. $T = 298.2$ K.

scattering wave vector, $q = (4\pi n \sin(1/2\ \theta))/\lambda$, where θ is the scattering angle, λ is the wavelength in a vacuum, and n is the refractive index of the medium. For spherical particles the apparent diffusion coefficient, D_m, is related to the apparent hydrodynamic radius, R_h^{app}, by the Stokes−Einstein relation. Of the two decays, the faster one corresponds to the difussion of the micellar aggregates. The slow decay could correspond to clusters of these aggregates, in equilibrium with the micelles, present in the system.[11,12]

Solutions were filtered with Millipore 0.2 μm filters, to remove dust particles from the scattering volume. All solutions were prepared and handled under a dust-free environment.

Kinetic Measurements. Rates of dehydrochlorination of DDT in the presence of hydroxide ions were determined using the same method as given in ref 5. The low solubility of DDT in water made it necessary to prepare its solutions in acetonitrile. The percentage of acetonitrile in the reaction mixture was always 2 vol %. In all cases hydroxide ion concentration was in large excess in order to work under pseudo-first-order conditions. Observed first-order rate constants, k_{obs}/s^{-1}, were obtained from the slopes of the $\ln(A_4 - A_t)$ against time plots, where A_t and A_4 are the absorbances at time t and at the end of the reaction, respectively. All experiments were repeated at least twice. Under the working conditions the first-order kinetic plots were linear for over more than three half-lives. The rate constants were reproducible within a precision better than 4%.

Results and Discussion

To test our data the reaction was carried out under the working conditions used by Nome et al.[2] The results obtained were in agreement with those in the literature.

Figures 1 and 2 show the dependence of the observed rate constant on the surfactant concentration in aqueous micellar solutions of Brij$_{35}$ and Triton X-100, respectively. The lowest surfactant concentration used was determined by the solubility of the DDT species, as well as by the solubility of the DDE product. In the case of the Triton X-100 micellar solutions, surfactant concentrations higher than 4×10^{-3} mol dm^{-3} could not be studied because a substantial light phenomenon does not permit the recording of the reaction spectrophotometrically.

Table 1 summarizes the cmc data for the two nonionic micellar solutions, in the absence and in the presence of various sodium hydroxide concentrations. These cmc data were obtained in the presence of acetonitrile 2%. None-
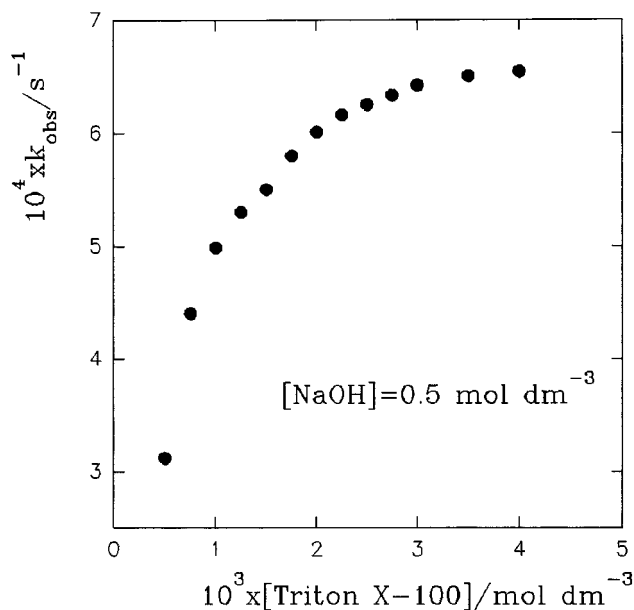
theless, Table 1 shows that the cmc values are independent of the presence of this small acetonitrile percentage. The cmc values are also nearly independent of the sodium hydroxide concentration.

To obtain information about the effect of the addition of NaOH on the size of the nonionic micellar aggregates of Brij$_{35}$ and Triton X-100, dynamic light scattering experiments have been carried out in the absence and in the presence of NaOH by changing surfactant concentration and scattering angles. The dependence of the micellar diffusion coefficient on surfactant concentration is linear for the two nonionic surfactants, at low [surfactant]. From the intercept at infinite dilution of the linear plot D_m against [surfactant], the hydrodynamic radii of the aggregates were obtained. These data are listed in Table 1. One can see from Table 1, that the presence of [NaOH] $= 0.5$ mol dm^{-3} does not affect their values much.

