JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 576–581

Determination of the hydrolysis rate of AOT in AOT–isooctane–water microemulsions using sodium nitroprusside as chemical probe†

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Received 3 September 2001; revised 22 February 2002; accepted 26 February 2002

ABSTRACT: The alkaline hydrolysis of sodium nitroprusside, $[Fe(CN)_5NO]^{2-}$, to yield $[Fe(CN)_5NO_2]^{4-}$ was studied in water in oil (w/o) AOT–isooctane–water microemulsions [AOT = sodium bis(2-ethylhexyl) sulphosuccinate]. Kinetic data show an initial increase of absorbance at 415 nm, due to the formation of $[Fe(CN)_5NO_2]^{4-}$. Following this initial increase, the absorbance started to decrease after a period of time which depends on the particular experimental conditions and returned to the initial value. This anomalous behaviour was interpreted as a result of competitive AOT hydrolysis consuming HO^- ions and regenerating $[Fe(CN)_5NO]^{2-}$. The influence of the microemulsion composition on the kinetic results was interpreted in terms of pseudophase formalism, assuming a uniform distribution of HO^- and $[Fe(CN)_5NO]^{2-}$ ions in the aqueous pseudophase. Analysis of the absorbance–time profiles enables us to obtain the second-order rate constants for hydrolysis of $[Fe(CN)_5NO]^{2-}$ in the water droplet, $= k_1^{NP} = 0.108\,M^{-1}\,s^{-1}$ (half that reported in pure water) and the second-order rate constant for hydrolysis of the surfactant (AOT), $= k_2^{AOT} = 4.4 \times 10^{-4}\,M^{-1}\,s^{-1}$, in the microemulsion. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: AOT; nitroprusside; hydrolysis; microemulsion; kinetics

INTRODUCTION

Microemulsions are stable, transparent solutions containing water, a hydrocarbon, a surfactant and, very often, a co-surfactant.[1] Structurally, they have been described as spherical drops of a disperse phase, separated from a continuous phase by a surfactant film.[2,3] The 'microemulsion-forming' surfactant used in this work was sodium bis(2-ethylhexyl)sulphosuccinate (AOT). This surfactant is one of the most widely investigated microemulsion formers[4,5] on account of the broad range of stability of its emulsions. In most instances oil-continuous microemulsions (w/o systems) have been used and the water droplets have proved useful as 'mini-reactors' for various types of syntheses. In preparative organic syntheses microemulsions are of interest to overcome incompatibility problems between non-polar organic compounds and inorganic salts. For this purpose, microemulsions can be regarded as an alternative to two-phase systems with added phase transfer reagents.[6]

A kinetic model based on the pseudophase formalism[7a] that accounts quantitatively for reactivity in microemulsions has been developed.[7b] When the reaction concerned takes place in the microdroplet only, the model can be simplified by referring the reactant concentrations to the disperse phase volume.[8] The use of these colloid systems as reaction media is hindered by the potential occurrence of side-reactions between some reactants and the surfactant. These side reactions complicate the quantitative interpretation of kinetic results and restrict the scope of microemulsions as reaction media.[9]

The alkaline hydrolysis of sodium nitroprusside (NP), $[Fe(CN)_5NO]^{2-}$, provided some of the earliest evidence for nucleophilic attack on a nitrosyl complex, which takes place via a well-known mechanism in aqueous medium.[10] Also, nitroprusside can be used as a source of NO^+ ions[11] and hence for nitrosation. Further, nitroprusside ion is widely used as the analytical and synthetic origin for a number of coordination compounds.

RESULTS AND DISCUSSION

The reaction of nitroprusside hydrolysis involves the nu-cleophilic attack of HO^- ion on the nitrosyl complex.

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†Presented at the 8th European Symposium on Organic Reactivity (ESOR-8), Cavtat (Dubrovnik), Croatia, September 2001.

