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Dehydrochlorination of 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane in Cationic Micellar Systems

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The reaction of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, DDT, with hydroxide ions (NaOH) was studied in cationic micellar aqueous solutions of tetradecyltrimethylammonium bromide, TTAB, and hexadecyltrimethylammonium bromide, CTAB, in the presence and in the absence of various added electrolytes (NaCl, NaF, NaBr, NaNO$_3$, and Na$_2$SO$_4$). In the absence of added salt, the influence of the variations of the surfactant concentration as well as of the total hydroxide ions concentration on the observed rate constant values has been investigated. Kinetic data show that for low [NaOH], a phase separation model can explain the experimental results. However, as the hydroxide ions concentration increases, an additional pathway across the micellar boundary becomes important. When added electrolytes are present in the micellar reaction medium, variations in k_{obs} depend on the nature of the anion of the salt, as well as on [salt]$_{added}$. For a given added electrolyte concentration the observed trend was k_{obs}(NaF) $> k_{obs}$(NaCl) $> k_{obs}$(Na$_2$SO$_4$) $> k_{obs}$(NaBr) $> k_{obs}$(NaNO$_3$). This trend can be explained by considering the affinity of the different anions for the positive sites at the micellar surface, which is the factor controlling the hydroxide ion concentration present in the micellar pseudophase. The kinetic effects of the added electrolytes show that the ion-exchange equilibrium constants are similar for the CTAB and TTAB aqueous micellar solutions.

Introduction

The effects of added salts on micelle-modified reactions are quite varied, ranging from inhibition to activation.[1-7] Such effects have been shown to be strongly dependent on the nature of the detergent headgroup, the initial counterion present, and the total ionic content of the system. We have recently been interested in the study of kinetic electrolyte effects in micellar systems.[8-10] The processes studied involved ionic reagents, and frequently, solubility problems were found when added salt concentration increased, precluding the experiments. The reaction of the dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, DDT, with hydroxide ion is a well understood mechanism. DDT is sparingly soluble in water,[11] and therefore, the possibility of the reaction taking place in the aqueous phase of a cationic micellar system is precluded. On the other hand, there is only one ionic reagent, the hydroxide ions; because of these two facts,

the equations that describe the dependence of the observed rate constant on the nature and concentration of added anions (included the hydroxide ions), in cationic micellar systems, will be quite manageable. Besides, previous experiments have shown that there are no solubility problems when different electrolytes were added to the cationic micellar reaction media. For these reasons the reaction DDT + OH$^-$ was studied in hexadecyltrimethylammonium bromide, CTAB, and tetradecyltrimethylammonium bromide, TTAB, aqueous micellar systems in the presence of various added electrolytes (NaF, NaCl, NaBr, NaNO$_3$, and Na$_2$SO$_4$). The concentrations of the surfactant, of the hydroxide ions, and of the added electrolytes were changed, and their influence on the observed pseudo-first-order rate constant, k_{obs}/s^{-1}, was investigated. In all the experiments the temperature was maintained at 298.2 K.

Experimental Section

Materials. The 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)-ethane, DDT, was purchased from Aldrich. Aqueous solutions of sodium hydroxide (obtained from Merck) were prepared, and their concentration of hydroxide ion was determined by titration. All the electrolytes used were obtained from Merck. Hexadecyltrimethylammonium bromide, CTAB, and tetradecyltrimethylammonium bromide, TTAB, were both from Aldrich and were used as received. The critical micelle concentrations, cmc, of the aqueous solutions of these two surfactants obtained by use of conductivity and surface tension measurements were in good agreement with those in the literature.

Water was obtained from a Millipore Milli-Q water system; its conductivity being less than 10^{-6} S cm^{-1}.

Conductivity Measurements. Conductivity was measured with a Crison MicroCM 2201 conductometer connected to a water flow thermostat maintained at 298.2 ± 0.1 K.

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Table 1. Pseudo-First-Order Rate Constants, k_{obs}/s^{-1}, for the Reaction DDT + OH^{-} in CTAB Aqueous Micellar Systems at [CTAB] = 6 × 10^{-3} mol dm^{-3}, T = 298.2 K

10^2[KOH]/mol dm^{-3}	$10^3 k_{obs}$/s^{-1} ^{a}	$10^3 k_{obs}$/s^{-1} ^{b}
0.10	0.77	0.75
0.24	1.71	1.70
0.43	3.80	3.83
0.60	4.56	4.6
0.80	5.78	5.7
1.60	11.9	11.7
3.10	13.6	13.8
3.72	24.3	24.0

^{a} Reference 12. ^{b} This work.

Kinetics. Rates of dehydrochlorination of DDT in the presence of hydroxide ions were determined following the appearance of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE) at 260 nm.[12] The rate measurements were performed using a Unicam UV-2000 UV−visible spectrophotometer. When the reactions lasted less than 20 min, a manual mixing apparatus was used. In all cases the DDT concentration in the reaction media was 2 × 10^{-5} mol dm^{-3}.