The structural data shown in Table 1 indicate that the presence of high sodium hydroxide concentrations does not affect substantially the characteristics of the nonionic micellar systems used as reaction media, compared to those when NaOH is not present. This will allow the discussion of the kinetic results by taking into account simple expressions which do not incorporate any parameter accounting for possible structural changes.

Figures 1 and 2 show an initial increase in the observed rate constant when [surfactant] increases; subsequently, k_{obs} reaches a plateau and then its value is independent of changes in surfactant concentration. In the case of the aqueous Triton X-100 micellar solutions, experimental problems precluded carrying out the experiments at high enough Triton X-100 concentration to see the plateau clearly. However, it seems reasonable to assume, from Figures 1 and 2, that the dependence of k_{obs} on the whole surfactant concentration range is similar for the two nonionic surfactants. Before going on with the discussion of the [surfactant] changes on k_{obs} shown in Figures 1 and 2, it is interesting to consider that the plots of $\log(k_{obs}/s^{-1})$ against $\log([NaOH]/mol\ dm^{-3})$ were good straight lines, with slopes close to 1, for the two nonionic micellar systems,

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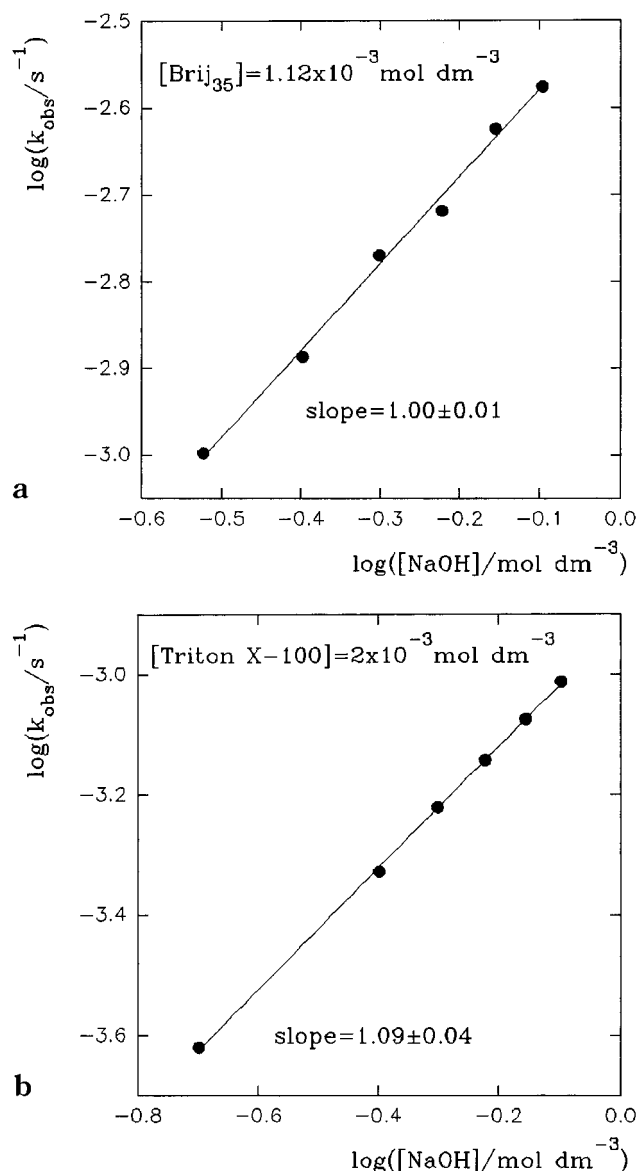
Figure 3. Plot of $\log(k_{obs}/s^{-1})$ against $\log([NaOH]/mol \; dm^{-3})$ for the reaction DDT + OH$^-$ at 298.2 K: (a) [Brij$_{35}$] = 1.12 × 10^{-3} mol dm^{-3}; (b) [Triton X-100] = 2 × 10^{-3} mol dm^{-3}.

at a given [surfactant] (see Figure 3). That is, the reaction follows a second-order rate law, first order with respect to each of the reagents. This can be explained as follows: Taking into account the low solubility of DDT in water, the DDT molecules will be localized in the micellar pseudophase. On the other hand, and considering the hydrophilic character of the hydroxide ions, the process is expected to take place mainly in the micellar surface of the nonionic micelles. Therefore, the reaction rate will depend on the hydroxide ions concentration in this region, [OH$_m^-$]. Since the interfacial electrical potential for a nonionic micelle is zero, the hydroxide ions concentration in the micellar pseudophase will be the same as that in the aqueous phase, [OH^-_m] = [OH^-_w], which explains the results.