Contract/grant sponsor: Ministerio de ciencia y technología, Universidad de Vigo; *Contract/grant number:* PB98-1098; *Contract/grant number:* BQU2001-3799; *Contract/grant number:* PGIDT01P-XI30106PR.

$$[\mathrm{Fe(CN)_5NO}]^{2-} + \mathrm{OH^-} \underset{}{\overset{\text{slow}}{\rightleftharpoons}} [\mathrm{Fe(CN)_5NO_2H}]^{3-}$$

$$k_1{}^{\mathrm{NP}} = 0.216\ \mathrm{M^{-1}\ s^{-1}}$$

$$K_1{}^{\mathrm{NP}} = 4.0 \times 10^{-4}\ \mathrm{M^{-1}}$$

$$k_{-1}{}^{\mathrm{NP}} = 5.4 \times 10^{2}\ \mathrm{s^{-1}}$$

$$[\mathrm{Fe(CN)_5NO_2H}]^{3-} + \mathrm{OH^-} \rightleftharpoons [\mathrm{Fe(CN)_5NO_2}]^{4-}$$

$$k_2{}^{\mathrm{NP}} = 4.0 \times 10^{7}\ \mathrm{M^{-1}}$$

very fast proton transfer

$$[\mathrm{Fe(CN)_5NO_2}]^{4-} \overset{+\mathrm{H_2O}}{\rightleftharpoons} [\mathrm{Fe(CN)_5(OH_2)}]^{3-} + \mathrm{NO_2}^-$$

$$k_{\mathrm{aq}} = 7.8 \times 10^{-3}\ \mathrm{s^{-1}}$$

$$K_{\mathrm{aq}} = 3.0 \times 10^{-4}\ \mathrm{M}$$

$$k_{-\mathrm{aq}} = 2.6 \times 10^{1}\ \mathrm{M^{-1}\ s^{-1}}$$

Scheme 1

Also worth considering here is the aquation[12] of the final com-plex $[\mathrm{Fe(CN)_5NO_2}]^{4-}$ to $[\mathrm{Fe(CN)_5H_2O}]^{3-}$ (see Scheme 1).

The underlying mechanism in an aqueous medium involves two consecutive equilibria similar to those for nitrosonium ion (see Scheme 2).[13]

The alkaline hydrolysis of NP was examined over a broad range of microemulsion compositions; thus, the surfactant (AOT) concentration was varied between 0.25 and 0.667 M and the mole ratio $W = [\mathrm{H_2O}]/[\mathrm{AOT}]$ from 10 to 30. All experiments revealed a 'peculiar' behaviour. Following an initial increase, the absorbance at 415 nm started to decrease after a period of time which depended on the particular experimental conditions. Also, the absorbance band at 415 nm returned to the initial absorbance value (Fig. 1). Such an anomalous behaviour resulted in atypical absorbance vs time profiles. In fact, the absorbance increased early during the reaction, then peaked and fell back to its initial level, without any other changes in the spectrum.

The above-described phenomenon can be attributed to the fact that the process is an equilibrium with known constants[14] in pure water and the surfactant used to form the microemulsion, AOT, can undergo alkaline hydrolysis which results in $\mathrm{HO^-}$ uptake.[15] If this process is included in the global hydrolysis of NP, then one has a mechanistic picture such as that in Scheme 1. The disappearance of $\mathrm{HO^-}$ in the hydrolysis of AOT displaces the equilibrium towards the reactants, i.e. to NP regeneration. Taking into account that the NP, NaOH and AOT concentrations in the medium were 1×10^{-3} M, 1×10^{-2} M and 0.25–0.667 M, respectively, all referred to the overall volume of the microemulsion, the hydrolysis of even a small proportion of AOT would completely displace the equilibrium. One other possible reason for the absorbance decrease could be aquation of the $[\mathrm{Fe(CN)_5NO_2}]^{4-}$ complex (see Scheme 1). However, from the equilibrium constant for the complex aquation in aqueous media,[16] this process should not take place. This allows one to exclude any other process different to AOT hydrolysis as responsible for reversing the direction of the reaction. Further evidence to discard this process is the UV–Vis spectra. There are no changes between the NP and the final products spectra. The aquation process will cause changes in the position of the UV–Vis bands.

The increase in absorbance with time of the $[\mathrm{Fe(CN)_5NO_2}]^{4-}$ complex at 415 nm, revealed as an increasing absorbance in Fig. 1, was fitted with a first-order integrated equation by examining the first part of the reaction. In all cases the value of k_{obs} decreased with increasing W but remained roughly constant regardless of AOT concentration at a fixed W value.

