Kinetics and mechanism of the reaction of 1-fluoro-2,4-dinitrobenzene with hydroxide ion in 'water in oil' microemulsions

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The nucleophilic aromatic substitution (S_NAr) reaction of fluoride by hydroxide ion in 1-fluoro-2,4-dinitrobenzene has been studied in water in oil (W/O) microemulsion media. The microemulsions used were sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–heptane–water or benzylhexadecyldimethylammonium chloride (BHDC)–benzene–water. The kinetic profile of the reaction was investigated as a function of variables such as (*a*) reactant concentrations, (*b*) surfactant structure and concentration and (*c*) amount of water dispersed in the microemulsion. The distribution constants (K) of the substrate between the micellar pseudo-phase and organic phase have been determined. They were used to evaluate the intrinsic second-order rate coefficient (k_r) of the S_NAr reaction in microemulsion solutions. In cationic W/O microemulsions the reaction is catalysed relative to homogeneous solutions, whereas in anionic W/O microemulsions the reaction is inhibited. A mechanism to rationalize the kinetic results is proposed.

Introduction

Water can be readily dispersed in an organic medium using a surfactant molecule as a dispersant. The structures formed are generally known as 'reversed micelles' or 'water in oil (W/O) microemulsions'. They are characterized by a microdroplet of water surrounded by a monolayer of surfactant molecules, with the hydrocarbon tails of the amphiphilic compound directed into the organic solvent.[1] In these systems there are three different compartments in which small probe molecules can be solubilized: the internal water pool, the interface formed by the surfactant molecules and the external organic phase.[2,3] In the last few years microemulsions have been extensively studied because of their applications. They are of interest in enzymatic catalysis, liquid–liquid extraction of proteins or minerals, solar energy conversion, preparation of submicron particles, *etc.*[4] An interesting application of microemulsions is as molecular scale reactors. In this regard, it has been shown that the presence of the microemulsion droplets can enhance or retard chemical reactions depending on the nature and composition of the microemulsions.[4-6] Several authors used the water pools of microemulsions as reaction media for ionic reactants.[7-9] They used sodium bis(2-ethylhexyl)sulfosuccinate (AOT) as surfactant and aliphatic hydrocarbons as dispersing media. In these cases the reactions in microemulsions exhibited simple kinetic behaviour and the rate of the reaction decreased with the size of the water pool and was almost independent of the nature of the organic solvent. However, the behaviour of the kinetic parameters of a reaction in microemulsions could also be dependent upon the characteristics of the reactants.

In nucleophilic aromatic substitution (S_NAr) reactions involving anionic nucleophiles and neutral substrates, an environment should be created in order to ensure sufficient contact between the reactants and, at the same time, maintain the nucleophilicity of the anions. In hydroxylic solvents, anions are usually highly solvated and thus they result in poor nucleophiles, but on the other hand they are not very soluble in non-polar solvents.[10,11] Therefore, the structure of the W/O microemulsions appears to be appropriate for facilitating reactions due to their capacity of solubilization of hydrophilic and lipophilic reactants.[12] Furthermore, the water activity inside the core of W/O microemulsions is lower than in pure water,[13] thus increasing the nucleophilicity of the anionic reactants.

The reaction of 1-fluoro-2,4-dinitrobenzene (FDNB) with hydroxide ion has been extensively studied in homogeneous[14-17] and micellar media.[10,18] In cationic micellar solutions a catalytic effect upon the rate of the reaction was found, little effect in non-ionic surfactants and an inhibitory effect with anionic surfactants was observed.[17,18] A similar behaviour was also observed for this reaction in 'oil in water' microemulsions made with octane, *tert*-amyl alcohol and cetyltrimethylammonium bromide (CTAB) or sodium lauryl sulfate (NaLS).[19]

In this work we report the kinetic parameters and mechanism of the nucleophilic aromatic substitution reaction of 1-fluoro-2,4-dinitrobenzene and hydroxide ion in W/O microemulsions made with anionic and cationic surfactants. The microemulsions were formed with sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–heptane–water or benzylhexadecyldimethylammonium chloride (BHDC)–benzene–water. Nucleophilic aromatic substitution of fluoride anion was observed. The results show that the rate of the reaction depends mainly on the nature of the surfactant molecules and the amount of water present in the microemulsion. The reaction rate is enhanced by about 40 times in cationic W/O microemulsions relative to aqueous solutions and by three orders of magnitude in relation to anionic W/O microemulsions. A detailed mechanism is also presented as a function of the FDNB partition between the surfactant aggregates and the organic solvent.

