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Reverse Micellar Aggregates: Effect on Ketone Reduction. 2. Surfactant Role

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Kinetics of the reduction of 3-chloroacetophenone (CAF) with sodium borohydride ($NaBH_4$) were followed by UV−vis spectroscopy at 27.0 °C in different reverse micellar media, toluene/BHDC/water and toluene/AOT/water, and compared with results in an isooctane/AOT/water reverse micellar system. AOT is sodium 1,4-bis-2-ethylhexylsulfosuccinate, and BHDC is benzyl-*n*-hexadecyl dimethylammonium chloride. The kinetic profiles were investigated as a function of variables such as surfactant and $NaBH_4$ concentration and the amount of water dispersed in the reverse micelles, $W_0 = [H_2O]/[\text{surfactant}]$. In all cases, the first-order rate constant, k_{obs}, increases with the concentration of surfactant as a consequence of incorporating the substrate into the interface of the reverse micelles where the reaction takes place. The reaction is faster at the cationic interface than at the anionic one probably because the negative ion BH_4^- is part of the cationic interface. The effect of the external solvent on the reaction shows that reduction is favored in the isooctane/AOT/water reverse micellar system than that with an aromatic solvent. This is probably due to BH_4^- being more in the water pool of the toluene/AOT/water reverse micellar system. The kinetic profile upon water addition depends largely on the type of interface. In the BHDC system, k_{obs} increases with W_0 in the whole range studied while in AOT the kinetic profile has a maximum at $W_0 \sim 5$, probably reflecting the fact that BH_4^- is part of the cationic interface while, in the anionic one, there is a strong interaction between water and the polar headgroup of AOT below $W_0 = 5$ and, above that, BH_4^- is repelled from the interface once the water pool has formed. Application of a kinetic model based on the pseudophase formalism, which considers the distribution of the ketone between the continuous medium and the interface and assumes that reaction takes place only at the interface, has enabled us to estimate rate constants at the interface of the reverse micellar systems. At $W_0 < 10$, it was considered that $NaBH_4$ is wholly at the interface and, at $W_0 \geq 10$, where there are free water molecules, also the partitioning between the interface and the water pool was taken into account. The results were used to evaluate CAF and $NaBH_4$ distribution constants between the different pseudophases as well as the second-order reaction rate constant of the reduction reaction in the micellar interface.

Introduction

Several surfactants are able to aggregate in nonaqueous solvents to yield reverse micellar systems. In recent years, these systems have attracted considerable attention, particularly because of their resemblance to biomembranes and their catalytic properties in chemical and enzymatic reactions. These systems have a molecular heterogeneity due to the amphiphilic nature of the surfactant which forms the interface between water and the nonaqueous solvent. Small solute particles can be located in three different compartments: (a) the external organic solvent, (b) the micellar interface formed by a surfactant monolayer, and (c) the internal water pool. In this way, these systems contain aqueous microdroplets entrapped in a film of surfactant and dispersed in a low-polarity bulk solvent.[1−19]

Among the anionic surfactants that form reverse micelles, the best known are the systems derived from the AOT (sodium 1,4-bis-2-ethylhexylsulfosuccinate) in

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different nonpolar media. AOT has a well-known V-shaped molecular geometry, giving rise to stable reverse micelles without cosurfactant. AOT has the remarkable ability to solubilize a large amount of water with values of W_0, ($W_0 = [H_2O]/[AOT]$), as large as 40−60 depending on the surrounding nonpolar medium, the solute, and the temperature; however, the droplets size depends only on the water amount, W_0.[2,3,5]

The system benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) in toluene was chosen as a cationic polar system in comparison with AOT. It is known that BHDC forms reverse micelles in nonpolar solvents and water can be solubilized up to W_0 of about 20 depending on the external solvent. These reverse micelles seem to have properties that are characteristics of other reverse micellar systems. This is brought out by the nature of the water pool in BHDC, which shows that properties (NMR, IR, QB absorption spectra) of bulk water are approached only when more water than necessary for surfactant solvation is present. Micellar sizes are similar to those reported for AOT reverse micellar systems.[11,20]

Ketone reduction, by $NaBH_4$ in the presence of surfactants in water, shows that micellar aggregates influence regioselectivity and stereoselectivity.[21−23] Studies performed in chiral reverse micellar systems[24] show that prochiral ketones are reduced to optically active alcohols. A systematic study[25] of the reaction performed in cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) in water shows, for a series of aromatic ketones, a decrease (20−50-fold) of the second-order reaction rate constants in the micellar pseudophase relative to those in water due to specific micellar interactions. In part 1 of our work (see ref 39), we have shown results on the reduction in isooctane/AOT/water reverse micellar system and how the ketone structure affects the kinetic results. Due to the lack of kinetic study in different reverse micellar media, we thought it worthwhile to kinetically investigate how different cationic and anionic interfaces and external solvents influence the reduction of 3-chloroacetophenone (CAF) in reverse micelles.

In this paper, we report data on the kinetics of reduction by $NaBH_4$ of the CAF in toluene/BHDC/water, toluene/AOT/water, and isooctane/AOT/water reverse micelles. These systems were chosen to compare the effects of organic solvents and anionic and cationic interfaces over the kinetic profiles. The results show that the reaction is faster in the cationic over the anionic systems and the addition of water can accelerate or retard the reaction depending on the nature of the interface. On the other hand, isooctane as an external solvent seems to allow the borohydride ion to be located more into the interfacial region, probably shrinking it, making reaction faster in isooctane/AOT/water than in toluene/AOT/water reverse micellar system.

Experimental Section

General Methods. UV−vis spectra were recorded on a spectrophotometer equipped with a multiple cell holder thermostated at 27.0 ± 0.1 °C. This temperature was chosen due to the BHDC Kraft point.[20] Control experiments of CAF reduction by $NaBH_4$ (under reverse micelle conditions) showed that CAF disappears and the correspondent alcohol is the only formed product (by GC analysis). Moreover, in the absence of $NaBH_4$, no reaction occurred and there were no changes in the UV−vis spectra.

