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Influence of *n*-Butyl and *n*-Hexyl Alcohols in the Dehydrohalogenation of DDT in Cationic Micelles of *N*-Cetyl-*N*,*N*,*N*-trimethylammonium Bromide, Chloride, and Hydroxide

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The incorporation of *n*-butyl and *n*-hexyl alcohols on cationic micelles of hexadecyltrimethylammonium bromide, chloride, and hydroxide (CTAB, CTAC, and CTAOH) decreases the rate of the basic dehydrohalogenation of DDT in simple cationic micelles. From the kinetic results and on the basis of the Berezin model the mean molar volume of micellar pseudophase for simple micelles and surfactant/alcohol system has been evaluated.

Introduction

A microemulsion is a transparent dispersion that normally contains oil, water, surfactant, and a cosurfactant which normally is an alcohol.[1] An oil-in-water microemulsion (o/w) consists of droplets with a hydrocarbon core surrounded by surfactant and cosurfactant, while a water-in-oil microemulsion (w/o) is related to a reverse micelle system.

The incorporation of oil and cosurfactant into surfactant micelles increases the mean volume of micellar aggregates[2] and microemulsions are often called swollen micelles.[3]

Different chemical reactions have been studied in such microemulsion systems as nucleophilic substitution,[4-7] hydrolysis,[8-11] oxidation and photooxidation,[12-16] reduction,[17] and Diels–Alder[18] reactions, and it is already reported that they act in the same way as typical aqueous surfactant solutions, so that microemulsions with cationic droplets catalyze bimolecular reactions with negative ions and inhibit reactions with positive ions, and vice versa.[19-22] This catalytic effect is mainly concerned with the concentration of reactants in the small volume of the droplets, and microemulsions have the advantage over single surfactant micelles that they can solubilize higher amounts of hydrophobic substrates. Another important differential factor with a simple surfactant micelle is the mean volume of the droplets.

In this paper we have studied the influence of *n*-butyl and *n*-hexyl alcohols on the dehydrohalogenation of *p*,*p*′-DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) in cationic micelles of CTAOH, CTAC, and CTAB. The experimental kinetic results in surfactant/alcohol/water (1:1) systems are the same as results in o/w microemulsions of surfactant/alcohol/hexane/water ($1{:}1{:}{}^1/_2$).

We report the results in surfactant/cosurfactant/water systems, and we compare these results with the ones obtained in simple cationic micelles of CTAB and CTAOH.[23] In order to explain the results in the surfactant/alcohol system we have used the Berezin model[24-26] that considers "effective concentrations" of reactants in the micellar pseudophase, using the mass-action model and ion-exchange model developed by Bunton[27,28] and Romsted,[29] to explain the ion distribution in solution between aqueous and micellar phases. This new treatment permits comparison of the molar volume of simple surfactant droplets with molar volumes of microemulsion droplets.

Experimental Section

Materials. The surfactant CTAB, Merck, was recrystallized from MeOH/Et$_2$O. The surfactant CTAOH was prepared according to the method described,[30] and the surfactant CTAC was prepared by ion exchange from CTAB on Amberlite 21K anionic resin. The absence of Br$^-$ in CTAOH was tested with silver ion. This surfactant was prepared and kept under N$_2$, and it was only used within 24 h after preparation. The pesticide DDT was purchased from U.S. Environmental Protection Agency Pesticides and Industrial Chemicals Repository (MD-8). Other reactants,

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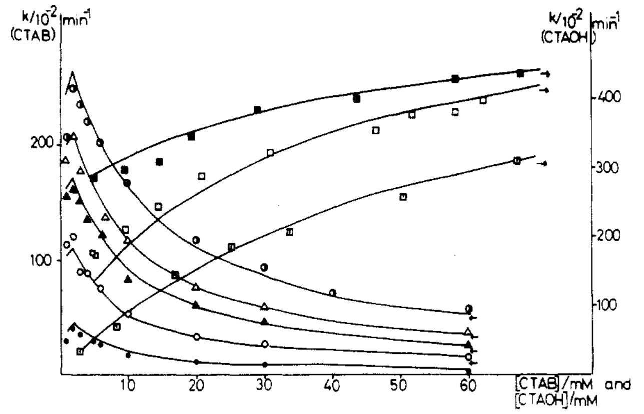

Figure 1. Variation of the pseudo-first-order rate constant, k_Ψ, in simple cationic micelles with CTAOH concentration [NaOH] (in M) = (⊡) 0, (□) 3.3×10^{-3}, (■) 3×10^{-2}, and with CTAB concentration [NaOH] (in M) = 3.3×10^{-3}, (○) 10^{-2}, (▲) 2×10^{-2}, (△) 3×10^{-2}, and (◑) 5×10^{-2}. Lines are predicted values with the theoretical model.

n-butyl and *n*-hexyl alcohols, NaOH, and KBr (Merck), were used without further purification.