The temperature for the kinetic runs was maintained at 298.2 ± 0.1 K by using a water-jacketed cell compartment. In all cases hydroxide ions 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 $\ln(A_\infty - A_t)$ against time plots, where A_t and A_∞ are the absorbances at time t and at the end of the reaction, respectively. Under the working conditions the first-order kinetic plots were linear over more than three half-lives. The rate constants were reproducible within a precision of about 5%.

Results

To test our data, the reaction was carried out under the working conditions used by Nome et al.[12] Conditions were as follows: [DDT] = 2 × 10^{-5} mol dm^{-3}; [CTAB] = 6 × 10^{-3} mol dm^{-3}; T = 298.2 K; KOH concentration varying from 10^{-3} mol dm^{-3} to 3.72 × 10^{-2} mol dm^{-3}. The wavelength used to follow the reaction was 260 nm. Table 1 shows that the obtained values are in good agreement with those in the literature.

Figures 1 and 2 show the dependence of the observed rate constant on the surfactant concentration in CTAB and TTAB micellar systems at a fixed hydroxide concentration of 0.01 mol dm^{-3}. Table 2 shows the dependence of the observed rate constant, k_{obs}, on the hydroxide ion concentration for different TTAB concentrations. Finally, Figure 3 shows the influence of several added electrolytes on k_{obs} for [surfactant] = 5 × 10^{-3} mol dm^{-3} and [NaOH] = 0.01 mol dm^{-3} for the CTAB and TTAB aqueous micellar solutions.

Discussion

The rate of a bimolecular reaction in a micellar solution can be expressed as

$$\text{rate} = k_{2w}[A]_w[B]_w + k_{2m}[A]_m[B]_m \tag{1}$$

Here k_{2w} and k_{2m} are the second-order rate constants in the aqueous and micellar phases and subscripts w and m refer to the aqueous and micellar phases of the system. This equation is consistent with a phase separation model. The concentrations of reagents in each phase will depend

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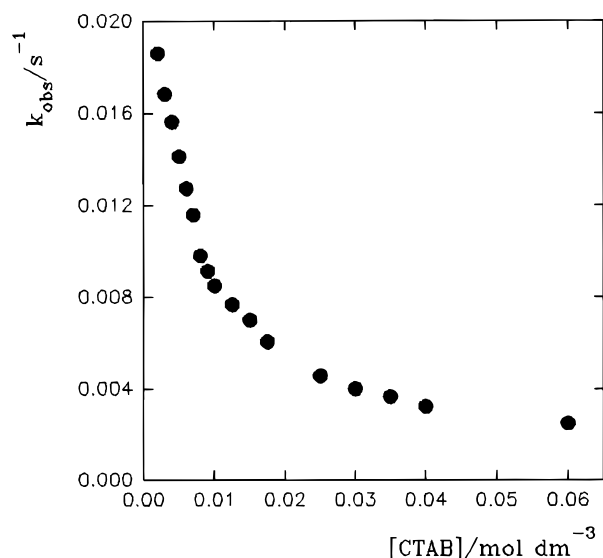
Figure 1. Plot of the observed rate constant, k_{obs}/s^{-1}, against the CTAB concentration for the reaction DDT + OH^{-} in aqueous solutions at [NaOH] = 0.01 mol dm^{-3}. T = 298.2 K.
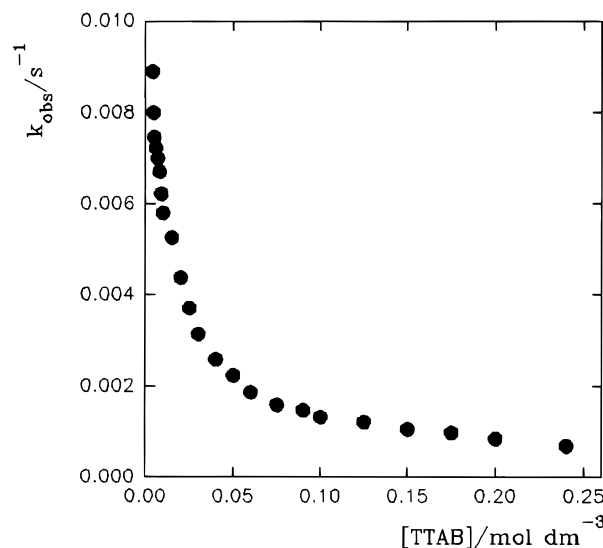
Figure 2. Plot of the observed rate constant, k_{obs}/s^{-1}, against the TTAB concentration for the reaction DDT + OH^{-} in aqueous solutions at [NaOH] = 0.01 mol dm^{-3}. T = 298.2 K.

on the partition coefficients for neutral species and on the ion-exchange phenomena if some of the reagents are ions.