Materials. 3-Chloroacetophenone (CAF 99%) and toluene (HPLC grade 99.7%) from Aldrich were used without further purification. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) from Sigma (>99%) were dried under reduced pressure and were kept under vacuum over P_2O_5 until use. $NaBH_4$ (98%) from Acros Organics was used as received. Water was triply distilled.

Procedures. A 0.5 M stock solution of surfactant was prepared by dissolving the necessary amount of surfactant in toluene. To obtain optically clear solutions, they were shaken in a sonicating bath. The appropriate amount of stock solution to obtain a given concentration of surfactant in the micellar media was transferred into the cell, and the water was added using a calibrated microsyringe. The amount of water present in the system is expressed as the molar ratio between water and the surfactant ($W_0 = [H_2O]/[surfactant]$). The stock solution of $NaBH_4$ (0.1 M) was prepared by dissolving in a water solution of NaOH (0.1 M) the necessary amount of solid, and the solution was stored in a refrigerator prior to use. NaOH (0.1 M) in the water stabilizes BH_4^-.[26−30] The appropriate amount of stock solution of $NaBH_4$ was added to the reverse micellar system. Ionic concentrations in the reverse micelles are referred to that of water, i.e., $[NaBH_4]_w = 0.1$ M. When the surfactant concentration is changed at a given value of W_0, total amounts of water and $NaBH_4$ differ in every case, but the ratio is always the same. The concentration of hydride species was assumed to be four times that of the analytical

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concentration[31,32] due to the presence in the BH_4^- ion of four identical hydrogen atoms.

Kinetics. Reactions were followed spectrophotometrically by the disappearance of the absorbance of CAF at 300 nm, [CAF] = 1.3×10^{-3} M at 27.0 ± 0.1 °C, using as blank a solution of surfactant of identical concentration and W_0. To start a kinetic run, a stock solution of the ketone was added (20 μL) to a thermostated cell containing $NaBH_4$ in the reverse micellar solution. First-order plots were obtained with an excess of $NaBH_4$. Kinetics fitted the first-order integrated equation in a satisfactory way ($r > 0.999$) for the whole period of time (almost $10t_{1/2}$). The mean standard deviation of the kinetic data, using different samples, was less than 5%.

Determination of the Binding Constant of Ketones (K_{ket}) to AOT Reverse Micellar System. According to the procedure followed in part 1,[39] the absorbances of toluene solutions of CAF at a fixed wavelength were recorded and averaged with different AOT concentrations (0−0.4 M) at $W_0 = 5$, 8, and 10, obtained by diluting the stock AOT solution (AOT 0.4 M, CAF 1.14×10^{-3} M) with the toluene CAF solution. Spectra were run at 27.0 °C, the blank being a solution of surfactant of identical concentration and W_0.

Values of K_{ket} were calculated with a least-squares fit to eq 1[33]

$$A^{\lambda} = \frac{(\epsilon^{f} + \epsilon^{b}[\mathrm{AOT}]K_{\mathrm{ket}})[\mathrm{ketone}]_{\mathrm{T}}}{(1 + K_{\mathrm{ket}}[\mathrm{AOT}])} \tag{1}$$

where A^{λ} is the absorbance at different AOT concentrations and ϵ^{f} and ϵ^{b} are the molar extinction coefficients for the ketones in isooctane and at the interface of the reverse micelles, respectively. [AOT] is the surfactant concentration and $[\mathrm{ketone}]_{\mathrm{T}}$ is the total ketone concentration. It should be borne in mind that precise spectroscopic estimation of the constants is ruled out by the impossibility of having all the ketone at the interface, and therefore, the value of ϵ^{b} can only be estimated. The spectroscopic estimation of K_{ket} was therefore based on the analysis of the spectroscopic data using a fitting procedure with the ϵ^{b} as an adjustable parameter.

K_{ket} values were also determined by using Ketelaar's eq 2[34−36]

$$\frac{1}{A^{\lambda\mathrm{tol}} - A^{\lambda}} = \frac{1}{(\epsilon^{f} - \epsilon^{b})[\mathrm{ketone}]_{\mathrm{T}}} + \frac{1}{(\epsilon^{f} - \epsilon^{b})[\mathrm{ketone}]_{\mathrm{T}}K_{\mathrm{ket}}}\,\frac{1}{[\mathrm{AOT}]} \tag{2}$$

where $A^{\lambda\mathrm{tol}}$ is the absorbance in toluene and the other terms are as defined above. By plotting the left-hand side term of eq 2 vs 1/[AOT], K_{ket} can be calculated from the slopes and intercepts.

These procedures were not feasible for the CAF solution in the BHDC reverse micelles due to very low values of the distribution constants, probably below the limit of sensitivity of the method. There were no spectral changes with the variation of [BHDC] between 0 and 0.4 M.