Kinetics. All the reactions were run at 25 ± 0.1 °C in the thermostated cuvettes of a Spectronic 2000 Bausch and Lomb spectrophotometer. Reactions were followed at 260 nm which corresponds to the absorbance of the reaction product. Stock solutions of surfactant and alcohol in water proportion 1:1 and surfactant, alcohol, and oil with a mole ratio $1:1:{}^1/_2$ were prepared. To the corresponding mixture and NaOH at a given concentration in the thermostated cuvettes, 0.1 mL of DDT stock solution (10^{-3} M in acetonitrile) was added so that the amount of CH_3CN in the reaction mixture was 3% and the mole ratio between surfactant, cosurfactant, and oil was constant. The concentrations were NaOH 0–10^{-1} M, CTAB, CTAC, and CTAOH 1×10^{-3} to 7×10^{-2} M, and DDT 3.3×10^{-5} M in all the experiments. The hydroxide ion was always in large excess over substrate, and the experimental results fit the first-order rate equation. Values of the pseudo-first-order rate constants were obtained by least-squares fit with correlation coefficients greater than 0.999.

Influence of Alcohol and Oil on the Cmc Value of CTAB. Butyl and hexyl alcohols do not affect the critical micellar concentration of CTAB (cmc = 0.0009 M) as was determined by conductivity measurements, but the value found for the CTAB/*n*-hexane/water ($1:{}^1/_2$) system is 0.001 M.

Experimental Results

The second-order rate constant for the reaction in water was obtained by extrapolating the second-order rate constants obtained in different ethanol–water mixtures to zero amount of ethanol.[23] From these results it is deduced that the small amount of alcohol used does not affect the rate of the reaction in the aqueous phase; that is, it is negligible as compared with the reaction in surfactant.

Experimental pseudo-first-order rate constants for DDT reaction in CTAB and CTAOH micelles at different OH^- concentration are represented by dots in Figure 1.

The influence of *n*-butyl and *n*-hexyl alcohols on reaction in CTAOH ([NaOH] = 0 M) and CTAB ([NaOH] = 5×10^{-2} M) with a mole ratio surfactant/alcohol 1:1 is shown in Figures 2 and 3, respectively, where it can be seen that *n*-butyl and *n*-hexyl alcohols inhibit the reaction more as the hydrocarbon chain of alcohol becomes larger. A wider study is represented in Figures 4–8. In Figure 4 are shown by dots the experimental pseudo-first-order rate constants for reaction in the mixture CTAB/butanol and CTAOH/butanol at different NaOH concentration. In Figure 5 are represented by dots the experimental pseudo-first-order rate constants for the reaction in CTAB/hexanol and CTAOH/hexanol systems at different NaOH concentration. In Figure 6 are represented by dots the experimental pseudo-first-order rate constants for reaction in CTAC/hexanol systems at different NaOH concentrations. In Figure 7 are shown by dots the experimental pseudo-first-order rate constants at fixed CTAB concentrations (2×10^{-3} M and 2×10^{-2} M) and different amounts of OH^- reactive ion for the reaction in the CTAB/butanol system, and in Figure 8 are represented by dots the experimental pseudo-first-order rate constants for the reaction in the CTAB/butanol system at a fixed CTAB concentration (2×10^{-3} M) and different amounts of KBr. In all the experiments (Figures 1–8) the mole ratio surfactant/alcohol, 1:1, was kept constant.

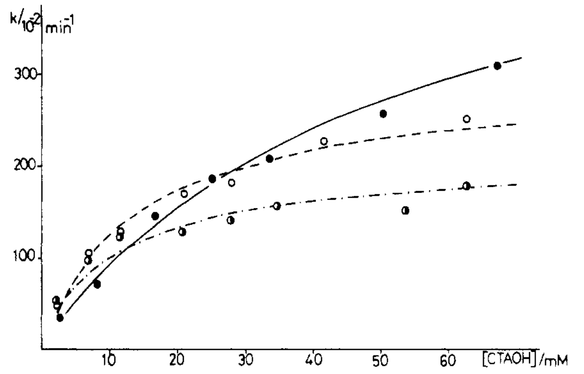

Figure 2. Variation of the pseudo-first-order rate constant, k_Ψ, with CTAOH concentration at fixed NaOH concentration: (●) in simple surfactant micelles, (○) in CTAOH/butanol (1:1) mixture, and (◑) in CTAOH/hexanol (1:1) mixture. Lines are predicted values with the theoretical model.