The reaction studied in this work involved a neutral molecule, the DDT species, and a univalent ion of opposite charge to that of the surfactant. Considering eq 1, the expression for the observed first-order rate constant in cationic CTAB and TTAB micellar solutions can be derived on the basis of the model proposed by Quina et al.[13]

$$k_{obs} = \frac{\dfrac{k_{2m}}{\bar{V}} K_S K_{OH^-/Br^-} \dfrac{[Br^-]_b}{[Br^-]_f} + k_{2w}}{(1 + K_S C_D)\left(1 + K_{OH^-/Br^-} \dfrac{[Br^-]_b}{[Br^-]_f}\right)} [OH^-]_T \tag{2}$$

In this equation, $\bar{V}$ is the effective volume, per mole of micellized surfactant, of the region surrounding the micelle

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Table 2. Observed Pseudo-First-Order Rate Constants, k_{obs}/s^{-1}, for the Reaction DDT + OH$^-$ at Different TTAB and Sodium Hydroxide Ion Concentrations, T = 298.2 K

10^3[NaOH] (mol dm^{-3})	$10^3 k_{obs}$/s^{-1} at different TTAB concentrations (10^2[TTAB]/mol dm^{-3})					
	0.5	3	4	5	6	24
2.5		0.64	0.61	0.56	0.41	0.17
3.6	2.57					
5.0	3.90	1.46	1.40	1.17	0.84	0.33
6.0	4.40					
7.5				1.73		
8.0	6.62		2.55			
10.0	7.92	3.23	2.82	2.23	1.86	0.67
12.5	10.2					
15.0	11.8	4.67				
17.5	13.4					
20.0	15.7	6.35	5.90	4.98	3.83	1.27
25.0	18.3	8.13				1.59
30.0		9.52	8.33	7.13	5.63	1.87
40.0		11.2	9.47	8.23	7.17	2.40
50.0		12.8	12.4	10.0	8.37	3.00
60.0		14.9	14.0	11.7	10.7	3.48
70.0		17.0	15.5	13.4	12.1	3.90
80.0		19.2	17.2	14.4	13.3	4.40
90.0		20.7	18.9	16.3	14.1	4.80
100.0		22.9	21.0	17.5	15.6	5.20
110.0				19.0	17.3	
125.0						7.89
150.0						9.47
200.0						12.2
225.0						13.8

within which the ions may be said to be *bound*. K_S is the binding constant of the DDT molecules to the cationic micelles, K_{OH^-/Br^-} is the ion-exchange constant, C_D is the micellized surfactant concentration, and T, b, and f refer to the total, bound, and free ionic species, respectively. Taking into account that the solubility of DDT in water at 298.2 K is smaller than 1.2 ppb[11] and that in the presence of CTAB and TTAB, at the smallest surfactant concentrations used in the reaction media, a DDT concentration of 2×10^{-5} mol dm^{-3} can be easily solubilized, it seems clear that $K_S C_D \gg 1$. Besides, considering the low solubility of DDT in water, the amount of this organic reagent in the aqueous phase of the micellar system would approach zero. Taking into account the above two points, eq 2 can be simplified to eq 3:

$$k_{obs} = \frac{k_{2m}}{C_D \bar{V}} \frac{K_{OH^-/Br^-} \dfrac{[Br^-]_b}{[Br^-]_f}}{1 + K_{OH^-/Br^-} \dfrac{[Br^-]_b}{[Br^-]_f}} [OH^-]_T \qquad (3)$$