Results

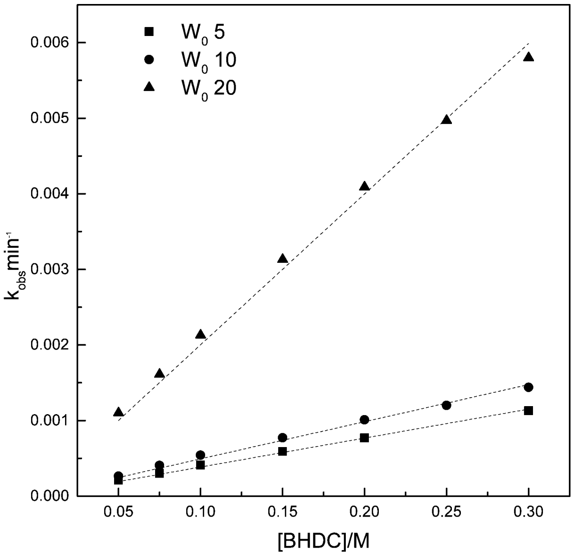
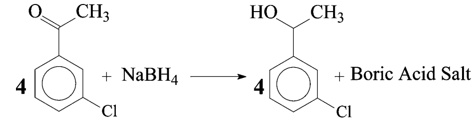


FIGURE 1. Dependence of k_{obs} on the BHDC concentration for the reaction between CAF and $NaBH_4$ in water/BHDC/toluene reverse micellar system at different W_0. [CAF] = 1.3×10^{-3} M. In all cases, $[NaBH_4]_{waterpool} = 0.1$ M. $[NaOH]_{waterpool} = 0.1$ M. The dotted line shows the fitting by eq 8 for $W_0 = 5$ and eq 9 for $W_0 = 10$ and 20.

SCHEME 1



Reaction of CAF with $NaBH_4$ in toluene/BHDC/water and toluene/AOT/water reverse micellar system yields the corresponding alcohol (Scheme 1) as in homogeneous media,[37,38] in direct micelles,[25] and AOT reverse micellar systems: see part 1.[39]

A large excess of $NaBH_4$ was always used, and reactions follow first-order kinetics. Effects of the microheterogeneous media were investigated as follows.

Reaction in Toluene/BHDC/Water Reverse Micellar Systems. (1) **Effects of BHDC Concentration.** Figure 1 shows the kinetic profile with varying BHDC concentrations at $W_0 = 5$, 10, and 20, where k_{obs} increases almost linearly with increasing [BHDC] over the whole range. These results probably indicate that saturation of CAF, in the micellar interface, is not reached in the range of the [surfactant] used. Moreover, Figure 1 shows that k_{obs} increases with the water content (W_0).

(2) Effect of $NaBH_4$ Concentration. Figure 2 shows the effect of $NaBH_4$ concentration on the reduction of CAF by $NaBH_4$ in cationic reverse micelles at 0.2 M of BHDC and W_0 = 5, 10, and 20. k_{obs}'s increase linearly with $[NaBH_4]$. The reaction is faster at high water content as observed with varying [BHDC].

(3) Effect of Water Dispersed, W_0. Figure 3 shows effects of changing W_0 on k_{obs} with [BHDC] = 0.3 M and $[NaBH_4]_w = 0.1$ M. The value of k_{obs} increases slowly with W_0 up to $W_0 \sim 10$, and then the rate constant increases noticeably. The maximum amount of water (W_0) that can be reached in this system is around 22 and the minimum

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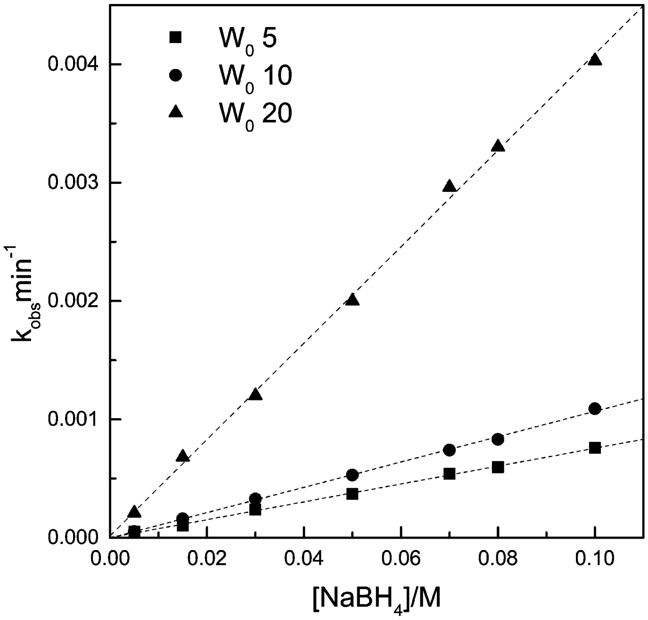


FIGURE 2. Variation of k_{obs} as a function of the $NaBH_4$ concentration for the reaction between CAF and $NaBH_4$ in water/BHDC/toluene reverse micellar system at different W_0. [CAF] = 1.3×10^{-3} M. In all cases, [BHDC] = 0.2 M. $[NaOH]_{waterpool}$ = 0.1 M. The dotted line shows the fitting by eq 8 for $W_0 = 5$ and eq 9 for $W_0 = 10$ and 20.

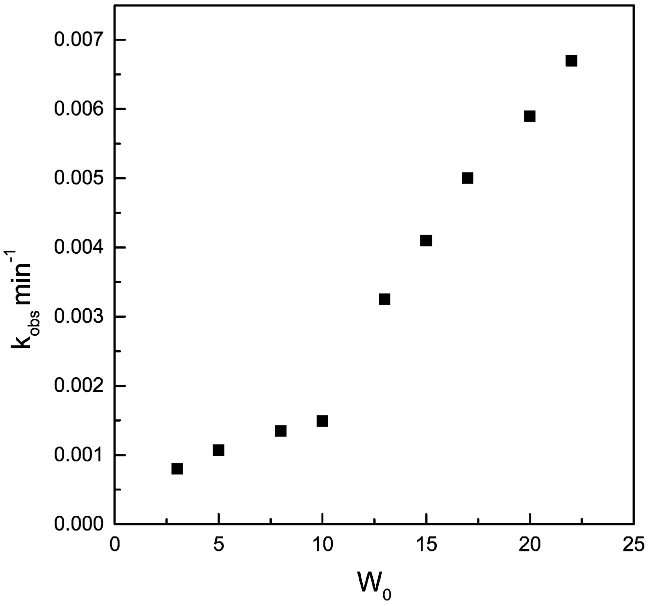


FIGURE 3. Variation of k_{obs} as a function of W_0 for the reaction between CAF and $NaBH_4$ in water/BHDC/toluene reverse micellar system. [CAF] = 1.3×10^{-3} M. In all cases, [BHDC] = 0.3 M. $[NaBH_4]_{waterpool}$ = 0.1 M. $[NaOH]_{waterpool}$ = 0.1 M.