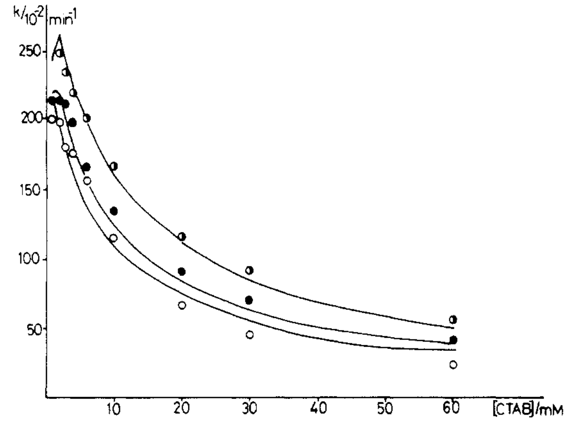

Figure 3. Variation of the pseudo-first-order rate constant, k_Ψ, with CTAB concentration at fixed NaOH concentration (5×10^{-2} M): (◑) in simple surfactant micelles, (●) in CTAB/butanol (1:1) mixture, and (○) in CTAB/hexanol (1:1) mixture. Lines are predicted values with the theoretical model.

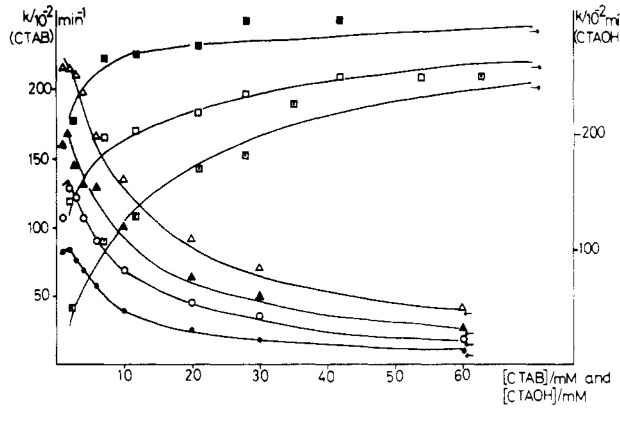

Figure 4. Variation of the pseudo-first-order rate constant, k_Ψ, with surfactant concentration in the CTAB/butanol (1:1) system: [NaOH] (in M) = (●) 1×10^{-2}, (○) 2×10^{-2}, (▲) 3×10^{-2}, and (△) 5×10^{-2} and in CTAOH/butanol (1:1) system: [NaOH] (in M) = (⊡) 0, (□) 1×10^{-2}, and (■) 3×10^{-2}. Lines are predicted values with the theoretical model.

As can be seen the reaction in micelles in the presence of alcohol is always slower than reaction in simple surfactant micelles, and

TABLE I: Values of Parameters That Best Fit the Experimental Results in Aqueous Micelles of CTAB and CTAOH and in the CTAOH/Butanol, CTAOH/Hexanol, CTAB/Butanol, CTAB/Hexanol, and CTAC/Hexanol Systems

system	k_m, M^{-1} min^{-1}	$\bar{V}$, M^{-1}	K_S, M^{-1}	K_{OH}', M^{-1}	K_{Br}^{OH}	K_{Cl}^{OH}
CTAOH	3	0.371	1500 + 27000([NaOH] + [KBr])	30		
CTAB	3	0.371	1500 + 27000 ([NaOH] + [KBr])		32	
CTAOH–butanol	3	0.80	1800 + 34000([NaOH] + [KBr])	80		
CTAOH–hexanol	3	1.20	3000 + 5 × 10^5([NaOH] + [KBr])	120		
CTAB–butanol	3	0.50	1800 + 2.8 × 10^4([NaOH] + [KBr])		32	
CTAB–hexanol	3	0.57	1500 + 7 × 10^4([NaOH] + [KBr])		32	
CTAC–hexanol	3	0.60	2800 + 2 × 10^5([NaOH] + [KBr])			11