Experimental

General

UV–VIS spectra were recorded on a Hewlett-Packard HP 8452 spectrophotometer. The HPLC measurements were performed on a Varian 5000 liquid chromatograph equipped with a UV–VIS variable wavelength detector (Varian 2550) operating at 250 nm for all assays. The solvent system used was 10% propan-2-ol in hexane. The column used was a Varian Micro-Pak SI-5 (150 mm × 4 mm ID).

Materials

1-Fluoro-2,4-dinitrobenzene (FDNB) from Aldrich and sodium hydroxide (Merck, PA) were used without further purification.

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), Sigma, was dried under reduced pressure and used without further modification. Benzylhexadecyldimethylammonium chloride (BHDC) was also from Sigma; it was recrystallized several times from ethyl acetate and dried under reduced pressure. Benzene, heptane and acetonitrile HPLC quality (Sintorgan) were used as received. Water was triply distilled.

Solution preparation

A solution of the surfactant was prepared in the appropriate organic solvent. Subsequently, aqueous sodium hydroxide of suitable concentrations was added to the surfactant solution. These mixtures were sonicated to obtain perfectly clear microemulsions. The amount of water present in the system was expressed as the molar ratio between water and the surfactant present in the microemulsion ($R = [H_2O]/[\text{Surf}]$).

Kinetics

Reactions were followed spectrophotometrically at 25 ± 1 °C. To start a kinetic run, a stock solution of FDNB was syringed (10 µl) (1 µl = 1 mm^3) into a thermostatted cell containing the microemulsion solution. The FDNB concentration was 2.5×10^{-4} mol dm^{-3}. The kinetic runs were performed by following the increase in the absorbance of the product of the reaction, 2,4-dinitrophenoxide ion at 400 nm. The value of the absorbance at an infinite reaction time was consistent with the value obtained from authentic samples of the product of the reaction within 3%.

Very good pseudo-first-order plots were obtained in excess of nucleophile. The concentration of sodium hydroxide in the water pools was changed between 0.015–0.150 mol dm^{-3}. The pseudo-first-order rate constants (k_{obs}) were obtained by a non-linear least-squares fit of the experimental concentration *vs.* time values. When AOT–heptane–water microemulsions were used, k_{obs} values were calculated from the initial rates.

Determination of distribution constant

The distribution of FDNB between the organic solvent and the micellar interface at different R values was evaluated using the Encinas–Lissi fluorescence quenching method.[20] Tris(2,2′-bipyridine)ruthenium(II) which is quenched by nitroaromatic compounds was used as the fluorescence probe.[21] The distribution constant of FDNB in microemulsion solutions was defined by eqn. (1) where $[\text{FDNB}]_b$ is the molar

$$K = \frac{[\text{FDNB}]_b}{[\text{FDNB}]_f[\text{Surf}]} \qquad (1)$$

concentration of FDNB that is bound to the micellar aggregates, $[\text{FDNB}]_f$ is the molar concentration of substrate in the organic phase; and [Surf] is the molar concentration of micellized surfactant in the microemulsion. The K values obtained for AOT microemulsions were *ca.* 8 ± 1.5 dm^3 mol^{-1}, independent of the value of R. In BHDC microemulsions a K value of 0.1 dm^3 mol^{-1} was estimated at $R = 20$.