Based on Scheme 1 and on the assumption that the rate-determining step of the process is the attack of $\mathrm{HO^-}$ ion on $[\mathrm{Fe(CN)_5NO}]^{2-}$, the kinetic equation in pure water was well established in the literature.[14,16–18] The following expression for the reaction rate can be obtained, showing a complex dependence of $[\mathrm{OH^-}]$:

$$\begin{aligned} r &= \frac{d[\mathrm{Fe(CN)_5NO_2}^{4-}]}{dt} \\ &= k_1^{\mathrm{NP}}[\mathrm{Fe(CN)_5NO^{2-}}][\mathrm{HO^-}] \qquad (1) \\ &\quad - \frac{k_{-1}^{\mathrm{NP}}}{K_2^{\mathrm{NP}}K_{\mathrm{W}}}[\mathrm{Fe(CN)_5NO_2}^{4-}][\mathrm{H^+}] \end{aligned}$$

where

$$K_1^{\mathrm{NP}} = \frac{[\mathrm{Fe(CN)_5NO_2H^{3-}}]}{[\mathrm{Fe(CN)_5NO^{2-}}][\mathrm{HO^-}]} = \frac{k_1^{\mathrm{NP}}}{k_{-1}^{\mathrm{NP}}}$$

$$K_2^{\mathrm{NP}} = \frac{[\mathrm{Fe(CN)_5NO_2}^{4-}]}{[\mathrm{Fe(CN)_5NO_2H^{3-}}][\mathrm{HO^-}]} = \frac{k_2^{\mathrm{NP}}}{k_{-2}^{\mathrm{NP}}}$$

$K_1{}^{\mathrm{NP}}$ and $K_2{}^{\mathrm{NP}}$ are the hydrolysis equilibrium constants

$$[\mathrm{Fe(CN)_5NO}]^{2-} \overset{\mathrm{OH^-}}{\rightleftharpoons} [\mathrm{Fe(CN)_5NO_2H}]^{3-} \overset{\mathrm{OH^-}}{\rightleftharpoons} [\mathrm{Fe(CN)_5NO_2}]^{4-}$$

$$\mathrm{NO^+} \overset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{HNO_2} \overset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{NO_2}^-$$

Scheme 2

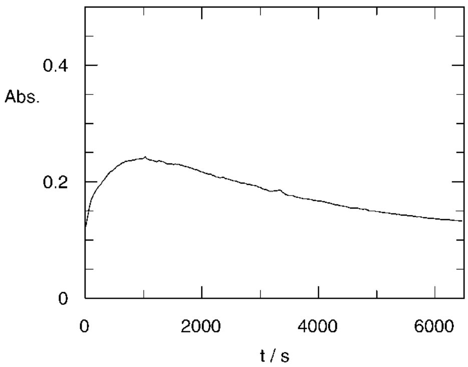


Figure 1. Variation of the absorbance ($\lambda = 415$ nm) with time in the reaction between NP and HO^- in AOT–isooctane–water microemulsions. [AOT] = 0.583 M, $[NP]_0 = 1 \times 10^{-3}$ M, [NaOH] = 1×10^{-2} M, W = 16; T = 25 °C All concentrations are refereed to the total volume of the microemulsion

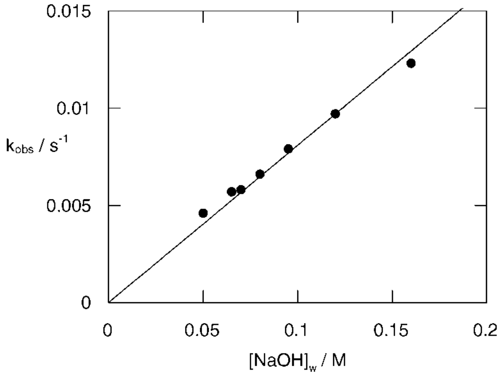


Figure 2. Variation of k_{obs} for the reaction between NP and HO^- in AOT–isooctane–water microemulsions. [AOT] = 0.6 M, $[NP]_0 = 1 \times 10^{-3}$ M, W = 20; T = 25 °C. [NaOH] is referred to the water volume in the microemulsion