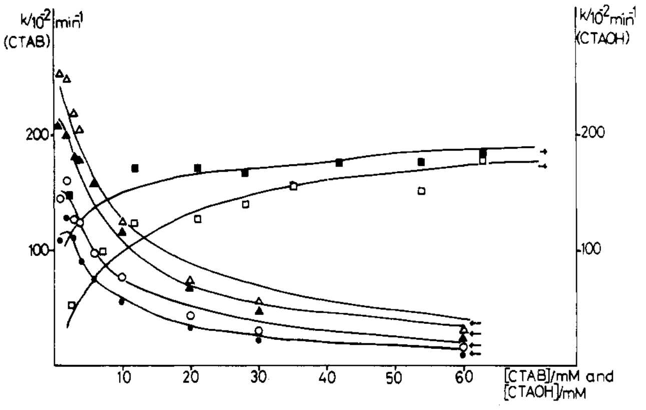

Figure 5. Variation of the pseudo-first-order rate constant, k_Ψ, with surfactant concentration in the CTAB/hexanol (1:1) system: [NaOH] (in M) = (●) 2 × 10^{-2}, (○) 3 × 10^{-2}, (▲) 5 × 10^{-2}, and (△) 6.67 × 10^{-2} and in the CTAOH/hexanol (1:1) system: [NaOH] (in M) = (□) 0 and (<<bds) 10^{-2}. Lines are predicted values with the theoretical model.

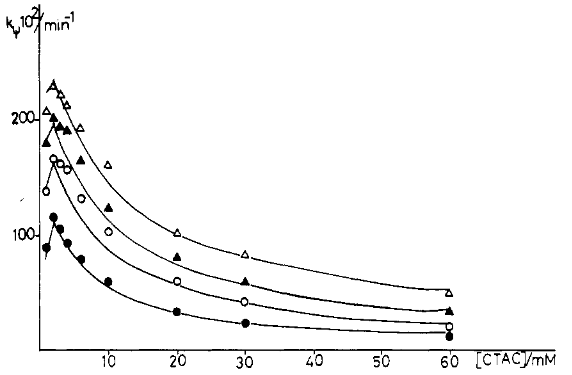

Figure 6. Variation of the pseudo-first-order rate constant, k_Ψ, with surfactant concentration in the CTAC/hexanol (1:1) system: [NaOH] (in M) = (●) 10^{-2}, 2 × 10^{-2}, 3 × 10^{-2}, and (△) 5 × 10^{-2}. Lines are predicted values with the theoretical model.

it can be concluded that the effect of alkoxide as nucleophile can be also considered negligible at this small amount of alcohol.

Discussion

Experimental results in simple micelles of CTAB and CTAOH can be explained with the pseudophase kinetic model proposed by Menger[27] and developed by Bunton and Romsted[28,29] that considers the micelle as a different phase from the aqueous phase and the reaction occurring in both phases so that a pseudo-first-order rate constant can be easily derived as

$$k_W = \frac{k_W[OH_T^-] + (k_M K_S - k_W)[OH_M^-]}{1 + K_S[Dn]} \qquad (1)$$

where k_W is the second-order rate constant in aqueous phase and k_M the pseudo-first-order rate constant in the micellar pseudophase written in terms of the mole ratio of micellar OH^- bound to the micellar head groups and with dimensions of a pseudo-first-order rate constant. K_S is the equilibrium binding constant of the substrate to the micelle, written in terms of micellized surfactant,

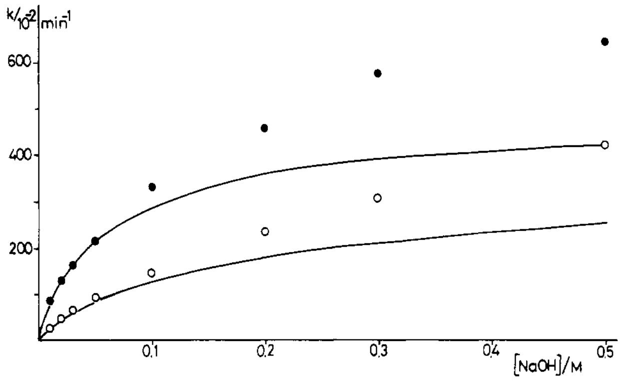

Figure 7. Variation of the pseudo-first-order rate constant, k_Ψ, in the CTAB/butanol (1:1) system, with NaOH concentration at fixed surfactant concentration: [CTAB] = (●) 2 mM and (○) 20 mM. Lines are predicted values with the theoretical model.