The reaction was studied at constant surfactant concentration while changing the total hydroxide concentration present in the reaction media. Table 2 shows the kinetic data. As can be observed, for any given [NaOH], there is a diminution of k_{obs} upon increasing surfactant concentration. Figures 1 and 2 show the dependence of k_{obs} on surfactant concentration at [NaOH] = 0.01 mol dm^{-3}. The diminution of k_{obs} as surfactant concentration increases can be explained by considering that an increase in surfactant concentration supposes an increase in the number of micelles present in the reaction media. This provokes a decrease in the hydroxide ions concentration in the reaction site and, therefore, a decrease in the observed rate constant.
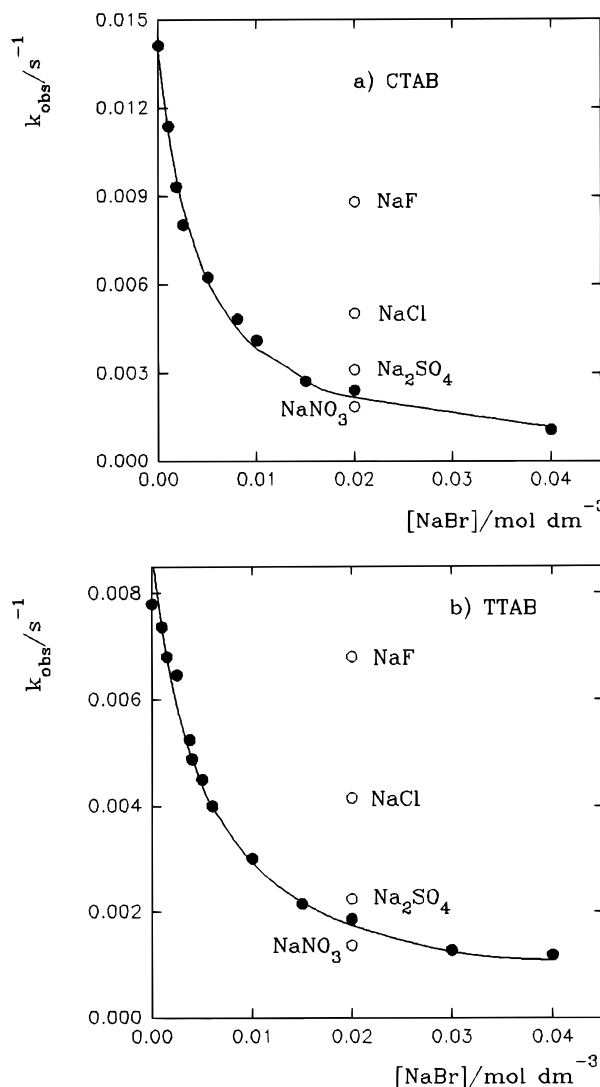
Figure 3. Influence of added NaBr concentration on the observed rate contant for the reaction DDT + OH$^-$ at [NaOH] = 0.01 mol dm^{-3} and [surfactant] = 5×10^{-3} mol dm^{-3}. T = 298.2 K: (a) CTAB; (b)TTAB. In both figures the effect of other added electrolytes on the kinetics is also shown.

Equation 3 cannot explain the kinetic data corresponding to the reaction DDT + OH$^-$ at high [NaOH].[12-14] For [OH$^-$] > 0.01 mol dm^{-3}, the observed rate constant is higher than that expected on the basis of eq 3, and an additional reaction pathway across the micellar boundary, in which the hydroxide ions in the aqueous phase will be able to react with the organic substrate, has to be considered. Equation 4 describes this model

$$k_{obs} = \frac{k_{2m} K_{OH^-/Br^-} \dfrac{[Br^-]_b}{[Br^-]_f}}{C_D \bar{V} \left(1 + K_{OH^-/Br^-} \dfrac{[Br^-]_b}{[Br^-]_f}\right)} [OH^-]_T + k_{2m/w}[OH^-]_T$$

$$(4)$$

Here $k_{2m/w}$ is the second-order rate constant for the reaction pathway at the micellar–water interphase. To calculate the [Br$^-$]$_b$/[Br$^-$]$_f$ values for the different total hydroxide ions concentrations, the following equations, together with

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Table 3. Conductometric Critical Micelle Concentration, cmc, Data for TTAB Aqueous Solutions in the Absence and in the Presence of Various Amounts of Added NaBr and NaNO$_3$, T = 298.2 K

	10^3cmc/mol dm^{-3}	
10^3 [salt]/mol dm^{-3}	NaBr	NaNO$_3$
0	3.64	3.64
1	3.20	3.23
2	2.92	2.88
3	2.69	2.62
4	2.37	2.33
5	2.29	2.22
6	2.10	1.98

the expression for the K_{OH^-/Br^-} equilibrium constant, were taken into account:

$$[Br^-_T] = C_T = [Br^-_b] + [Br^-_f] \tag{5}$$

$$[Br^-_w] = cmc + \alpha C_D + [OH^-_b] \tag{6}$$

$$[Br^-_b] = (1 - \alpha) C_D - [OH^-_b] \tag{7}$$

$$[OH^-_T] = [OH^-_b] + [OH^-_f] \tag{8}$$

In these equations [OH^-_T] is the total analytical concentration of added OH$^-$ ions, and [OH^-_b], [OH^-_f], [Br^-_b], and [Br^-_f] refer to the analytical concentrations of bound and free ions, respectively. α is the dissociation degree of the cationic micelles, and it was taken as 0.2 for the two cationic micellar systems. cmc is the critical micelle concentration and values equal to 9.1×10^{-4} and 3.6×10^{-3} mol dm^{-3} were considered for CTAB and TTAB micellar solutions, respectively. K_{OH^-/Br^-} and $\bar{V}$ were taken as 0.08 and 0.37 dm^3 mol^{-1} for the two micellar systems. In this regard, the value of the effective volume per micellized surfactant (which Berezin et al. approximate as the partial molar volume of the surfactant[15]), $\bar{V}$, would be different for CTAB and TTAB surfactants. However, this difference will not affect discussion of the results, and for this reason, the authors have considered the same value for both systems. With respect to the K_{OH^-/Br^-} constant, at first one would expect it to be similar for the two cationic micellar systems. Nonetheless the authors have tried to investigate this point. Table 3 shows the cmc values of the TTAB aqueous solutions in the presence of several NaNO$_3$ and NaBr concentrations. The NaNO$_3$ electrolyte was chosen in order to minimize the errors in the cmc measurements, given that changing [NaNO$_3$] in the dilute concentration range provokes substantial changes in the cmc of the aqueous TTAB solutions. The cmc data in the presence of added common salt, NaBr, obey the usual relationship[16]

$$\log(cmc) = A - B \log(cmc + [NaBr]_{added}) \tag{9}$$

In the presence of an added foreign salt, as NaNO$_3$, the cmc data corresponding to the TTAB solutions can be well reproduced by the expression[17]

$$\log(cmc) = A - B \log(cmc + K_{NO_3^-/Br^-}[NaNO_3]) \tag{10}$$

where $K_{NO_3^-/Br^-}$ is the ion-exchange constant or counterion selectivity coefficient between the nitrate and bromide ions. In this case, the value obtained from eq 10 was $K_{NO_3^-/Br^-}$ (TTAB) = 1.1, which is equal with that corresponding to the CTAB aqueous micellar solutions.[18,19] It seems that the ion-exchange processes between Br$^-$ and NO$_3^-$ anions at the micellar surface of the CTAB and TTAB micelles are similar. This can be taken as indicative that the ion-exchange mechanism for other anions is also similar. Therefore, the use of K_{OH^-/Br^-} = 0.08 for the TTAB micellar solutions seems justified. Nonetheless, this point will be considered again below.

Solid lines in Figure 4 show the result of the treatment of the experimental data by using eq 4. Table 4 summarizes the kinetic parameters obtained from the theoretical treatment of the data. It is interesting to note that the fittings were done for the same [NaOH] range in the cases of TTAB 0.03, 0.04, 0.05, 0.06, and 0.24 mol dm^{-3}, but not for [TTAB] = 5×10^{-3} mol dm^{-3}. In this regard, the authors tested the influence of the [NaOH] range in the kinetic parameters values obtained from the fittings, by considering the kinetic data for the reaction DDT + OH$^-$ (KOH) at [CTAB] = 6×10^{-3} mol dm^{-3} taken from the work of Nome et al.[12] When the fitting was done, with the kinetic data corresponding to a potassium hydroxide concentration range up to 0.4 mol dm^{-3}, one obtains k_{2m} = $(1.7 \pm 0.1) \times 10^{-2}$ mol^{-1} dm^3 s^{-1} and $k_{2m/w}$ = $(1.76 \pm 0.08) \times 10^{-1}$ mol^{-1} dm^3 s^{-1}. If, on the other hand, one takes the kinetic data for a [KOH] range only up to 0.113 mol dm^{-3}, the results were k_{2m} = $(1.0 \pm 0.1) \times 10^{-2}$ mol^{-1} dm^3 s^{-1} and $k_{2m/w}$ = $(3.1 \pm 0.2) \times 10^{-1}$ mol^{-1} dm^3 s^{-1}. Then, it is clear that the k_{2m} and $k_{2m/w}$ values obtained from the fittings depend on the [OH$^-$] range considered. This is expected since the reaction pathway across the micellar boundary is more important the higher the hydroxide ions concentration is in the reaction medium. In fact, eq 3 can fit the experimental kinetic data for [OH$^-$] < 0.01 mol dm^{-3} in TTAB micellar solutions, as well as for CTAB micellar solutions as pointed out by Nome et al.[12] Table 4 shows that the k_{2m} and $k_{2m/w}$ values obtained for TTAB 0.03, 0.04, 0.05, and 0.06 mol dm^{-3} were practically the same (considering errors). For [TTAB] = 5×10^{-3} mol dm^{-3} the highest hydroxide ions concentration used was 0.025 mol dm^{-3}, and therefore, comparison to the others is not possible. At this point it is worth noting that the model proposed by Quina et al.[13] was developed under the assumption that the fraction of the total solution volume excluded by the micellar phase was small. This is expected to be true for [surfactant] < 0.1 mol dm^{-3}, especially in the presence of an added electrolyte. For [TTAB] = 0.24 mol dm^{-3} this condition could not be fulfilled, and for this reason, the parameter values obtained for this surfactant concentration will not be discussed. From the above results, one can say that a phase separation model, which assumes a closed thermodynamic system and partition between the micellar and aqueous pseudophases, can explain the kinetic results for low concentrations of hydroxide ions. However, as this concentration increases, an additional pathway across the micellar boundary becomes important and it could be the dominant factor in the reaction process at sufficiently high [OH$^-$]. This can be explained by considering that an increase in the sodium