Results and discussion

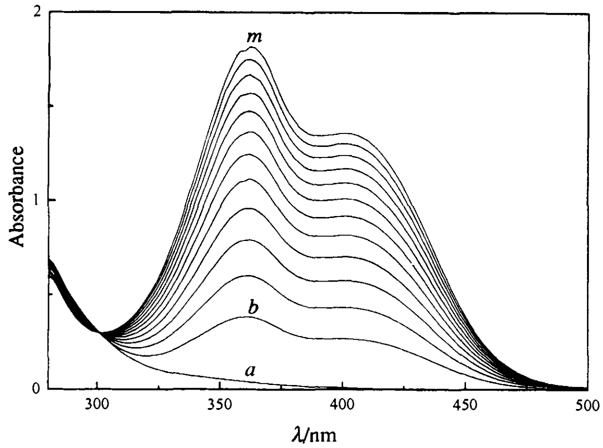


Fig. 1 UV–VIS spectra for the reaction of FDNB with hydroxide ion in BHDC–benzene–water microemulsions: (*a*) spectrum of FDNB in BHDC–benzene–R = 20 microemulsion with acid water pool; (*b–m*) spectra recorded every 15 s after reactants were mixed. [BHDC] = 0.102 mol dm^{-3}; $R = 20$; [FDNB] = 2.5×10^{-4} mol dm^{-3} and $[\text{NaOH}]_W$ = 0.152 mol dm^{-3}

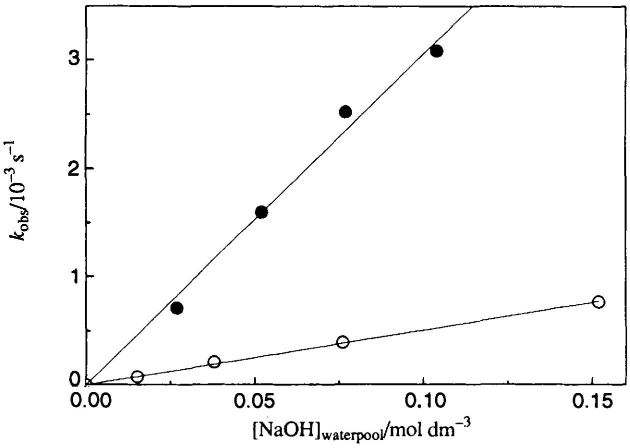
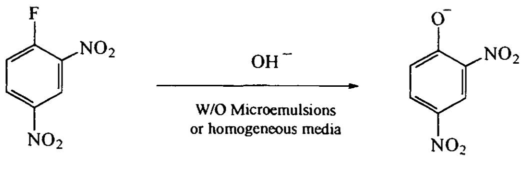


Fig. 2 Variation of the pseudo-first-order rate constant (k_{obs}) with the hydroxide ion concentration in BHDC and AOT W/O microemulsions at R = 20: (●) BHDC (0.102 mol dm^{-3})–benzene–water; (○) AOT (0.252 mol dm^{-3})–heptane–water

The reaction of 1-fluoro-2,4-dinitrobenzene with hydroxide ion in homogeneous solutions and in W/O microemulsions produces 2,4-dinitrophenoxide ions [reaction (2)]. Fig. 1 shows the absorption spectra of a typical run in BHDC–benzene–water microemulsions. The rising absorption is due to the absorbance of the 2,4-dinitrophenoxide ion. A clear isosbestic point can be observed at *ca.* 300 nm, thus evidencing the clearness of the reaction. This result was checked by HPLC chromatography. In AOT–heptane–water microemulsions the results were similar. On the other hand, no changes in the absorption spectra were observed when the substrate was added to surfactant solutions or to microemulsion solutions with acid water pools.



(2)

In order to gain some insight into the mechanism of this reaction in W/O microemulsions, the influence of several variables were investigated as follows.

Reactant concentration

The reactions were carried out in the presence of a large excess of nucleophile over substrate. In all cases, excellent pseudo-first-order plots were obtained indicating that the reaction is first-order in the substrate. The k_{obs} values obtained at different substrate concentrations ($1 \leqslant [\text{FDNB}]/10^{-4}$ mol dm$^{-3} \leqslant 5$) were the same, providing further evidence that the reaction is first-order in FDNB.