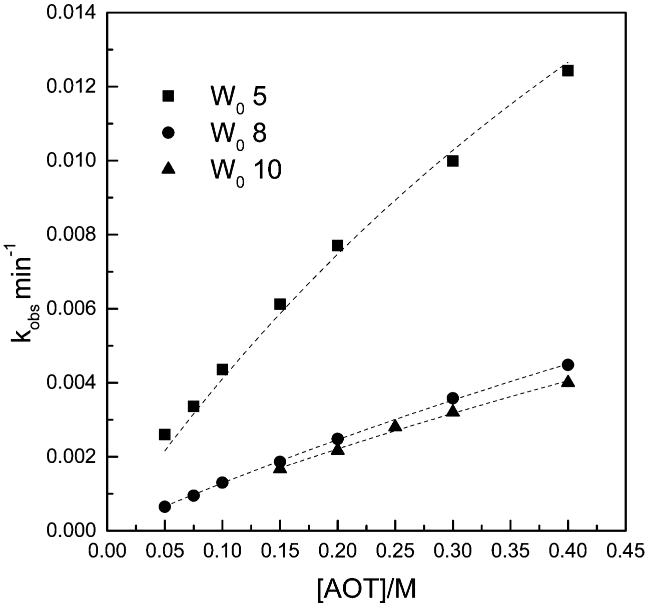


FIGURE 4. Dependence of k_{obs} on the AOT concentration for the reaction between CAF and $NaBH_4$ in water/AOT/toluene reverse micellar system at different W_0. [CAF] = 1.3×10^{-3} M. In all cases, $[NaBH_4]_{waterpool}$ = 0.1 M. $[NaOH]_{waterpool}$ = 0.1 M. The dotted line shows the fitting by eq 8 for $W_0 = 5$ and eq 9 for $W_0 = 8$ and 10.

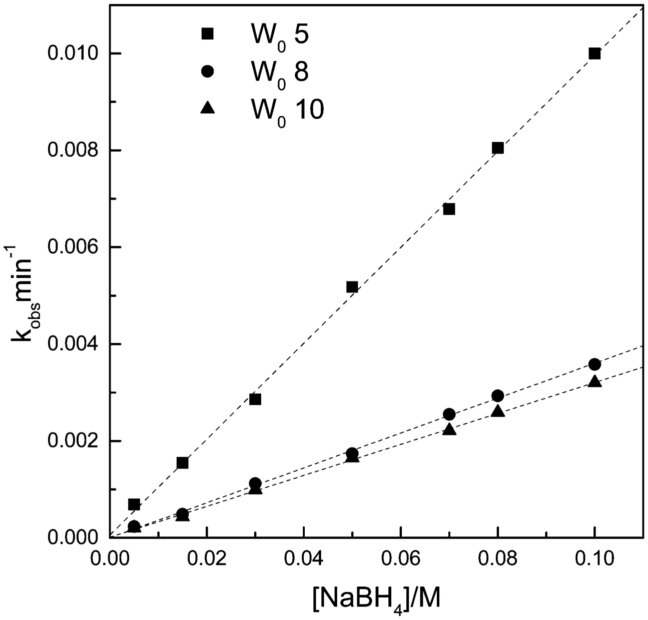


FIGURE 5. Variation of k_{obs} as a function of the $NaBH_4$ concentration for the reaction between CAF and $NaBH_4$ in water/AOT/toluene reverse micellar system at different W_0. [CAF] = 1.3×10^{-3} M. In all cases, [AOT] = 0.3 M. $[NaOH]_{waterpool}$ = 0.1 M. The dotted line shows the fitting by eq 8 for $W_0 = 5$ and eq 9 for $W_0 = 8$ and 10.

W_0 is 3. Reverse micelles with water content below 3 were not obtained at the temperature used.

Reaction in Toluene/AOT/Water Reverse Micellar System. (1) Effects of AOT Concentration. The kinetics of the reaction was studied by varying AOT concentrations between 0 and 0.4 M, keeping the other conditions fixed. For $W_0 = 10$, the lowest [AOT] reached was 0.15 M. Figure 4 shows the kinetic results at W_0 = 5, 8, and 10 for CAF: k_{obs} increases on increasing AOT concentrations in the whole range. These results are probably showing that saturation of the ketones in the micellar interface is not reached in the range of surfactant concentrations used. Moreover, from Figure 4 it can be inferred that k_{obs} diminishes with increasing water content (W_0).

Effect of $NaBH_4$ Concentration. To study the effect of $NaBH_4$ concentration, the reaction was carried out by

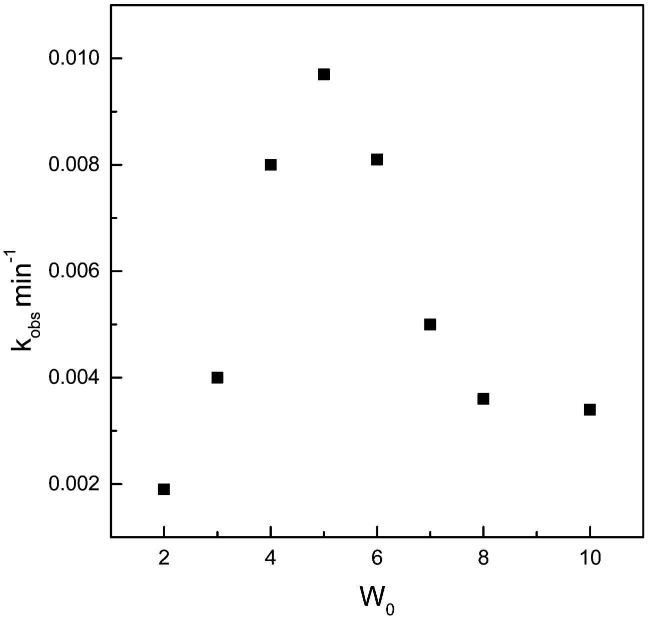


FIGURE 6. Variation of k_{obs} as a function of W_0 for the reaction between CAF and $NaBH_4$ in water/AOT/toluene reverse micellar system. [CAF] = 1.3×10^{-3} M. In all cases, [AOT] = 0.3 M. $[NaBH_4]_{waterpool}$ = 0.1 M. $[NaOH]_{waterpool}$ = 0.1 M.