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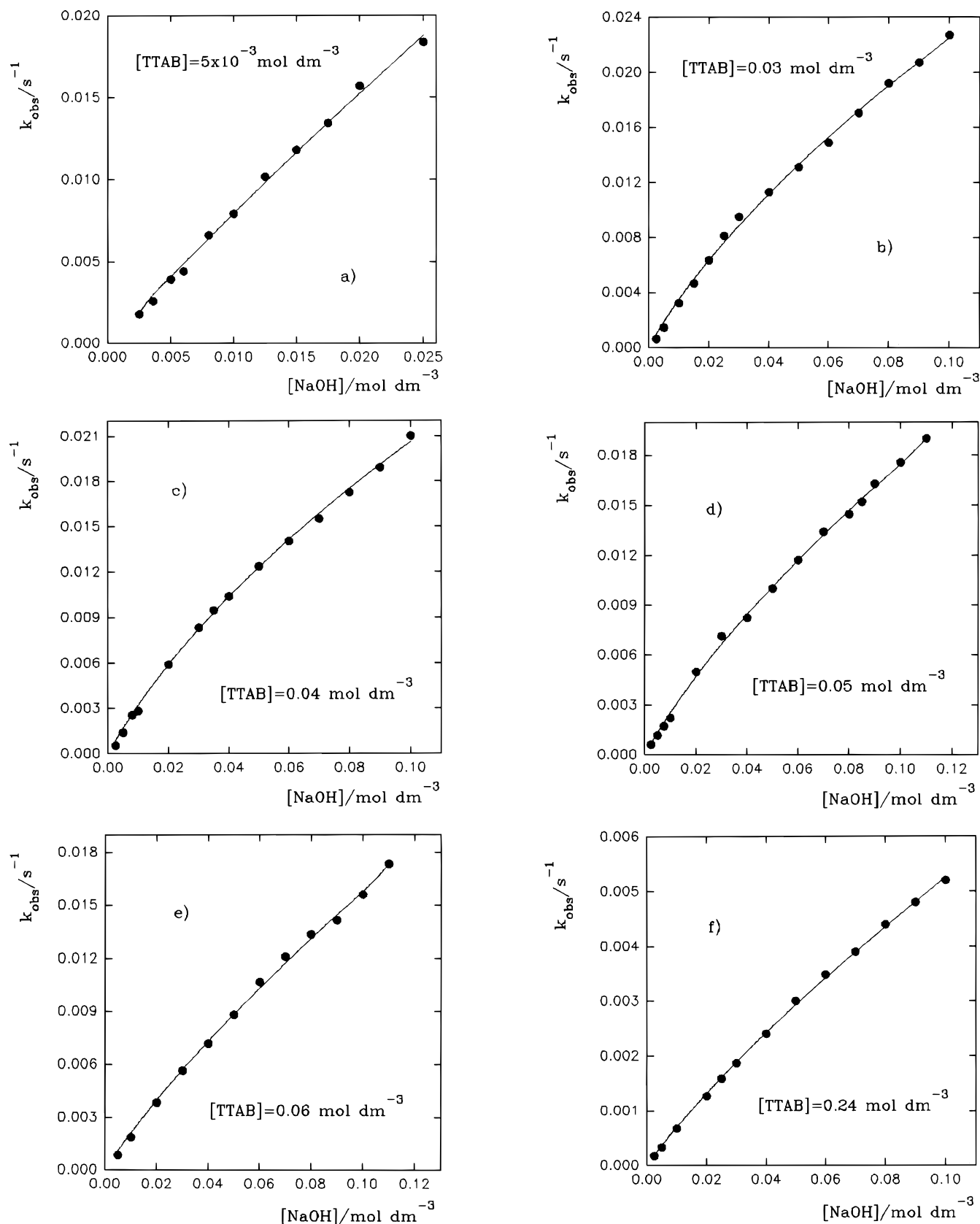
Figure 4. Plots of the observed rate constant, k_{obs}/s^{-1}, against sodium hydroxide concentration at various surfactant concentrations in TTAB aqueous micellar solutions. (a) [TTAB] = 5 × 10^{-3} mol dm^{-3}; (b) [TTAB] = 0.03 mol dm^{-3}; (c) [TTAB] = 0.04 mol dm^{-3}; (d) [TTAB] = 0.05 mol dm^{-3}; (e) [TTAB] = 0.06 mol dm^{-3}; (f) [TTAB] = 0.24 mol dm^{-3}. T = 298.2 K.

hydroxide concentration, that is, an increase in an electrolyte concentration, decreases the thickness of the diffuse double layer.[20,21] The net effect would be an overall increase of the [OH$^-$] in the inner part of the diffuse double layer. As a consequence, the possibility of reaction between a micellar bound substrate and ions adsorbed at the inner part of the double layer close to the shearing surface increases.