The effect of changing the hydroxide ion concentration on the observed reaction rate constant, k_{obs}, is shown in Fig. 2. In all cases, the experimental data show a linear dependency with nucleophile concentration, indicating a first-order behaviour in relation to the nucleophile. Furthermore, it can be observed from Fig. 2 that in AOT–heptane–water solutions the reaction rate is lower than in BHDC–benzene–water solutions. This difference can be explained by electrostatic effects. In cationic interfaces, an anionic nucleophile, *e.g.* the hydroxide ion, is part of the electric double layer linked to the polar head of the surfactant molecules. This suggests that the effective concentration of OH^- at the interface of cationic microemulsions is higher than at the interface of the anionic one, and thus the reaction is favoured. On the other hand, the electrostatic repulsions do not favour the incorporation of hydroxide ions into the anionic interface of W/O microemulsions and the reaction is inhibited. This result is similar to those found in many other rate enhancements of bimolecular reactions by cationic micelles with anionic nucleophiles.[10,18]

Water content

From the slopes shown in Fig. 2, the apparent second-order rate constants (k_{app}) for the reaction can be obtained. In most cases k_{app} increases with the amount of water present in the microemulsion. In Fig. 3 these variations are shown as a function of R for AOT and BHDC microemulsions, respectively. However, the change with R is dependent on the type of microemulsion. For the anionic microemulsions [Fig. 3(*a*)] the apparent second-order rate constants increase markedly between $12.5 < R < 20$. These changes can be understood taking into account the fact that the water pools of the W/O microemulsions consist of a layer of 'bound' water associated with the polar head groups of the surfactant and 'free' water molecules at the centre of the water pools.[22] At values of $R < 10$, the water molecules in the water pool are firmly coupled to the polar head of the surfactant molecules and the fluidity of the micellar pseudo-phase is low relative to bulk water.[23] This effect hinders major contact between the reactants. As the size of the water pools increase, the proportion of the 'free' component increases until the water environment closely resembles that of bulk water.[22] In this situation, hydroxide ions can easily reach the micellar interface to produce the reaction with the substrate molecules.

On the other hand, in BHDC microemulsions, the dependency of k_{app} with R is almost linear, [Fig. 3(*b*)]. In this system the hydroxide ions are present as counterions at the cationic interface. Moreover, the surfactant layer rigidity in BHDC–benzene–water microemulsions decreases with the value of R.[24] Then, the increase in the k_{app} values with R could be due only to a larger accessibility of the substrate molecules in the micellar interface. Therefore, this effect allows a better contact between the nucleophiles and substrate molecules, thus favouring the S_NAr reaction at the micellar interface.

Surfactant concentration

For the AOT–heptane–water microemulsions a downward curvature of the k_{app} with the surfactant concentration was observed, as shown in Fig. 4. This effect on the k_{app} values could be expected due to higher incorporation of the substrate into the micellar aggregates with the increase of surfactant concentration.

However, in BHDC–benzene–water microemulsions the dependency of k_{app} on the BHDC concentrations seems to be linear, Fig. 5. This result suggests that the saturation of the substrate molecules in the micellar interface is not reached in the surfactant concentration range used.

The above results support other evidence that the nucleophilic aromatic substitution in W/O microemulsions occurs at the micellar interface and not in the water pools and the product formed during the reaction (2,4-dinitrophenoxide ion) is solubilized in the micellar pseudo-phase. Furthermore, the neutral substrate (FDNB) is partitioned between the organic solvent and the micellar aggregates, and this partition is dependent on the nature of the microemulsion.

The mechanism assumed for this S_NAr reaction in W/O

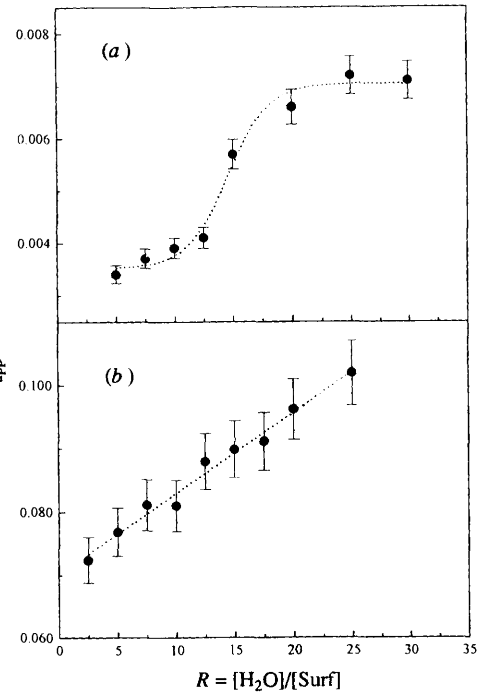


Fig. 3 Dependency of the apparent second-order rate constant (k_{app}) with R: (*a*) AOT (0.252 mol dm^{-3})–heptane–water; (*b*) BHDC (0.252 mol dm^{-3})–benzene–water