using 0.3 M of AOT at $W_0 = 5$, 8, and 10. The results are shown in Figure 5, where k_{obs} increases linearly with $[NaBH_4]$. The reaction is fastest at low water content as was observed by varying [AOT].

Effect of Water Dispersed, W_0. The effects of changing the value of W_0 on k_{obs}, keeping AOT and $(NaBH_4)_w$ concentrations constant, are shown in Figure 6. Values of k_{obs} increase as W_0 increases up to $W_0 \sim 5$ and then decrease until $W_0 \sim 8$ to finally remain practically constant. The maximum W_0 that can be reached in this system is about 10.

Discussion

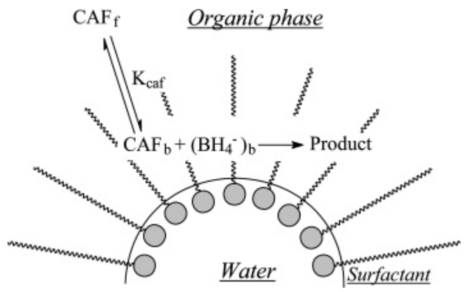
In regard to the reaction environment, $NaBH_4$ is not soluble in low polarity organic solvents and CAF is poorly soluble in water, and consequently, the reaction can only occur at the interface of the aggregate, with the surfactant providing a new region where the reactants can be in contact.[6-9,15,40,41] Therefore, in the kinetic model we considered for BH_4^- only the equilibrium partitioning between water and the reverse micellar interface and for the CAF only the partitioning between the organic phase and the reverse micellar interface.

As in part 1[39] and on the same basis, we write the following equations:

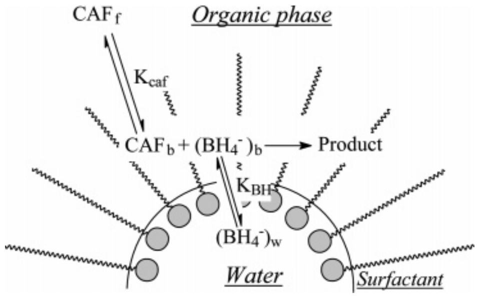
$$K_{CAF} = \frac{n_{CAF}{}^{b}}{[CAF]_f} \tag{3}$$

$$K_{BH} = \frac{n_{NaBH_4}{}^{b}}{n_{NaBH_4}{}^{w}} \tag{4}$$

SCHEME 2



SCHEME 3



where K_{CAF} and K_{BH} are distribution constants of CAF and $NaBH_4$ between the organic phase and the interface and between the interface and the water pool, respectively. $n_{CAF}{}^{b}$, $n_{NaBH_4}{}^{b}$, and $n_{NaBH_4}{}^{w}$ are the occupation numbers of CAF and $NaBH_4$ respectively. Super- and subscripts f, b, and w indicate the organic phase, the micellar pseudophase, and the water pool, respectively. The occupation number is $n = [\text{solute}]_b/[\text{surf}]$, where surf represents the surfactant. The occupation number is defined according to the place where the substrate is located inside the aggregate, in the case of CAF there is only the occupation number relative to the CAF at the interface ($n_{CAF}{}^{b} = [CAF]_b/[\text{surf}]$); on the other hand, $NaBH_4$ is wholly in the aggregate (reverse micelle surface and water pool), and therefore, there are two occupation numbers relative to $NaBH_4$, the one relative to $NaBH_4$ at the surface ($n_{NaBH_4}{}^{b} = [NaBH_4]_b/[\text{surf}]$) and the one relative to $NaBH_4$ in the water pool ($n_{NaBH_4}{}^{w} = [NaBH_4]_w/[\text{surf}]$).[5]

At $W_0 < 10$, the mechanism summarized in Scheme 2 can be proposed[6,41] (curvature and relative size are arbitrary and drown only for illustration purposes).

At $W_0 \geq 10$ Scheme 3 can be proposed[6-8] (curvature and relative size are arbitrary and drown only for illustration purposes).

The rate of the reaction can be expressed by eq 5 at $W_0 < 10$ and by eq 6 at $W_0 \geq 10$

$$\frac{d[P]}{dt} = k'_b[CAF_b][NaBH_4]_T \tag{5}$$

$$\frac{d[P]}{dt} = k'_b[CAF_b][NaBH_4]_b \tag{6}$$

where [P] is the concentration of the obtained product and k'_b is the bimolecular interfacial rate constant. The concentrations in square brackets refer to the total volume of reverse micelles.