To rationalize the dependence of k_{obs} on [surfactant] shown in Figures 1 and 2, a simple mass action model can be considered. This model expresses the observed rate constant as:

$$k_{obs} = \frac{k_w + k_m K_m [\text{Surfactant}_m]}{1 + K_m [\text{Surfactant}_m]} \qquad (1)$$

In this equation the subscripts w and m refer to the aqueous and micellar pseudophases, respectively. k_w and k_m are the first-order rate constants in the aqueous and micellar phases, K_m is the equilibrium binding constant of the DDT molecules to the nonionic micelles, and [Surfactant$_m$] is the micellized surfactant concentration, equal to the total surfactant concentration minus the cmc. At first, one could consider the possibility of the reaction taking place in the aqueous phase as well as the micellar phase. However, if the value of k_w estimated by Rezende et al.[3] is considered ($k_w = 1.05 \times 10^{-3} s^{-1}$ under our working conditions), eq 1 cannot fit the kinetic data. A much smaller value of k_w would be necessary. Along with this, eq 1 cannot explain the plateau reached by k_{obs} at high surfactant concentrations (neither did the linear behavior shown in Figures 4 and 5, see below). With this in mind, and taking into account the low solubility of DDT in water, eq 2 will be considered. This equation can explain the experimental

$$k_{obs} = \frac{k_m K_m [\text{Surfactant}_m]}{1 + K_m [\text{Surfactant}_m]} \qquad (2)$$

kinetic data shown in Figures 1 and 2. When the surfactant concentration is high, one can assume that $1 \ll K_m$[Surfactant$_m$] and then eq 2 is simplified as:

$$k_{obs} = k_m \qquad (3)$$

that is, no dependence of the observed rate constant value on surfactant concentration would be expected, as in fact is found. Figure 1 shows that $k_m = 17 \times 10^{-4} s^{-1}$ for Brij$_{35}$ micellar solutions. Equation 2 can also be written as:

$$\frac{1}{k_{obs}} = \frac{1}{k_m} + \frac{1}{k_m K_m} \frac{1}{[\text{Surfactant}_m]} \qquad (4)$$

That is, the plot of 1/k_{obs} against 1/[Surfactant$_m$] is expected to be a straight line within the surfactant concentration range for which the observed rate constant depends on [Surfactant]. Figures 4 and 5 show these plots for Brij$_{35}$ and Triton X-100, respectively. The cmc values used were 5.5×10^{-5} mol dm^{-3} for Brij$_{35}$ and 2.3×10^{-4} mol dm^{-3} for Triton X-100. From these plots one obtains $K_m = 1.07 \times 10^5$ mol^{-1} dm^3 for Brij$_{35}$ and $K_m = 2.89 \times 10^4$ mol^{-1} dm^3 for Triton X-100. Besides, for the latter a $k_m = 7.0 \times 10^{-4}$ s^{-1} value was obtained. One can see that k_m and K_m values are higher for Brij$_{35}$ than for Triton X-100. The length of the hydrophobic core of the Brij$_{35}$ micelles is much longer (and the hydrophobic core a little more polar) than that of the Triton X-100 micelles.[14] However, the main difference between these two surfactants is the presence of a long linear hydrocarbon chain, C$_{12}$H$_{23}$, in the case of Brij$_{35}$ instead of a p-(1,1,3,3-tetrabutyl)phenoxy group in Triton X-100. The differences in the characteristics of the two nonionic micelles result in different k_m and K_m values, although a clear relationship is not evident.

At this point it is worth noting the difference in the rate of the reaction DDT + OH$^-$ when the micellar reaction media changes. At a given hydroxide ions concentration, the reaction is always much faster in cationic than in nonionic micellar solutions.[2-5] In anionic micellar solutions, even at really high [NaOH], the process is slow ($k_{obs} < 10^{-7} s^{-1}$ [15]). These results can be rationalized by considering that the process takes place in the micellar