for sodium nitroprusside (see Scheme 1) and K_W is the ionic product of water. From Eqn. (1) we can obtain the following expression for k_{obs}

$$k_{obs} = k_1^{NP}[OH^-] + \frac{k_{-1}^{NP}}{K_2^{NP} K_W}[H^+] \tag{2}$$

Under the prevailing experimental conditions, $[HO^-] \geq 3.37 \times 10^{-2}$ M (referred to the water phase volume), the first term in Eqn. (2) yields $k_1^{NP}\lfloor HO^- \rfloor \geq 1.68 \times 10^{-2}$ s^{-1}. Simple calculations yields a limiting value of $(k_{-1}^{NP}/K_2^{NP}\ K_W)[H^+] \leq 3.56 \times 10^{-4}$ s^{-1}, such that Eqn. (2) can be simplified to $k_{obs} = k_1^{NP}[HO^-]$, which was found experimentally to be obeyed by all compositions of microemulsions studied; in fact, k_{obs} varied linearly with the NaOH concentration (see Fig. 2) at a fixed composition of microemulsion.

Taking into account the high negative charge of the complex and the fact that it is insoluble in low-polarity solvents, we can assume that it will not be present either in the organic phase or at the interface. Consequently, the simplest model available for interpreting the experimental results involves the assumption that the reaction only takes place inside the microdroplet and that both reactants are uniformly distributed within it. The former assumption is consistent with the fact that the aqueous microdroplet is the only zone where HO^- ions can 'reside.' The assumption of a uniform distribution of HO^- ions in the microdroplets is probably an over-simplification since electrostatic repulsion between hydroxyl ions and charged AOT heads probably leads to HO^- concentrating in the centre of the microdroplet. However, based on the high ion concentrations inside the microdroplets, assuming a uniform distribution of HO^- ions in the aqueous pseudophase appears to be sensible. We can thus express the HO^- concentration in the aqueous pseudophase as

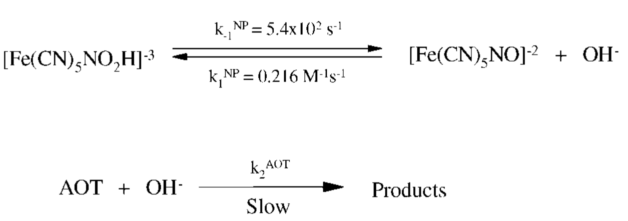
$$[HO^-]_W = \frac{[HO^-]_T V_T}{V_W} \tag{3}$$

where the subscript w denotes the effective concentration of HO^- ions in the aqueous droplet and V_T and V_w are the volumes of the microemulsion and aqueous phase, respectively.

Based on this model, one can estimate the effective concentration of HO^- ions in the aqueous phase and use it to derive the corresponding second-order constants $k_1{}^{NP}$ from the k_{obs} values, via the following equation:

$$k_1^{NP} = \frac{k_{obs}}{[HO^-]_W} = \frac{k_{obs} V_W}{[HO^-]_T V_T} \tag{4}$$

The $k_1{}^{NP}$ values obtained from Eqn. (4) remained constant with changes in W at a fixed AOT concentration. This behaviour was also found for each AOT concentration studied. ${}^{m}k_1{}^{NP}$ has been defined as the average second-order rate constant, $k_1{}^{NP}$, at each fixed AOT concentration. This value of ${}^{m}k_1{}^{NP}$ is constant for each AOT concentration (see Table 1). From these results, we



Scheme 3

Table 1. Variation of pseudo-first-order rate constants and second-order rate constants of the reaction between NP and HO^- in AOT–isooctane–water microemulsions: $[NP]_0 = 1 \times 10^{-3}$ M, $[NaOH] = 1 \times 10^{-2}$ M (referred to the total volume of the microemulsion); $T = 25$ °C