If $[NaBH_4]_T \gg [CAF]$ the reaction has a first-order kinetics form. Then with eqs 3–6, together with the mass

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TABLE 1. Kinetic Parameters and Distribution Constants for the Reaction of CAF and $NaBH_4$ in Different Reverse Micellar Systems at 27 °C

	k_b/M^{-1} min^{-1}				10^2K_{CAF}/M^{-1}		
system	$W_0 = 5$[a,b,c]	$W_0 = 10$[a] $W_0 = 8$[b]	$W_0 = 20$[a] $W_0 = 10$[b] $W_0 = 15$[c]	water (k_w)/M^{-1} min^{-1}	$W_0 = 5$[a,b]	$W_0 = 10$[a] $W_0 = 8$[b]	$W_0 = 20$[a] $W_0 = 10$[b] $W_0 = 15$[c]
toluene/BHDC	0.28[d] ± 0.04	0.49[e] ± 0.04	1.61[e] ± 0.04		0.12[d] ± 0.02	0.11[e] ± 0.02	0.14[e] ± 0.02
	0.30[f] ± 0.05	0.52[g] ± 0.05	1.65[g] ± 0.05	3.46 ± 0.02			
toluene/AOT	0.045[h] ± 0.002	0.036[i] ± 0.002	0.032[i] ± 0.002		90[h] ± 5	120[i] ± 5	110[i] ± 5
	0.043[j] ± 0.002	0.037[k] ± 0.002	0.033[k] ± 0.002		89[l]	110[l]	130[l]
					80[m]	100[m]	120[m]
isooctane/AOT[n]	0.21 ± 0.04	0.16 ± 0.04	0.15 ± 0.04		220 ± 10	210 ± 10	200 ± 10

[a] W_0's for the toluene/BHDC/water system. [b] W_0's for the toluene/AOT/water system. [c] W_0's for the isooctane/AOT/water system. [d] From Figure 1 fitted by eq 8 (k_b was obtained by correction with eq 10; see text). [e] From Figure 1 fitted by eq 9 (k_b was obtained by correction with eq 10; see text). [f] From Figure 2 fitted by eq 8 (k_b was obtained by correction with eq 10; see text). [g] From Figure 2 fitted by eq 9 (k_b was obtained by correction with eq 10; see text). [h] From Figure 4 fitted by eq 8 (k_b was obtained by correction with eq 10; see text). [i] From Figure 4 fitted by eq 9 (k_b was obtained by correction with eq 10; see text). [j] From Figure 5 fitted by eq 8 (k_b was obtained by correction with eq 10; see text). [k] From Figure 5 fitted by eq 9 (k_b was obtained by correction with eq 10; see text). [l] From eq 1. The errors here were not included and are higher than the ones which come from the fitting due to the reason expressed in the Experimental Section. They are estimated to be around 50%. [m] From eq 2, note that the errors here were not included and are higher than the ones which come from the fitting due to the reason expressed in the Experimental Section. They are estimated to be around 50%. $K_{BH} = 100 \pm 10$ from eq 9 in the system toluene/BHDC/water. K_{BH} 0.50 ± 0.02 from eq 9 in the system toluene/AOT/water. Parameter values are calculated using 0.995 confidence level in nonlinear regression. [n] Data taken from ref 39.

balance for the ketones and $NaBH_4$, we obtain the final expression for the rate (eq 7) and k_{obs} (eq 8 for $W_0 < 10$ and eq 9 for $W_0 \geq 10$)

$$\frac{d[P]}{dt} = k_{obs}[CAF]_T \tag{7}$$

with

$$k_{obs} = \frac{(4k'_bK_{CAF}[NaBH_4]_T[surf])}{(1 + K_{CAF}[surf])} \tag{8}$$

$$k_{obs} = \frac{(4k'_bK_{CAF}K_{BH}[NaBH_4]_T[surf])}{(1 + K_{CAF}[surf])(1 + K_{BH})} \tag{9}$$

We note that, if $K_{BH} \gg 1$, eq 9 converges to eq 8.

To obtain the micellar second-order rate constants k_b for absolute comparison of reactivity in different media, the molar reaction volume at the interface should be known. This can be taken from the molar volume of AOT and BHDC in the reverse micellar system, which can be taken as 0.38 and 0.44, respectively.[6-8,42]

In this way, a conventional second-order rate constant (with conventional units $M^{-1}s^{-1}$) is given by[6,25]

$$k_b = k'_b\bar{v} \tag{10}$$

where $\bar{v}$ is the surfactant molar volume.

Reaction in the Toluene/BHDC/Water System. The increase of k_{obs} with increasing BHDC concentration (Figure 1) at all W_0's that have been studied could be due to the gradual incorporation of CAF into the micellar aggregate, but there is no interface saturation, probably reflecting the low value of the distribution constant. Moreover, the dependence of k_{obs} on the surfactant concentration seems to be linear. Equations 8 and 9 show that when the distribution constant of the ketone is very low and the product K_{CAF}[surf] is negligible, in comparison to unity, k_{obs} would exhibit a linear relationship with the surfactant concentration. In fact, as noted above, we could not calculate the distribution constant of CAF in toluene/BHDC/water by UV spectroscopy.

By fitting the experimental data with eq 8 for $W_0 = 5$ and eq 9 for the other W_0's (Figure 1), values of K_{CAF}, K_{BH}, and k_b can be obtained, and the results are shown in Table 1. The value of K_{BH} is shown in footnote *m* of Table 1. As can be inferred, k_b is higher at $W_0 = 20$ than at the other W_0 used, as was previously shown. Even at the maximum amount of water, CAF is less reactive in the micellar interface than in water, probably because reaction is occurring at the interface and not in the water pool.

The partition constants for CAF are very small and practically independent of W_0, indicating the high affinity of the substrate for the organic pseudophase and that reaction happens at the interface as pointed out above. Even with a very small amount of CAF in the interface, k_b at $W_0 = 20$ is only 0.5 times lower than in water, probably reflecting the fact that cationic interfaces are stabilizing the transition state. For other aromatic ketones, reductions by $NaBH_4$ were studied in normal micelles of CTAB and CTAC with a ~50-fold decrease of the second-order reaction rate constants in the cationic micellar pseudophase relative to those in water.[25] It seems, however, that cationic reverse micelles are enhancing the reaction rates probably because of the higher $NaBH_4$ concentration at the interface of these kinds of aggregates.