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Table 1. Structural Parameters Obtained by Surface Tension, Fluorescence, and Light Scattering Measurements, $T =$ 298.2 K

species present in the solution	surfactant	method	cmc/mol dm^{-3}
none	Brij$_{35}$	surface tension	5.8×10^{-5}
	Brij$_{35}$	fluorescence	5.6×10^{-5}
	Triton X-100	surface tension	2.3×10^{-4}
	triton X-100	fluorescence	2.4×10^{-4}
2% acetonitrile	Brij$_{35}$	surface tension	5.6×10^{-5}
	Brij$_{35}$	fluorescence	5.9×10^{-5}
	Triton X-100	surface tension	2.3×10^{-4}
	Triton X-100	fluorescence	2.6×10^{-4}
[NaOH] = 0.5 mol dm^{-3}	Brij$_{35}$	surface tension	5.1×10^{-5}
	Brij$_{35}$	fluorescence	5.4×10^{-5}
	Triton X-100	surface tension	2.6×10^{-4}
	Triton X-100	fluorescence	2.2×10^{-4}

species present in the solution	surfactant	method	$R_H/$Å
none	Brij$_{35}$	light scattering	44[a]
	Triton X-100	light scattering	45,[b] 31[c]
[NaOH] = 0.5 mol dm^{-3}	Brij$_{35}$	light scattering	42
	Triton X-100	light scattering	39

[a] Reference 12. [b] Reference 11. [c] Reference 13.

Figure 4. Plot of $(1/k_{obs})/s$ against $(1/[\text{Surfactant}])/\text{mol}^{-1}$ dm^3 for the reaction DDT + OH$^-$ in aqueous Brij$_{35}$ micellar solutions. $T =$ 298.2 K.
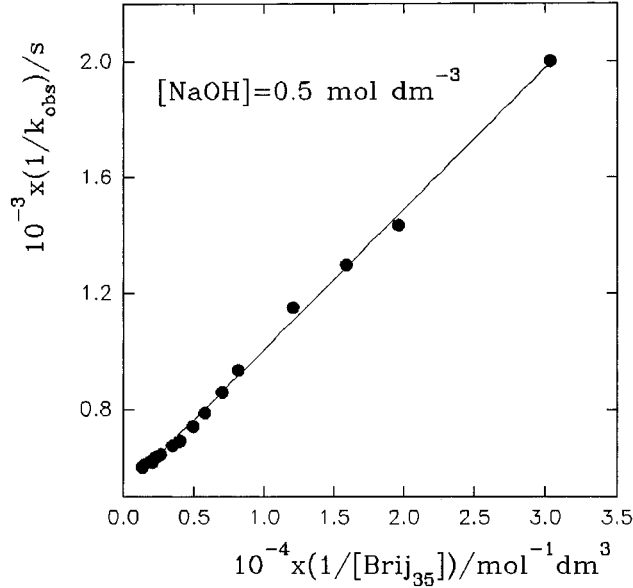

Figure 5. Plot of $(1/k_{obs})/s$ against $(1/[\text{Surfactant}])/\text{mol}^{-1}$ dm^3 for the reaction DDT + OH$^-$ in aqueous Triton X-100 micellar solutions. $T =$ 298.2 K.

surface of the micelles, ionic and nonionic. The reaction rate will be controlled by the hydroxide ion concentration in this region, and [OH$_m$-] will depend on the interfacial electrical potential. Taking the nonionic micelles (zero interfacial electrical potential) as reference, in cationic micelles the local interfacial hydroxide ion concentration will be higher than that in the bulk water because of the positive interfacial electrical potential. Therefore, the reaction rate has to be faster than that in nonionic micelles, as is fo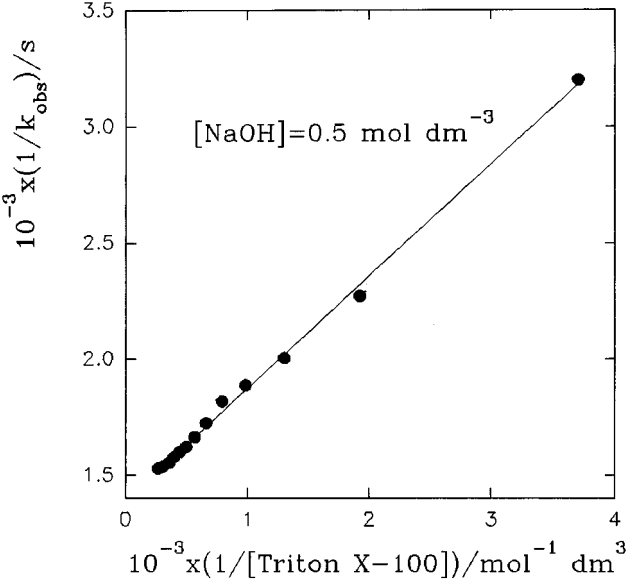und. In anionic micelles, the hydroxide ions will be repelled from the negatively charged micellar surface and, therefore, the reaction rate will be slower than that in nonionic micelles.