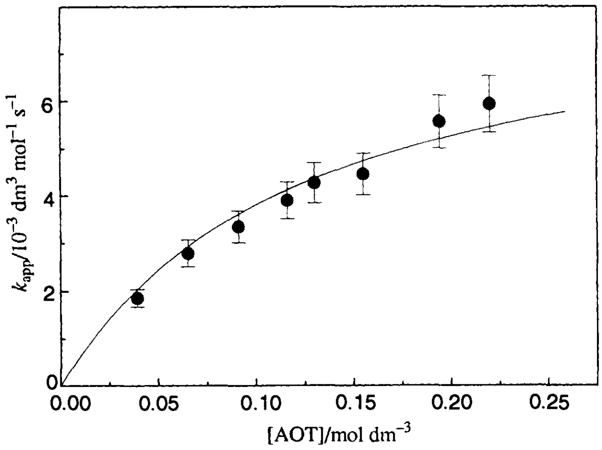


Fig. 4 Variation of the apparent second-order constant (k_{app}) with the surfactant molar concentration in AOT–heptane–water ($R = 20$) microemulsions. The line shows the fitting by eqn. (8), using a FDNB distribution constant of 8 dm^3 mol^{-1}.

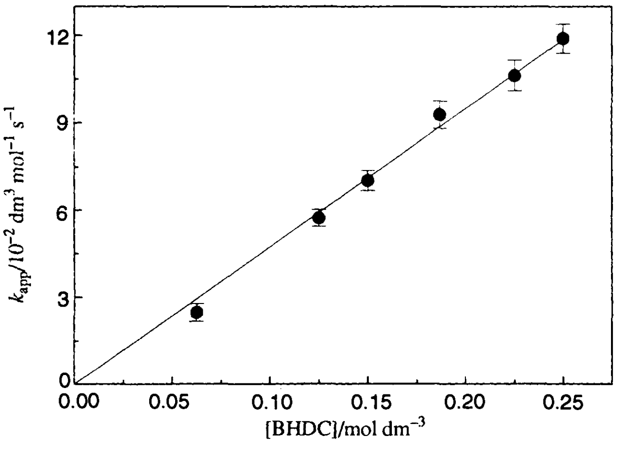


Fig. 5 Variation of the apparent second-order constant (k_{app}) with the surfactant molar concentration in BHDC–benzene–water ($R = 20$) microemulsions. The line shows the fitting by eqn. (8).

microemulsions solutions can be summarized by the following scheme where $FDNB_f$, $FDNB_b$ indicates the substrate in the

$$FDNB_f + Surf \overset{K}{\rightleftharpoons} FDNB_b \qquad (3)$$

$$FDNB_b + OH^-_w \xrightarrow{k_r} Product \qquad (4)$$

organic phase and in the micellar pseudo-phase, respectively, Surf represents the micellized surfactant molecules, OH^-_w is the hydroxide ion in the water pools; k_r is the intrinsic second-order rate constant of the reaction and K is the distribution constant of the substrate between the organic phase and micellar pseudo-phase (see Experimental). In this case the water domains can be considered as a pseudo continuous phase because the rate of reaction is much lower than the exchanges between droplets in the microemulsion systems.[24,25]

The rate of the reaction can be expressed by eqn. (5). The

$$\frac{d[\mathrm{Product}]}{dt} = k_r[\mathrm{FDNB}]_b[\mathrm{OH}^-]_w \qquad (5)$$