Analyzing the distribution constant of $NaBH_4$ at $W_0 =$ 10 and 20 it appears that this large value is reflecting that, due to electrostatic attraction, the effective concentration of $NaBH_4$ at the interface of cationic reverse micellar system is very high. In the interior of the water microdroplets OH^- and Cl^- were present and competing with the BH_4^- at the surface of the reverse micelle surface. Previous studies[25] carried out in direct cationic micelles of CTAC have shown that exchange between OH^- and BH_4^- can be neglected because addition of a large amount of hydroxide ion did not affect the reactivity of BH_4^-. Similarly, the favorable ion exchange constant of BH_4^- over Cl^-[25] and of Cl^- over OH^-,[43-45] measured in cationic direct micelle, encourage us to assume that

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the majority of borohydride is at the interface so that we can neglect the influence of OH^- and Cl^- on the reaction kinetic.

Also if the data of Figure 1 are fitted with eq 8, k_b at $W_0 = 10$ and 20 are 0.48 ± 0.02 and 1.58 ± 0.02, respectively. It appears that, in toluene/BHDC/water reverse micelles, BH_4^- is practically anchored at the interface without partitioning into to the water pool.

Equations 8 and 9 also show that, if [AOT] and W_0 are fixed, there should be a linear relationship between k_{obs} and [$NaBH_4$] and by the introduction of the values of K_{CAF} and K_{BH} the values of k_b could be recalculated for each system at $W_0 = 5$, 10, and 15 by fitting the new set of experimental data (k_{obs} vs [$NaBH_4$]) with these equations. The results are compared in Table 1, and good estimates of k_b within experimental error are obtained by two independent methods.

The kinetic profile upon the addition of water (Figure 3) shows that k_{obs} increases modestly with W_0 up to 10 which probably indicates that the strong interactions between BH_4^- ion and the cationic polar head of the BHDC are competing for the nucleophilic attack of the ion on CAF when there is only hydration water ($W_0 <$ 8−10) at a rigid interface.[11,46] At $W_0 > 10$, the interfacial rigidity in benzene/BHDC/water reverse micelles decreases with the value of W_0,[41,47] so the sharp increase in k_{obs} with the water amount observed above $W_0 > 10$ could be due to a higher accessibility of the reactants in the micellar interface. This effect allows a better contact between CAF and $NaBH_4$, favoring reaction at the micellar interface. In other words, at a low W_0 level, unsolvated BHDC interacts with BH_4^- stabilizing the initial state of the ion more effectively than when it is fully solvated at $W_0 > 10$. Moreover, previous studies[25] in normal micelles have shown that BH_4^- has a higher affinity for a cationic surfactant than Cl^- and Br^-.

Reaction in the Toluene/AOT/Water System. Comparison between the Different Interfaces. To analyze the effect of different interfaces on the rates of reduction of CAF by $NaBH_4$, the kinetic profile was investigated in toluene/AOT/water anionic reverse micellar system.

As shown in Figure 4, k_{obs} increases with increasing AOT concentration at all W_0's studied. This is probably due to the gradual incorporation of CAF into the reverse micellar surface. There is no interfacial saturation but the profile is not as linear as was observed in the toluene/BHDC/water reverse micelles, probably reflecting a low value of the distribution constant however higher than in the cationic micelles. By fitting the experimental data with eq 8 at $W_0 = 5$ and eq 9 for $W_0 = 8$ and 10 (Figure 4), values of K_{CAF}, K_{BH}, and k_b were obtained and are in Table 1. The literature value of the molar volume of AOT, $\bar{v}$, is 0.38.[6−8,48] Also in Table 1 can be found values for the CAF distribution constants obtained independently by UV spectroscopy that are in a very good agreement with those obtained kinetically. As can be inferred, k_b is lower at $W_0 = 10$ than at 5 as seen in Figure 4. As previously discussed for the BHDC system, eqs 8 and 9 also show that, if [AOT] and W_0 are fixed, there should be a linear relationship between k_{obs} and [$NaBH_4$], and by the introduction of the proper values of K_{CAF} and K_{BH}, values of k_b can be recalculated for each system at $W_0 =$ 5, 8, and 10 by fitting the new set of experimental data with these equations (Figure 5). The results are compared in Table 1. The k_b values obtained by two independent methods agree reasonably.

Values of k_b at every W_0 studied are always higher in toluene/BHDC than in toluene/AOT, reflecting the fact that anionic reactants, such as the borohydride, are more tightly bound to a cationic interface. In this way, the local effective concentration of the ions is greater in a cationic interface than in an anionic one making reaction faster. This fact could be confirmed by looking at values of K_{BH} in both systems, the $K_{BH(toluene/BHDC)}/K_{BH(toluene/AOT)}$ ratio being 200. The catalytic effect of the cationic interface over the anionic one was also found in other types of reaction where not only ions are involved[1,41,49,50] but also neutral molecules.[8,9b] In other words, a critical point in micellar second-order kinetics is the value attributed to $\bar{v}$ that is derived from partial molar factor. A reduced "real reaction volume" that cannot be measured in any way corresponds to a change in reaction rate.

It is interesting to note that the value of K_{CAF} is lower in the toluene/BHDC than in the toluene/AOT system. It seems that CAF has less affinity for cationic interfaces as observed with other aromatic compounds in different reactions.[8,9b,41] Literature ^1H NMR spectroscopic data[51] show a specific interaction between AOT headgroups and benzene. It appears that the aromatic ring of CAF is responsible for its stronger interaction with the polar headgroup of AOT than with BHDC. Accordingly, stronger interactions between the Na^+ and an aromatic compound than $^+N(Me)_4$ and the π system are reported in the literature.[52]

The kinetic profile upon addition of water is quite peculiar (Figure 6). At $W_0 > 5$, the kinetic profiles show that the rate diminishes with the water amount until $W_0 = 8$ and then is practically constant. For $W_0 < 5$, the rate increases with W_0. Our interpretation of those data is that up to $W_0 = 5$ water is solvating the AOT polar headgroup, making less relevant Na^+ BH_4^- ion pairing, so that the rate increases. At $W_0 \geq 5$ CAF is also being solvated and rates decrease.

