

Application of the pseudophase ion-exchange model to reactivity in quaternary water in oil microemulsions

Luis García-Río and Pablo Hervella

Received (in Montpellier, France) 3rd January 2007, Accepted 14th February 2007

First published as an Advance Article on the web 14th March 2007

DOI: 10.1039/b618874e

The nucleophilic attack of a bromide ion on benzyl chloride (BCl) and the acid denitrosation of *N*-methyl-*N*-nitroso-*para*-toluenesulfonamide (MNTS) in quaternary microemulsions of TTABr and SDS containing 1-hexanol as cosurfactant were studied. The experimental results were examined in the light of a kinetic model which allows the quaternary microemulsion to be reduced to a pseudo-ternary microemulsion, by considering the cosurfactant partition between the continuous medium and the interface of the microemulsion to be determined by Shulman titration. The incorporation of the alcohol into the interface alters the interfacial volume to be used in constructing the kinetic model. The second step of the process involves determining how the reactants partition among the different microenvironments of the pseudo-ternary system, the interface being the sole reactive region in the microemulsion. Accounting for the results obtained in the acid denitrosation of MNTS required using the ion-exchange formalism. Based on the results, the product of the fraction of neutralized charge at the interface and the rate constant is independent of the water content of the system. This suggests that the degree of dissociation of the surfactant at the interface does not depend on the water content of the microemulsion. Under the assumption of a surfactant fraction of neutralized charge of $\beta = 0.8$, we calculated the rate constants at the interface for both processes. Such rate constants were smaller than in the aqueous medium and consistent with the effects found in nitroso group transfer reactions in microemulsions.

Introduction

Water-in-oil microemulsions are usually described as nano-sized water droplets dispersed in a non-polar solvent with the aid of a surfactant monolayer. Some surfactants can form no microemulsions by themselves and require the presence of a cosurfactant (usually an alcohol) to be stable; however, ternary systems consisting of a surfactant, water and a non-polar solvent are the most simple possible in this context and have thus been the most widely studied in this respect.¹ The interest of these complex fluids lies in their usefulness for oil recovery,² solubilization of proteins³ and amino acids,⁴ in enzymatic reactions,⁵ as alternatives to phase-transfer catalysts⁶ and in the preparation of monodisperse colloid-size particles.⁷ This array of applications of reversed micelles has been propitiated by their aggregates possessing three solubilization sites, namely: the non-polar continuum, the micellar interface and the intramellar water pool. Despite the vast scope of application of microemulsions, their influence on the processes they can host has scarcely been examined, particularly in those cases involving a reaction between a hydrophobic substrate and an ionic species bound to the interface. In bimolecular reactions between an organic substrate and a univalent ion of

charge opposite to that of the interface, the pseudo-phase ion-exchange formalism has been applied to aqueous ionic micelles.⁸ The pseudo-phase ion-exchange model for micelles assumes reactions to take place in the two pseudo-phases simultaneously. Micelles act as a separate phase and the surfactant behaves like an ion-exchange resin, the partitioning of ionic species being described by an ion-exchange constant. The apparent failure of the pseudo-phase ion-exchange model⁹ with reactive counterion surfactants and at high detergent or salt concentrations in the presence of an excess of highly hydrophilic counterions (such as OH[−] or F[−]) has been shown to arise from the assumption that the degree of dissociation of the counterion, α , remains constant.

The properties of water within drops and at the microemulsion interface are very strongly affected by the water content of the microemulsion. The state of water within AOT reversed micelles and the influence of W ($W = [\text{H}_2\text{O}]/[\text{AOT}]$) on micellar properties have been examined by using a variety of techniques¹⁰ which have revealed that the properties of surfactant-trapped water differ from those of bulk water and change strongly with the water content at W values below about 10. The anomalous behavior of water at low W values has been ascribed to local interactions of water molecules with Na⁺ counterions and sulfosuccinate ion. Little is known about the physicochemical properties of other surfactant systems, particularly as regards the state of solubilized water. The cationic surfactant cetyltrimethylammonium bromide has for several years been known to form reversed micelles in

Departamento Química Física, Facultad de Química, Universidad de Santiago de Compostela. Avenida. De las Ciencias s/n, 15782 Santiago de Compostela, Spain. E-mail: qflgr3cn@usc.es; Fax: +34 981 595012

various solvents including 1-hexanol, chloroform and dichloromethane.¹¹ There is infrared¹² and ¹H-NMR^{11e,13} spectral evidence for a change in the properties of water in these cationic reversed micelles as *W* is raised; also, the ¹³C-NMR chemical shifts for the surfactant are consistent with the proposed change in local structure. These changes in water properties in microemulsions can alter the amount of charge that is neutralized at the interface.