$[\mathrm{FDNB}]_b$ can be calculated by a simple mass balance using the distribution constant K and the analytical concentration of FDNB, $[\mathrm{FDNB}]_T$ [eqn. (6)]. Substituting eqn. (6) into eqn. (5)

$$[\mathrm{FDNB}]_b = \frac{K[\mathrm{Surf}]}{(1 + K[\mathrm{Surf}])}[\mathrm{FDNB}]_T \qquad (6)$$

we can obtain the final expression [eqn. (7)] for the reaction rate,

$$\frac{d[\mathrm{Product}]}{dt} = \frac{K[\mathrm{Surf}]}{(1 + K[\mathrm{Surf}])}k_r[\mathrm{OH}^-]_w[\mathrm{FDNB}]_T = k_{app}[\mathrm{OH}^-]_w[\mathrm{FDNB}]_T \qquad (7)$$

where

$$k_{app} = \frac{K[\mathrm{Surf}]}{(1 + K[\mathrm{Surf}])}k_r \qquad (8)$$

If $[\mathrm{OH}^-]_w \gg [\mathrm{FDNB}]_T$ we assumed a pseudo-first-order behaviour for the kinetics of the reaction and eqn. (7) can be written as eqn. (9),

$$\frac{d[\mathrm{Product}]}{dt} = k_{obs}[\mathrm{FDNB}]_T \qquad (9)$$

with

$$k_{obs} = k_{app}[\mathrm{OH}^-] \qquad (10)$$

The experimental results show agreement with the mechanism proposed. A linear relationship between k_{obs} and hydroxide ion concentration was found (Fig. 2) as predicted by eqn. (10). The variation of k_{app} with the surfactant concentration can be explained from eqn. (8). This equation claims that k_{app} should exhibit a non-linear dependency with the surfactant concentration, if the product K[Surf] is significant. The intrinsic second-order rate constant of the reaction (k_r) in W/O microemulsions can be calculated from eqn. (8) and the value of K. The distribution constants K for FDNB in AOT–heptane–water were calculated using a fluorescence quenching method.[20] They were independent of the R values. This is an indication that the substrate is only partitioned between the micellar interface and the organic solvent, and completely excluded from the water pools. An average value 8.0 ± 1.5 dm^3 mol^{-1} between $5 \leqslant R \leqslant 30$ was found. Fig. 4 shows the fitting of the k_{app} values using eqn. (8) with the average K value calculated for FDNB in AOT microemulsions at $R = 20$. The fitting of the experimental points is quite good and the intrinsic second-order rate constant (k_r) value in this medium is shown in Table 1. This table also contains the values of the second-order rate constant of the reaction measured in water and acetonitrile–water (1:1) solutions in order to make comparisons. The k_r value is larger in the acetonitrile–water mixture than in water solutions due to an enhancement of the hydroxide ion nucleophilicity with the amount of the dipolar aprotic solvent.[10]

Table 1 Intrinsic second-order rate constants, k_r,[a] for the reaction of 1-fluoro-2,4-dinitrobenzene with hydroxide ion in W/O microemulsions and homogeneous media at 25 °C

Solvent	k_r/dm^3 mol^{-1} s^{-1}
AOT–heptane–water (R = 20)	0.009
BHDC–benzene–water (R = 20)	$\geqslant$4.71
Water	0.125
Water–Acetonitrile (1:1)	0.185

[a] Error estimated ± 5%.

The linear dependency of k_{app} with BHDC, shown in Fig. 5, can also be explained from eqn. (8). It turns into a linear relationship only if the distribution constant of the solute is very low and the product K [Surf] $\ll 1$. This assumption is valid because of the impossibility of calculating the distribution constant of FDNB in BHDC–benzene–water microemulsions using the Encinas–Lissi method, which does not allow distribution constant values below 0.1 dm^3 mol^{-1} to be calculated. This result is not surprising if the aromatic nature of the solute and organic solvent is taken into account and it shows that the FDNB resides principally in the organic phase of the microemulsion solutions. However, an evaluation of the K and k_r values in BHDC microemulsions from the fitting of the experimental data to eqn. (8) could be made. A higher limit value for K of 0.1 dm^3 mol^{-1} was estimated for the partition of FDNB in BHDC–benzene–water (R = 20) microemulsions. Under this condition the fitting of eqn. (8) is linear to within 5%. From this estimation the k_r value in these media is at least three orders of magnitude higher than in AOT microemulsions and one order of magnitude relative to homogeneous media, Table 1.

These results show that the BHDC–benzene–water microemulsions are a very interesting media for substitution reactions with anionic nucleophiles due to their incorporation as counterions in the micellar interfaces, which allows a greater contact with the substrate molecules. Presumably, under these conditions the hydroxide ion is less hydrated than in bulky solutions and in anionic W/O microemulsions and therefore its nucleophilicity is enhanced.

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