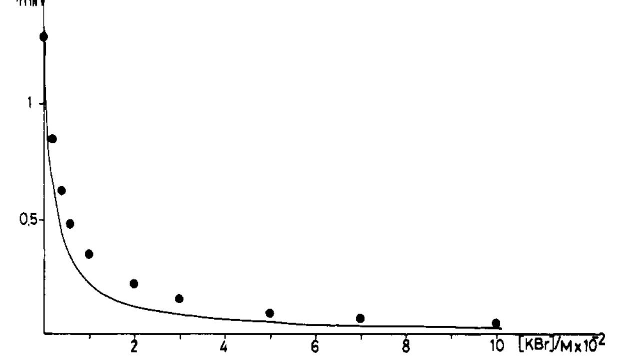

Figure 8. Variation of the pseudo-first-order rate constant, k_Ψ, in the CTAB/butanol (1:1) system, with KBr concentration at fixed surfactant and NaOH concentration: (●) [NaOH] = 2 × 10^{-2} M and [CTAB] = 2 mM. Lines are predicted values with the theoretical model.

$[OH_T^-]$ is the total concentration of hydroxide ion and $[OH_M^-]$ the concentration of this ion bound to micelle, Dn is the micellized surfactant whose concentration is given by [Dn] = [D] − cmc, and cmc is the critical micelle concentration.

For a reaction where the reactive ion OH^- is the micelle counterion as in CTAOH micelles, the distribution of this ion between aqueous and micellar pseudophases can be expressed by a mass-action equilibrium with an equilibrium constant K_{OH}' so that $[OH_M^-]$ is given by

$$K_{OH}'[OH_M^-]^2 - (K_{OH}'[Dn] + K_{OH}'[OH_T^-] + 1)[OH_M^-] + K_{OH}'[Dn][OH_T^-] = 0 \qquad (2)$$

with the fraction of neutralized micellar head groups, β, given by $\beta = [OH_M^-]/[Dn]$. Equation 2 predicts that β increases with surfactant concentration.

In the case of two ions competing for the micellar head groups, as in CTAB micelles, Romsted[29] proposes a model considering β as a constant and ions binding to micelles according to the exchange model developed for resins, so that for OH^- as reactive ion and Br^- as micelle counterion the following expression for $m_{OH} = [OH_M^-]/[Dn]$ can be easily deduced

$$m_{\mathrm{OH}}^{2} + m_{\mathrm{OH}}\left[\frac{[\mathrm{OH_T}^-] + K_{\mathrm{Br}}^{\mathrm{OH}}[\mathrm{Br_T}^-]}{(k_{\mathrm{Br}}^{\mathrm{OH}} - 1)[\mathrm{Dn}]} - \beta\right] - \frac{[\mathrm{OH_T}^-]\beta}{(k_{\mathrm{Br}}^{\mathrm{OH}} - 1)[\mathrm{Dn}]} = 0 \quad (3)$$

where $K_{\mathrm{Br}}^{\mathrm{OH}}$ is the ion exchange equilibrium constant of OH^- for Br^- in the micellar surface and $[\mathrm{Br_T}^-]$ is the total concentration of bromide ion.

The experimental results in Figure 1 can be fitted to eq 1 and 3 for CTAB, and to eq 1 and 2 for CTAOH by using simulation techniques, and the values of parameters that best fit the results in Table I, as already reported.[23]

In order to explain the results in microemulsions it is more convenient to use the Berezin treatment which considers the molar volume of micellar pseudophase and which will permit one to compare the volume of simple surfactant micelles with the volume of microemulsion droplets.

Berezin introduced the partition coefficients for the substrate

$$P_{\mathrm{S}} = [\overline{\mathrm{S_M}}]/[\overline{\mathrm{S_W}}] \quad (4)$$

where $[\bar{\mathrm{S}}_{\mathrm{M}}]$ is the effective concentration of substrate in the micellar pseudophases given by

$$[\overline{\mathrm{S_M}}] = [\mathrm{S_M}]/[\mathrm{Dn}]\bar{V} \quad (5)$$

and $\bar{V}$ is the volume of micellar pseudophase per mole of micellized surfactant, so that $[\bar{\mathrm{S}}_{\mathrm{M}}]$ is the moles of micellized substrate per unit volume of micellar pseudophase. $[\overline{\mathrm{S_W}}]$, the effective free substrate, should be given by

$$[\overline{\mathrm{S_W}}] = \frac{[\mathrm{S_W}]}{1 - [\mathrm{Dn}]\bar{V}} \quad (6)$$

for reasonable values of [Dn] (<0.1 M), $[\mathrm{Dn}]\bar{V} \ll 1$, and $[\overline{\mathrm{S_W}}] \approx [\mathrm{S_W}]$.[20,29]