Some additives are known to dramatically alter the degree of micelle dissociation in aqueous micellar systems.¹⁴ Thus, the degrees of ionization of SDS¹⁵ and TTABr¹⁶ increase with increasing alcohol concentration. The degree of micelle ionization, α , reflects electrostatic interactions between charged micelle surfaces and counterions, and provides a rough measure of the fraction of counterions in close proximity to micelle surfaces with their solvation layer still intact¹⁷ that are in contact with the micelle solvation layer. These interactions are essentially determined by the charge density of the micelle surface, which is strongly affected by surface solubilization of the alcohol. Thus, they depend much less on the amount of alcohol added, up to a fairly large content, as the micelle and counterion solvation layers are likely to remain largely composed of water molecules, even at fairly large alcohol concentrations, in alcohol-water mixtures.¹⁸ As a result, changes in α with the alcohol concentration are essentially due to the alcohol penetrating micelles rather than to its presence in the intermicellar region.

In this work, we examined two types of kinetic processes between a hydrophobic substrate and an ionic species that reacts by binding to the microemulsion interface. Specifically, we studied the nucleophilic attack of bromide ions on benzyl chloride (BCl) in TTABr–1-hexanol–isooctane–water microemulsions and the acid denitrosation of *N*-methyl-*N*-nitroso-*para*-toluenesulfonamide (MNTS) in SDS–1-hexanol–isooctane–water microemulsions (Scheme 1). All the experiments were conducted at a constant [1-hexanol] : [TTABr] ratio of 4 : 1 or a constant [1-hexanol] : [SDS] ratio of 5 : 1. The surfactant counterion was the reactive species in the former case; the latter, required applying the ion-exchange formalism at the microemulsion interface to Na⁺ as counterion and H⁺ as reactive ion.

The results obtained are explained in the light of a kinetic model where the quaternary microemulsion is transformed into a pseudo-ternary one and the change in interfacial volume is assumed to result from incorporation of the cosurfactant into the interface. Subsequently applying the pseudo-phase ion-exchange model allowed the interfacial rate constants for the target nucleophilic substitution and hydrolysis reactions to

be determined. Based on the results, the reaction rate at the interface of the quaternary microemulsion is smaller than in water and aqueous micelles by effect of the decreased polarity of the interface relative to micellar systems.

Experimental

Tetradecyltrimethylammonium bromide (TTABr) and sodium dodecyl sulfate (SDS) were supplied by Sigma and used without further purification. 1-Hexanol and isooctane were Aldrich products in the highest commercially available purity. *N*-Methyl-*N*-nitroso-*para*-toluenesulfonamide (MNTS (Aldrich 99%)) and benzyl chloride (Merck >99%) were used as received.

Microemulsions of the desired compositions were prepared from stock water–surfactant–isooctane–alcohol microemulsions by adding appropriate amounts of isooctane and water. A constant alcohol : surfactant mole ratio of 4 : 1 for TTABr and 5 : 1 for SDS was used throughout. Densities were measured with a pycnometer.

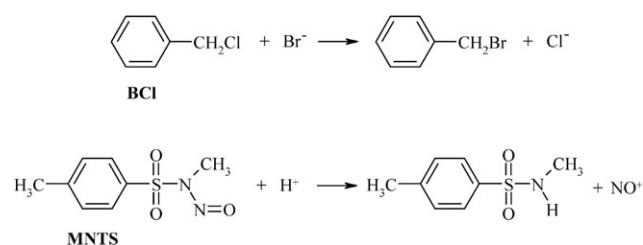
Reactions were monitored at 25.0 °C on a Varian Cary 500 Scan UV-vis-NIR spectrophotometer equipped with thermostated cell holders. The acid denitrosation of MNTS was studied by monitoring the disappearance of the substrate at 260 nm. The conditions used in all cases were such that the nitroso compound concentration was always much smaller than the [H⁺]. Typically, such conditions included [MNTS] = 1.91 × 10^{−4} M and [HCl] = 6.67 × 10^{−3} M. All kinetic data fitted a first-order integrated equation with *r* > 0.999. In what follows, *k*_{obs} is used to denote the pseudo first-order rate constant. The nucleophilic attack of bromide ions on benzyl chloride is a very slow reaction, so it was examined *via* the initial rate method. Kinetic experiments involved monitoring the absorbance change at 249 nm for (5–10)% of the reaction time, using a substrate concentration [BCl] = 1.17 × 10^{−3} M. The slope of each absorbance-time plot was converted into a rate constant *via* the overall absorbance change. The reaction was also examined using the integration method in several control tests that involved measuring the absorbance change over at least 4 lifetimes and fitting absorbance-time data pairs to a first-order integral equation. The *k*_{obs} values obtained with both methods were identical.

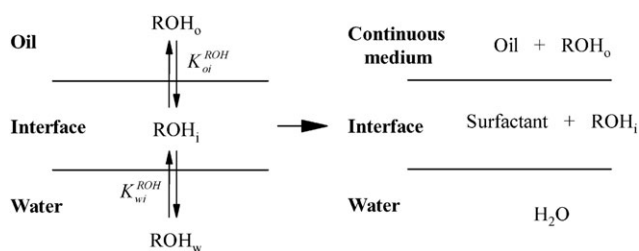
Results and discussion

Alcohols can be regarded as cosolvents that partition between the aqueous and oil-rich bulk phases on the one hand, and the interfacial layer on the other, thereby decreasing the effective hydrophilicity of the amphiphile and the effective hydrophobicity of the oil. In order to simplify the analysis of kinetic data, a quaternary microemulsion can be transformed into a pseudo-ternary one. Scheme 2 depicts the way the alcohol partitions among the different pseudo-phases.