At $W_0 \sim 8$, the water pool is formed and BH_4^- is ejected from the anionic interfacial reaction region. At $W_0 > 8$, [BH_4^-] at the interface is practically constant as is the reaction rate. These results agree with the previous statement that the reaction is taking place at the interface of the aggregate and not in the water pool. It can be seen from Table 1 that the reaction is faster in pure water than in the reverse micelles media. It must be noted that W_0 cannot be superior than 10 while in toluene/BHDC/water reverse micellar systems values of around 25 can be reached. This profile is quite different

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from the one found in the cationic system (Figure 3) where BH_4^- is part of the double layer of the cationic interface while in the anionic one it is ejected into the water pool due to electrostatic repulsion.

Solvent Effects on Anionic Interface. To investigate the effect of external solvent on the CAF reduction by $NaBH_4$, it is useful to compare the results in toluene/AOT/water reverse micellar system with those in isooctane/AOT/water aggregates.[39]

The reaction (Table 1) is faster in the isooctane/AOT/water system and the CAF distribution constant is higher in these aggregates. In the literature,[11,46,53] several differences can be found comparing behaviors of reverse micelles of AOT/alkanes with those of AOT/aromatic hydrocarbon. The thermodynamics of micellization show that clustering of benzene molecules around AOT headgroups appears to be more ordered than with saturated alkanes such as isooctane.[54] At the same value of W_0, the aggregation number of AOT is five times higher in the alkanes[55] than in benzene.[56]

Moreover, while AOT reverse micelles in saturated hydrocarbons solubilize large amounts of water; those reverse micelles in benzene solubilize only small amounts of water.[57] However, ^{1}H NMR spectroscopy shows that free water can be detected in AOT−benzene reverse micellar systems at low W_0 values.[51] Furthermore, these studies give evidence of specific interactions between AOT headgroups and benzene. ^{13}C NMR spectroscopy[58] shows that the extent of water penetration into AOT reversed micelles is greater in aromatic than in saturated hydrocarbons. In short, it seems that reversed micelles of AOT in benzene or toluene are smaller but have greater water penetration in the nonpolar pseudophase of the micelle than with AOT in alkanes. It seems that, due to the greater water penetration in the toluene/AOT system and the presence of free water, at lower W_0, BH_4^- is more in the water pool and, for these reasons, the reaction is slower than in isooctane/AOT reverse micellar system. Note that the value of K_{BH} in the isooctane/AOT system is higher (0.7) than that in the toluene/AOT one. The K_{CAF} value in toluene/AOT is about half that in isooctane/AOT reverse micellar systems, which is not surprising if the aromatic natures of the solute and organic solvent are considered;[9b,41] i.e., CAF has a higher affinity for the organic phase when toluene rather than an alkane is the external solvent.

Conclusions

The influence of different interfaces and the external solvent on the mechanism of the reaction between CAF and $NaBH_4$ were investigated in water/AOT/toluene and water/BHDC/toluene and also compared with that in water/AOT/isooctane reverse micellar system by UV -spectroscopy. A kinetic model based on the pseudophase formalism, which considers the distributions of the ketone among the continuous medium and the interface and the assumption that reaction takes place only at the interface, has enabled us to estimate rate constants in the interface of the different reverse micellar systems. At $W_0 = 5$, it was considered that all $NaBH_4$ is at the interface and, at $W_0 \geq 10$, where there are free water molecules, partitioning between the interface and the water pool was also considered. Rate constants increase with the surfactant concentration for every system and at every water content (W_0) as a consequence of incorporating the substrates into the interface of the reverse micellar system but the saturation of the interface by the substrate is never reached due to the low value of K_{CAF}.

The reaction is faster in the cationic interface than in the anionic one probably because BH_4^- is part of a cationic interface. Moreover, the distribution constant of CAF is around 900 times higher in AOT reverse micelles than in BHDC reverse micelles, showing that the presence of the $NaBH_4$ in the interface is the key factor. The high value of K_{CAF} in AOT/toluene reverse micellar systems is probably due to a specific interaction between the aromatic ketone and the polar head of the surfactant.

The effect of the external solvent on the reaction shows that reduction is favored in isooctane/AOT over toluene/AOT reverse micellar systems, probably due to BH_4^- being largely present in the water pool of the toluene/AOT reverse micelles. Also, K_{CAF} is lower in the presence of toluene as a solvent, due to the aromatic nature of both molecules.

Effects of water addition differ largely depending on the type of interface. In toluene/BHDC/water reverse micellar systems, k_{obs} increases with W_0 probably due to the fact that the layer rigidity diminishes with the amount of water making possible a larger accessibility of the reactants in the micellar interface. By solvating the BHDC headgroup reducing BH_4^- N^+ pairing, these effects allow better contact between CAF and $NaBH_4$, favoring reaction at the micellar interface. On the other hand, in toluene/AOT/water, k_{obs} is at a maximum at W_0 ca. 5, probably showing that, below this value, water is interacting strongly with the polar head of the surfactant, leaving the ketones and the borohydride (located at the interface) more reactive. Above this threshold water molecules probably start to interact with CAF, and once the water pool is formed, BH_4^- is ejected from the anionic interfacial reaction region.

These results seem to provide a good model for predicting a reduction of the ketones in reverse micellar systems. Moreover, this study can be extended to control the stereoselectivity of the reaction since interiors of these aggregates, which are similar to the polar parts of enzymes, are the reactive centers of the whole system, and a chiral environment can easily be created by dissolving asymmetric solutes in the interior.

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