The relation between this partition coefficient for the substrate, P_{S}, and the substrate binding constant to micelle, K_{S}, is given by

$$P_{\mathrm{S}} = K_{\mathrm{S}}\frac{1 - [\mathrm{Dn}]\bar{V}}{\bar{V}} \simeq \frac{K_{\mathrm{S}}}{\bar{V}} \quad (7)$$

In the same way it is possible to define effective concentrations for ions in solution (X) (OH^- reactive ions and micelle counterion Br^-) as

$$[\overline{\mathrm{X_M}^-}] = \frac{[\mathrm{X_M}^-]}{[\mathrm{Dn}]\bar{V}}$$

$$[\overline{\mathrm{X_W}^-}] = \frac{[\mathrm{X_W}^-]}{1 - [\mathrm{Dn}]\bar{V}} \approx [\mathrm{X_W}^-] \quad (8)$$

A pseudo-first-order rate constant can be derived as

$$k_{\Psi} = \frac{k_{\mathrm{m}}P_{\mathrm{S}}[\overline{\mathrm{OH_M}^-}][\mathrm{Dn}]\bar{V} + k_{\mathrm{W}}(1 - [\mathrm{Dn}]\bar{V})[\overline{\mathrm{OH_W}^-}]}{1 + [\mathrm{Dn}]\bar{V}(P_{\mathrm{S}} - 1)} \quad (9)$$

where k_{m} is defined in terms of the effective concentration of reactive ion, OH^-, in micellar phase so that $k_{\mathrm{m}} = \bar{V}k_{\mathrm{M}}$. This expression reduces to eq 10 considering $(1 - [\mathrm{Dn}]\bar{V}) \approx 1$, the same

$$k_{\Psi} = \frac{k_{\mathrm{W}}[\mathrm{OH}^-] + \left[\frac{k_{\mathrm{m}}K_{\mathrm{S}}}{\bar{V}} - k_{\mathrm{W}}\right][\mathrm{OH_M}^-]}{1 + K_{\mathrm{S}}[\mathrm{Dn}]} \quad (10)$$

as eq 1 for the kinetic model developed for simple ionic micelles where $k_{\mathrm{m}} = k_{\mathrm{M}}\bar{V}$.

Equation 3 and 10 can be used to explain the experimental results in CTAB, CTAB/butanol/water, CTAB/hexanol/water, and CTAC/hexanol/water systems and eq 2 and 10 to explain the results in CTAOH, CTAOH/butanol/Ater, and CTAOH/hexanol/water systems (Figures 1–8).

In the fitting of the results by simulation techniques the parameters β, k_{W}, and cmc have been taken as fixed parameters and k_{m}, K_{S}, K_{OH}', and $K_{\mathrm{Br}}^{\mathrm{OH}}$ as adjustable ones. k_{W} is the second-order rate constant in aqueous solution whose value is 0.126 L mol^{-1} min^{-1}. For the value of the cmc when the surfactant used is CTAB, the following variation[31] with ions has been used as for simple surfactant aqueous micelles, as alcohol in the small proportion used does not affect the cmc

$$\mathrm{cmc} = 10^{(-3.7671-0.2133\ \log\ (\mathrm{cm}+[\mathrm{OH}^-]+[\mathrm{Br}^-]))} \quad (11)$$

and from results in the literature[32] the following empirical expression has been deduced and used for the variation of cmc in CTAC/alcohol mixture with ions

$$\mathrm{cmc} = 10^{(-3.5016-0.2133\ \log\ (\mathrm{cm}+[\mathrm{OH}^-]+[\mathrm{Br}^-]))} \quad (12)$$

where cm is the critical micellar concentration without ions in solution with a value 0.0009 M for CTAB and 0.0013 M for CTAC.[33] β can be taken as constant according to the results in the literature[5] which show that β is not too much affected by microemulsion composition at small concentrations of alcohol and oil, and if the surfactant/alcohol ratio is kept constant, the values used in the literature are in the range 0.6–0.8.[5,7] In this paper we have used for β in the CTAB and CTAB/alcohol mixture the value of 0.8 and in the CTAC/alcohol mixture the value of 0.71 as for aqueous surfactant solution.[29]

Values of parameters k_{m}, K_{S}, K_{OH}', and $K_{\mathrm{Br}}^{\mathrm{OH}}$ that best fit the experimental results in these surfactant/alcohol mixtures are given in Table I and the calculated values of the pseudo-first-order rate constants are the lines in Figures 2–8.