[AOT] (M)	W	k_{obs} (s^{-1})	k_1^{NP} (M^{-1} s^{-1})	$^{m}k_1^{NP}$ (M^{-1} s^{-1})
0.667	10	0.00933	0.1120	0.1118
0.667	12	0.00783	0.1122	
0.667	14	0.00723	0.1123	
0.667	15	0.00582	0.1126	
0.667	18	0.00501	0.1085	
0.667	20	0.00459	0.1100	
0.667	22	0.00432	0.1137	
0.667	24	0.00382	0.1135	
0.600	10	0.01053	0.1159	0.1100
0.600	12	0.00747	0.0996	
0.600	14	0.00770	0.1181	
0.600	16	0.00687	0.1191	
0.600	18	0.00590	0.1143	
0.600	20	0.00509	0.1102	
0.600	22	0.00403	0.0954	
0.600	24	0.00420	0.1091	
0.600	26	0.00404	0.1151	
0.600	28	0.00327	0.0991	
0.600	30	0.00352	0.1138	
0.583	10	0.01167	0.1244	0.1096
0.583	12	0.00940	0.1191	
0.583	14	0.00580	0.0850	
0.583	16	0.00702	0.1194	
0.583	18	0.00493	0.0938	
0.583	20	0.00455	0.0956	
0.583	22	0.00496	0.1140	
0.583	24	0.00436	0.1105	
0.583	26	0.00416	0.1136	
0.583	28	0.00393	0.1153	
0.583	30	0.00368	0.1153	
0.500	10	0.01330	0.1197	0.1049
0.500	12	0.00863	0.0920	
0.500	14	0.00894	0.1132	
0.500	16	0.00776	0.1112	
0.500	18	0.00596	0.0974	
0.500	20	0.00539	0.0970	
0.500	22	0.00563	0.1126	
0.500	24	0.00491	0.1062	
0.500	26	0.00387	0.0902	
0.500	28	0.00418	0.1059	
0.500	30	0.00401	0.1084	
0.417	10	0.01365	0.1047	0.1085
0.417	12	0.01160	0.1044	
0.417	14	0.01075	0.1146	
0.417	16	0.00946	0.1136	
0.417	18	0.00886	0.1210	
0.417	20	0.00798	0.1196	
0.417	22	0.00666	0.1110	
0.417	24	0.00534	0.0961	
0.417	26	0.00472	0.0927	
0.417	28	0.00529	0.1111	
0.417	30	0.00464	0.1053	
0.333	10	0.02062	0.1237	0.0973
0.333	12	0.01248	0.0915	
0.333	14	0.01141	0.0951	
0.333	16	0.01005	0.0971	
0.333	18	0.00844	0.0929	
0.333	20	0.00814	0.0977	
0.333	22	0.00703	0.0937	
0.333	24	0.00636	0.0911	
0.333	26	0.00602	0.0941	
0.333	28	0.00563	0.0955	
0.333	30	0.00543	0.0977	
0.300	10	0.02200	0.1184	0.1110
0.300	12	0.01771	0.1181	
0.300	14	0.01568	0.1164	
0.300	16	0.01343	0.1164	
0.300	18	0.01298	0.1254	
0.300	20	0.01061	0.1131	
0.300	22	0.00933	0.1120	
0.300	24	0.00819	0.1092	
0.300	26	0.00644	0.0902	
0.300	28	0.00594	0.0890	
0.300	30	0.00722	0.1132	
0.250	10	0.02619	0.1222	0.1076
0.250	12	0.01768	0.0943	
0.250	14	0.01707	0.1081	
0.250	16	0.01453	0.1065	
0.250	18	0.01299	0.1093	
0.250	20	0.01322	0.1190	
0.250	22	0.00939	0.0939	

can conclude that the assumption of a reaction where the reactants are uniformly distributed in the aqueous core is correct.

This model reveals that the primary effect of changes in microemulsion composition is to change the 'effective' reactant concentrations. The effect of AOT–isooctane–water microemulsions on the intrinsic reactivity of NP towards HO^- is an inhibition. The value of the second-order rate constant in the water droplet of the microemulsion is $k_1^{NP} = 0.108$ M^{-1} s^{-1}, i.e. half the reported second-order rate constant in pure water. The reactivity difference in water and in microemulsion-encapsulated water can be ascribed to the different properties of water in water-in-oil (w/o) microemulsions.[19–22]

The decreased absorbance observed over time (see Fig.