Table 4. Kinetic Parameters Obtained from the Theoretical Treatment of the Data by Using Equation 4

[TTAB]/mol dm^{-3}	k_{2m}/mol^{-1} dm^3 s^{-1}	$k_{2m/w}$/mol^{-1} dm^3 s^{-1}
5×10^{-3}	1.8×10^{-3}	6.1×10^{-1}
0.03	1.6×10^{-2}	1.0×10^{-1}
0.04	2.0×10^{-2}	7.3×10^{-2}
0.05	1.8×10^{-2}	7.5×10^{-2}
0.06	1.4×10^{-2}	8.5×10^{-2}
0.24	1.4×10^{-2}	3.8×10^{-2}

Table 5. Ion-Exchange Constants for the CTAB Aqueous Micellar Solutions Taken from Reference 19a

X^-	K_{X^-/OH^-}	X^-	K_{X^-/OH^-}
F^-	1.02	Br	0.048
Cl^-	0.24	NO_3^-	0.04
SO_4^{2-}	0.077		

Figure 3 shows the kinetic data obtained in CTAB and TTAB micellar solutions in the presence of various electrolytes at [surfactant] = 5×10^{-3} mol dm^{-3} and [NaOH] = 0.01 mol dm^{-3}. The highest electrolyte concentration added was 0.04 mol dm^{-3}, and given that the hydroxide ions concentration present in the reaction media is low, eq 3 would be suitable to explain the kinetic data. To test this, the relation $[Br^-]_b/[Br^-]_f$ was calculated in the reaction medium when the [NaBr] changes. The values of the different magnitudes that appear in this equation were the same as those considered above. Nonetheless, eqs 5 to 8 have changed and now:

$$[Br^-_T] = C_T + [NaBr]_{added} = [Br^-_f] + [Br^-_b] \quad (11)$$

$$[Br^-_f] = cmc + \alpha C_D + [OH^-_b] + [NaBr]_{added} \quad (12)$$

$$[Br^-_b] = (1 - \alpha)C_D - [OH^-_b] \quad (13)$$

$$[OH^-_T] = [OH^-_b] + [OH^-_f] \quad (14)$$

The experimental kinetic data were fitted by using eq 3, and the results of the fittings are the solid lines in Figure 3. It can be seen that the theoretical values agree well with the experimental ones. The k_{2m} values obtained from the fittings were 2.54 ± 0.05 and 2.48 ± 0.4 mol^{-1} dm^3 s^{-1} for the CTAB and TTAB micellar solutions, respectively.

Figure 3 shows the changes observed in k_{obs} when adding a given amount of an electrolyte, depending on its nature. Actually, it depends on the nature of the anion of the added salt. For [salt]$_{added} = 2 \times 10^{-2}$ mol dm^{-3} and [NaOH] = 0.01 mol dm^{-3} the observed trend was $k_{obs}(F^-) > k_{obs}(Cl^-) > k_{obs}(SO_4^{2-}) > k_{obs}(Br^-) > k_{obs}(NO_3^-)$. The trend was the same for the two cationic micellar systems. To explain this trend in a simple way, one can consider the ion-exchange equilibrium constants given for the CTAB aqueous micellar solutions by Bartet et al.,[19a] which appear in Table 5. These equilibrium ion-exchange constants give information about the affinity of different anions for the micellar surface sites of CTAB micelles, referring to that of the hydroxide anion. Given that the observed rate constant depends on the hydroxide concentration in the reaction site, the addition of an electrolyte would modify k_{obs} as a function of the affinity of the added anions for the surface micellar sites. Actually, the kinetic effects of the added anions at a constant [NaOH] will be the result of the competition between the OH$^-$ anions and the X$^-$ added