From the obtained values of k_{M} for the reaction in simple surfactant micelles, the k_{m} value can be calculated taking into account that the molar volume of the micellar pseudophase in the simple micelles of CTA$^+$ is 0.371 M^{-1}.[32] Considering that the reaction media in single micelles of CTAOH and CTAB and in microemulsion droplets with CTAOH, CTAB, and CTAC should be the same, as the alcohol incorporation would not change too much the dielectric constant of micellar surface,[36] the kinetic rate constant, k_{m}, in simple micelles and microemulsion droplets with CTAOH, CTAB, and CTAC should be the same.[5,10,37] The values of the molar volume of microemulsion droplets, $\bar{V}$, in all these mixtures have been determined. This molar volume reported in Table I shows that $\bar{V}$ increases as the hydrocarbon chain of the alcohol increases, and it is larger with CTAOH surfactant than with CTAC surfactant and with CTAB surfactant, showing that alcohol penetration is in the order CTAOH > CTAC > CTAB.

The molar volume of micellar pseudophase, $\bar{V}$, can be expressed as[7]

$$\bar{V} = V/n_{\mathrm{surf.}} = \bar{V}_{\mathrm{surf.}} + \frac{n_{\mathrm{ROHM}}}{n_{\mathrm{surf.}}}\bar{V}_{\mathrm{ROHM}} \quad (13)$$

where $\bar{V}_{\mathrm{surf.}}$ and $\bar{V}_{\mathrm{ROHM}}$ are the molar volumes of micellized surfactant and alcohol, respectively, and where the molar volumes of *n*-butyl and *n*-hexyl alcohols are 0.092 and 0.125 M^{-1} as obtained from the density values. The molar ratio of micellized alcohol to micellized surfactant $n_{\mathrm{ROHM}}/n_{\mathrm{surf.}}$ in the droplets should be near 1 if all the alcohol was incorporated into the surfactant micelles. But according to the results in the literature[5,34] the incorporation of *n*-butyl and *n*-hexyl alcohols to CTAB micelles can be expressed by an equilibrium constant given by

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$$K_{\mathrm{ROH}} = \frac{[\mathrm{ROH_M}]}{[\mathrm{ROH_W}]([\mathrm{CTAB}] + [\mathrm{ROH_M}])} \tag{14}$$

where $[\mathrm{ROH_M}]$ and $[\mathrm{ROH_W}]$ denote the amount of alcohol in the micellar and aqueous phases, respectively. The values of these equilibrium constants reported are 1.0 and 10.2 $\mathrm{M^{-1}}$ for *n*-butyl and *n*-hexyl alcohols, respectively,[34] and from these values the ratio $n_{\mathrm{ROHM}}/n_{\mathrm{surf.}}$ in expression 13 can be calculated at different surfactant concentrations. This ratio increases as the concentration of the mixture CTAB/alcohol (1:1) increases and the molar volume of micellar pseudophase also increases. Although the predicted variation in this volume is small in the range of surfactant and alcohol concentration used, using this variation for $\bar{V}$ in the fitting of the experimental results does not make any variation in the parameter values found.

From the parameters in Table I it can be deduced that values of K_S increase with increasing $\bar{V}$, according to the results in the literature[5,20,21] and K_S values in CTAOH/alcohol mixtures are always larger than K_S values in the CTAC/alcohol mixtures, and these are larger than K_S values in CTAB/alcohol mixtures. All these values are larger in the surfactant/hexanol mixture than in surfactant/butanol mixture.

In the case of kinetic results at high amounts of ions, Figure 7 and 8, it is necessary to consider an empirical variation in K_S with ions as reported in Table I that can be explained by a salting-out effect.[35] Solid lines in Figures 7 and 8 show the calculated values for the pseudo-first-order rate constant at a high ion concentration. This treatment that considers β as a constant only explains the experimental results at a low concentration of ions in solution, as can be seen in Figures 7 and 8. This is the same effect found in simple surfactant micelles and the same effect has been found for the reaction in CTAB/hexanol/water systems and in CTAC/hexanol/water systems.