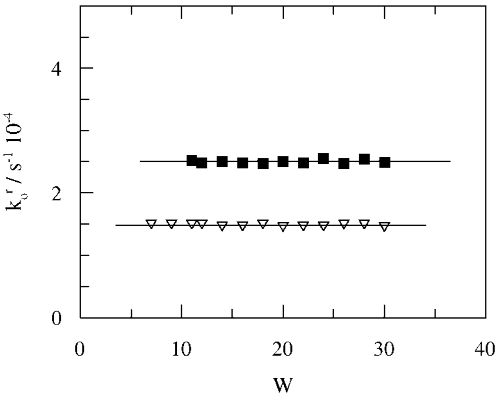


Figure 3. Variation of the pseudo-first-order rate constant for the recovery of NP, k_0^r. $[NP]_0 = 1 \times 10^{-3}$ M, $[NaOH] = 1 \times 10^{-2}$ M (concentration referred to total volume of microemulsion). (■) [AOT] = 0.5 M; (▽) [AOT] = 0.3 M; T = 25 °C

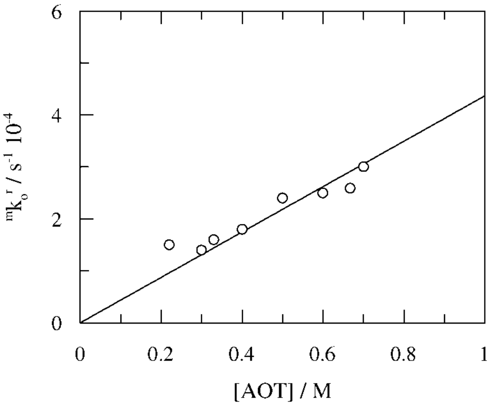


Figure 4. Variation of the average pseudo-first-order rate constant of the recovery of NP, $^{m}k_0{}^{r}$. $[NP]_0 = 1 \times 10^{-3}$ M, [NaOH] = 1×10^{-2} M (concentration referred to total volume of microemulsion); $T = 25\,°C$

1) could be the result of the hydrolysis equilibrium being displaced by HO^- uptake in the alkaline hydrolysis of AOT and of the consequent regeneration of sodium nitroprusside (Scheme 3). A kinetic study of NP recovery provided a hydrolysis constant for AOT. The recovery of NP was examined over a broad range of microemulsion compositions; the surfactant concentration was varied between 0.25 and 0.667 M and the mole ratio, *W*, from 10 to 30. The kinetic runs were analyzed using the second part of the absorbance–time plots. These experimental data were fitted to the first-order rate equation, and in all cases the fits were satisfactory.

In view of these experimental results, we can say that the pseudo-first-order rate constant for the recovery of $[Fe(CN)_5NO]^{2-}$, $k_{obs}{}^{r}$, does not change with *W* but increases with increasing AOT concentration (see Fig. 3). $^{m}k_{obs}{}^{r}$ has been defined as the average of the pseudo-first-order rate constant at each fixed AOT concentration for different *W* values. Taking into account the values of the rate constants ($k_{-1}{}^{NP}$ and $k_{-2}{}^{NP}$ shown in Scheme 3), $^{m}k_{obs}{}^{r}$ corresponds to the AOT hydrolysis pseudo-first-order rate constant, and hence the second-order rate constant of AOT hydrolysis, $k_2{}^{AOT}$, can be written as $k_2{}^{AOT} = {}^{m}k_{obs}{}^{r}/[AOT]$. Thus, the variation of the first-order rate constant, $^{m}k_0{}^{r}$, provides a hydrolysis second-order rate constant for AOT $k_2{}^{AOT} = 4.4 \times 10^{-4}$ M^{-1} s^{-1}. Figure 4 shows the variation of the rate constant for the reverse reaction, $^{m}k_0{}^{r}$, with surfactant concentration.