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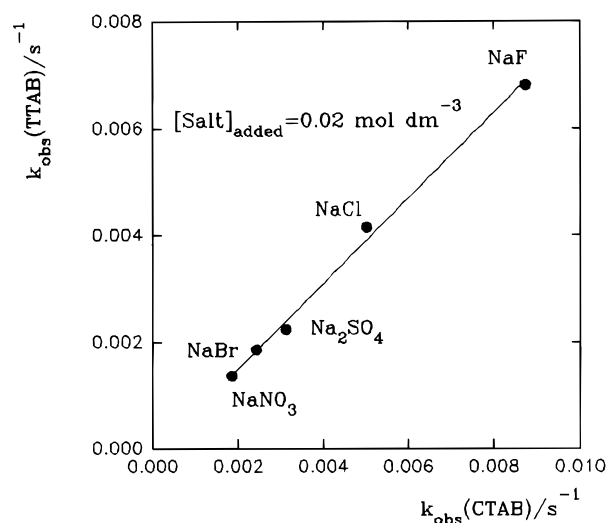
Figure 5. Plot of the observed rate constant values for the reaction DDT + OH$^-$ in TTAB aqueous micellar solutions, k_{obs}(TTAB)/s^{-1}, against those in CTAB micellar solutions, k_{obs}(CTAB)/s^{-1}, when various added electrolytes are present in the micellar reaction medium. T = 298.2 K.
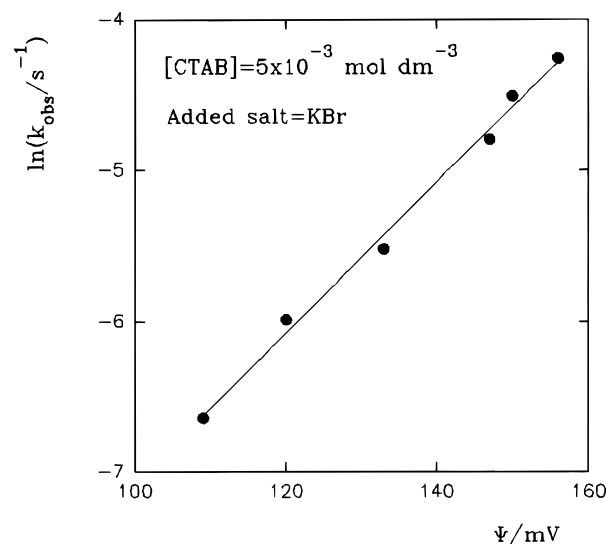
Figure 6. Plot of the ln(k_{obs}/s^{-1}) against the electrical surface potential, Ψ, for the reaction DDT + OH$^-$ in CTAB aqueous solutions in the presence of various amounts of KBr.

anions for the sites occupied by the Br$^-$ anions at the micellar surface. If K_{X^-/OH^-} decreases, the affinity of the X$^-$ anions for the micellar surface sites, referring to that of OH$^-$ ions, will be greater and, as a consequence, OH$^-$ concentration at the micellar surface will be smaller and so will k_{obs}. That is, the effects of added electrolytes reflect the *local concentration* of the reactive hydroxide ions in the micellar pseudophase. With this in mind, one would expect k_{obs} to be higher in the presence of NaF 2×10^{-2} mol dm^{-3} (K_{F^-/OH^-} = 1.02) than in the presence of NaNO$_3$ 2×10^{-2} mol dm^{-3} (=0.043), as in fact is observed. On this basis, the expected trend would be $k_{obs}(F^-) > k_{obs}(Cl^-) > k_{obs}(SO_4^{2-}) > k_{obs}(Br^-) > k_{obs}(NO_3^-)$, in agreement with that found experimentally. Figure 5 shows the plot of k_{obs}(TTAB) against k_{obs}(CTAB) for [surfactant] = 5×10^{-3} mol dm^{-3}, [NaOH] = 0.01 mol dm^{-3}, and [salt]$_{added}$ = 2×10^{-2} mol dm^{-3} for the different added electrolytes studied. A good straight line is obtained. This can be taken as indicative that the ion-exchange equilibrium constants are similar for the two cationic micellar systems, in agreement with the ideas mentioned above.

Another way to treat the added electrolyte effects on micellar-modified reactions is through consideration of the changes in the electrical surface potential of the micelles, Ψ, provoked by the presence of the added salt. From a simple electrostatic point of view, an increase in the added electrolyte concentration would decrease the electrical surface potential Ψ, and therefore, the tendency of the negatively charged hydroxide ions to be located at the positively charged micellar surface would be smaller. That is, one expects a decrease in k_{obs} as [salt]$_{added}$ increases. To investigate this, the reaction was followed in CTAB micellar aqueous solutions in the presence of various amounts of KBr. The surface potential of these cationic micellar solutions was obtained by Johnson et al.[22] Figure 6 shows the plot of $\ln(k_{obs}/s^{-1})$ against the surface potential, Ψ/mV, for [CTAB] = 5×10^{-3} mol dm^{-3}, [NaOH]=0.01 mol dm^{-3}, and several KBr concentrations

up to 0.04 mol dm^{-3}. A good straight line is observed, which indicates that the ion-binding mechanism, to the CTAB micelles, is the factor controlling the added electrolyte kinetic effects since, in these systems, this mechanism controls the electrical surface potential changes upon changing the added electrolyte concentration.[22] The same result was reached by using the two models.

The added electrolyte kinetic effects studied in this work can be explained on the basis of the pseudophase model. However, it would be interesting to investigate added electrolyte effects on reactions at limit conditions; that is, under working conditions for which the pathway across the interfacial boundary will be that which controls the process. We are currently investigating this field.

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