The exchange constant $K_{\mathrm{Br}}^{\mathrm{OH}}$ is the same for the reaction in simple CTAB micelles as for reactions in CTAB/butanol/water and CTAB/hexanol/water systems. This effect is consistent with other results in the literature showing that addition of organic additives to CTAB does not make appreciable changes in counterion binding that is also explained by Lindblom[37] who considers that incorporation of hexanol in the surfactant micelles of CTAX induces a transition from spherical to rod-shaped micelles which leads to an enforced counterion binding that compensates for lowered micellar surface charge density as alcohol molecules locate a micellar surface.

Nevertheless the distribution equilibrium constant for the reactive ion between the aqueous and micellar phases K_{OH}' increases with the incorporation of alcohol into the surfactant micelles of CTAOH, and its value is larger for the CTAOH/hexanol mixture than for the CTAOH/butanol mixture. This effect can be explained considering that the distribution equilibrium of ions between aqueous and micellar phases should be expressed in terms of effective concentrations so that K_{OH}' is given by

$$K_{\mathrm{OH}}' = \frac{[\overline{\mathrm{OH^-}}]\bar{V}}{[\overline{\mathrm{OH_W^-}}]([\mathrm{Dn}] - [\mathrm{OH_M^-}]/[\mathrm{Dn}])} \tag{15}$$

TABLE II: Experimental Values of the Pseudo-First-Order Rate Constant for the Reaction in CTAB/Hexanol (1:1) and in CTAB/Hexane/Hexanol ($1{:}^1/_2{:}1$) Mixtures at Different Surfactant Concentrations at Fixed NaOH Concentration ([NaOH] = 5×10^{-2} M)

[CTAB], 10^3 $\mathrm{M^{-1}}$	CTAB/hexanol (1:1)	CTAB/hexane/hexanol ($1{:}^1/_2{:}1$)
1	2.05	2.11
2	1.99	2.15
3	1.80	1.92
4	1.77	1.82
10	1.15	0.99
20	0.66	0.60
30	0.46	0.41
60	0.24	0.20

and $K_{\mathrm{OH}}' = \bar{K}_{\mathrm{OH}}\bar{V}$, if $\bar{K}_{\mathrm{OH}}$ is the equilibrium distribution given by

$$\bar{K}_{\mathrm{OH}} = \frac{[\overline{\mathrm{OH_M^-}}]}{[\overline{\mathrm{OH_W^-}}]\left[\dfrac{[\mathrm{DN}] - [\mathrm{OH_M^-}]}{[\mathrm{Dn}]}\right]} \tag{16}$$

and effectively $K_{\mathrm{OH}}'\bar{V}$ is nearly constant with a value of 100. It should be taken into account that $K_{\mathrm{Br}}^{\mathrm{OH}}$ expressed in terms of effective concentration is the same as that expressed in terms of analytical concentrations and its value is independent of the droplet volume.

From these obtained values of K_{OH}', $K_{\mathrm{Br}}^{\mathrm{OH}}$, and $K_{\mathrm{Cl}}^{\mathrm{OH}}$ it can be deduced that the selectivity of the micellar surface of $\mathrm{CTA^+}$ for $\mathrm{Br^-}$, $\mathrm{Cl^-}$, and $\mathrm{OH^-}$ ions is in the order $\mathrm{Br^-} > \mathrm{Cl^-} > \mathrm{OH^-}$, and the opposite order is found for the molar volume of micellar pseudophase. That means that, the more neutralized the micellar surface is, the less is the penetration of the alcohol and smaller the molar volume of micellar pseudophase.

The experimental kinetic results for the reaction in the microemulsion CTAB/hexanol/water with a molar ratio ($1{:}1{:}^1/_2$) are the same as for reaction in the mixture CTAB/hexanol (1:1), as can be seen in Table II, and that means that the oil in this small proportion and for this small alcohol concentration does not affect the micelle structure. It is not possible to increase the amount of oil in the mixture because it produces precipitation.

From all of these results it can be concluded that the incorporation of butyl and hexyl alcohols to CTAB, CTAOH, or CTAC cationic micelles decreases the rate of the dehydrohalogenation of *p,p'*-DDT. This effect is explained by the increase of the mean volume of the droplets that decreases the effective concentration of reactants in the micellar pseudophase, and from the kinetic experimental results the molar volume of micellized surfactant has been determined.

Registry No. CTAB, 57-09-0; CTAC, 112-02-7; CTAOH, 505-86-2; DDT, 50-29-3; butanol, 71-36-3; hexanol, 111-27-3.