CONCLUSIONS

The proposed model is usually employed to convert analytical concentrations (referred to the total volume of the microemulsions) into local concentrations (referred to the volume of the water pool phase). It allows us to estimate the effective concentration of HO^- ions in the aqueous phase, and therefrom the corresponding second-order reaction constants, $k_1{}^{NP}$. The second-order rate constant for the reaction between NP and NaOH was found to be $k_1{}^{NP} = 0.108$ M^{-1} s^{-1}, so the reactivity of NP for HO^- ions is roughly halved. This decrease can be ascribed to changes in the properties of microemulsion-encapsulated water, and in particular this effect can be attributed to a decrease in the polarity of the microdroplet water.[19,20] The reason why we do not find any influence of the microemulsion composition on the reactivity is due to the fact that the main changes in the properties of microemulsions are in the range of low values of *W* (*W* = 0–11),[23] and our experimental data were obtained in the range *W* = 10–30. In this range of *W* values, the changes in the polarity and the properties of the water microdroplets are not so drastic as at small values of *W*.[19,20] Another point is that at *W* = 10–30 at least two different water domains[19,20,24–27] are present in the microdroplet: the water pool core and the water involved in the solvation of AOT head groups. In this way, the apparent availability of all water is due to the exchange of water molecules between these two domains. This exchange is fast, hence it will have no influence upon the chemical process. For this reason, our reaction will 'observe' a uniform water domain the properties of which are an average of the properties of the two water domains present in the microdroplets. This assumption is confirmed with the appearance of only one ^{1}H NMR signal for water protons.

The decrease in the observed rate constant, k_{obs}, with increase in *W* can be ascribed to dilution of HO^- ions in an increased amount of water in the system. The model correctly reflects that the most significant effect of changes in the microemulsion composition is that of altered 'effective' concentrations for the reactants.

Taking into account the equilibrium constant for this process confirms that the surfactant undergoes slow hydrolysis; by virtue of the relative concentrations of the different reactants present in the medium, the surfactant hydrolysis reverses the hydrolysis equilibrium for sodium nitroprusside and leads to full recovery of the reactants. Hence the analysis of the kinetic profiles for the reversal of NP hydrolysis allowed us to determine the hydrolysis constant for AOT to be $k_2{}^{AOT} = 4.4 \times 10^{-4}$ M^{-1} s^{-1}. This value suggests that AOT hydrolysis must be considered in those cases where a significant amount of HO^- ions is present in the microemulsion core.

EXPERIMENTAL

AOT and isooctane were supplied by Aldrich. AOT was dried in a vacuum desiccator for 2 days and used without further purification. Sodium Nítroprusside (NP) and NaOH were purchased from Merck and used as received.

Kinetic profiles were obtained by UV spectroscopic monitoring of the appearance of $[Fe(CN)_5NP_2]^{4-}$ ion at

415 nm, using a Spectronic 3000 diode-array spectrophotometer. The temperature was kept at 25 ± 0.1 °C.

Kinetic experiments were conducted under pseudo-first-order conditions, the NP concentration being at least 10 times lower than that of NaOH throughout. Absorbance–time data were fitted with a first-order integrated equation and were reproducible to within 5%:

$$A = A_{\mathrm{i}} + \Delta A \mathrm{e}^{-kt} \tag{5}$$

where A is the absorbance, A_{i} the initial absorbance, ΔA the variation of absorbance in the reaction and k the rate constant.

The increase in absorbance with time of the $[\mathrm{Fe(CN)_5NO_2}]^{4-}$ complex at 415 nm was fitted with a first-order integrated equation by examining the first part of the reaction. For this fit only 70–75% of the first reaction was used to avoid any competition between the hydrolysis of NP and the recovery reaction. In all cases no deviations from the linearized first-order rate equation were found. The decrease in absorbance (second part of the absorbance–time plots) was fitted to the first-order rate equation, and in all cases the fits were satisfactory. To avoid the possibility of competition between the two consecutive reactions, a double exponential equation was used to fit the global process [Eqn. (6)]. The values of the two observed rate constants were compatible with the two separate analysis in all cases. Another point is that the observed rate constant of the second step is not greater than 10% of that of the first step. This means that in all of the cases the two reactions can be analyzed separately.

$$A = A_{\mathrm{i}} + \Delta A_1 \mathrm{e}^{-k_1 t} + \Delta A_2 \mathrm{e}^{k_2 t} \tag{6}$$

where A is the absorbance, A_{i} the initial absorbance, ΔA_1 and ΔA_2 the variation of absorbance due to both reactions and k_1 and k_2 the rate constants of the two reactions.

Acknowledgements

Financial support from (Projects BQU2001-3799, PGIDT01PXI30106PR and PB98 1098) is gratefully acknowledged.

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