The alcohol, 1-hexanol, will initially partition among the three microemulsion pseudo-phases in accordance with the partition constants *K*_{oi}^{ROH} and *K*_{wi}^{ROH}, which are defined as:

$$K_{oi}^{\text{ROH}} = \frac{[\text{ROH}]_i}{[\text{ROH}]_o} Z K_{wi}^{\text{ROH}} = \frac{[\text{ROH}]_i}{[\text{ROH}]_w} W \quad (1)$$





Scheme 2

where $[\text{ROH}]_o$, $[\text{ROH}]_i$ and $[\text{ROH}]_w$ denote the alcohol concentrations in the continuous phase, interface and bulk water, respectively, referred to the total microemulsion volume. Parameters Z and W bear their usual meaning (*i.e.* $Z = [\text{Isooctane}]/[\text{Surfactant}]$ and $W = [\text{H}_2\text{O}]/[\text{Surfactant}]$). By virtue of the very low solubility of 1-hexanol in water, the quaternary microemulsion can be transformed into a pseudo-ternary one consisting of isooctane and 1-hexanol as the continuous phase, the surfactant (TTABr or SDS) and 1-hexanol as the interface, and water as the aqueous phase.

Partitioning of the alcohol in the microemulsion

In the present paper, we investigated the surface composition of the w/o droplets by dilution method, in which TTABr or SDS is used as the surfactant, n-hexanol as the cosurfactant, and isooctane as the oil with addition of different amounts of water. For a stable w/o microemulsion, a critical amount of n-hexanol (cosurfactant) distributes between the bulk oil phase and the droplet surface, whereas the surfactant almost solely resides on the droplet surface since it is insoluble in isooctane.¹⁹ Supposing the number of moles of n-hexanol at the interface and in bulk oil phase being n_a^i and n_a^o , respectively, the total number of moles of n-hexanol n_a equals to the sum of both, where the number of moles of n-hexanol in water, n_a^w , is negligible because of its very small solubility:

$$n_a = n_a^i + n_a^o \quad (2)$$

Other conditions remaining the same, the ratios between the number of moles of alcohol in oil (n_a^o) and the number of moles of oil (n_o), and between the mole fraction of alcohol at the interface (X_a^i) and that in the oil (n_a^o) are fixed: $K = n_a^o/n_o$ and $K_d = X_a^i/X_a^o$, where K and K_d are the appropriate constants, the latter being the distribution constant. Addition of oil in the system would change K and K_d by abstracting the alcohol in it and making the system unstable. Since the stability of the microdispersion of water is affected by a threshold population of alcohol at the interface and consequently in the bulk oil, the addition of alcohol can reestablish the threshold stable condition of the system by restoring the required magnitudes of both K and K_d .

Representing the number of moles of alcohol in water and at the interface by n_a^w and n_a^i , respectively, by using $K = n_a^o/n_o$, the total number of moles of alcohol in the microemulsion system, n_a^t per mole of added surfactant can be represented as:^{20,21}

$$\frac{n_a^t}{n_s} = \frac{n_a^w + n_a^i}{n_s} + K \frac{n_o}{n_s} \quad (3)$$

where n_s is the number of moles of surfactant present in the system. In the dilution experiment at a constant n_s , n_a^t and n_o

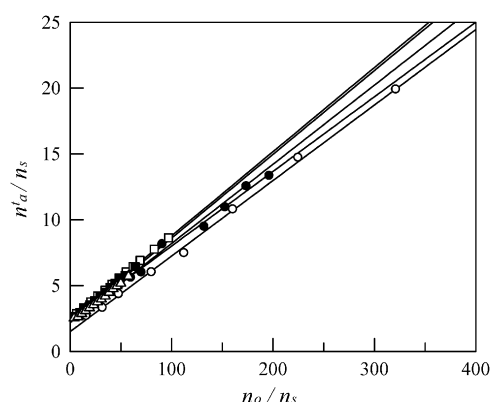


Fig. 1 Plot of n_a^t/n_s vs. n_o/n_s according to eqn (3) for w/o TTABr-isooctane-water-hexanol microemulsion systems at 25.0 °C with different TTABr concentrations: (○) 0.0019; (●) 0.0030; (□) 0.0043; (■) 0.0060 and (Δ) 0.0078 M.

are varied so as to get a series of n_a^t/n_s and n_o/n_s values whose graphical plotting according to eqn (3) can yield the values of n_a^i and n_a^o from the intercept and slope if n_a^w is negligible (see Fig. 1 and Fig. 2).

The alcohol distribution constant, K_{oi}^{ROH} , between the continuous medium and the interface of the microemulsions can be obtained as the ratio between the intercept/slope of plots like those showed in Fig. 1 and Fig. 2 for TTABr and SDS-based microemulsions:

$$K_{oi}^{\text{ROH}} = \frac{[\text{ROH}]_i}{[\text{ROH}]_o} Z = \frac{n_a^i n_o}{n_a^o n_s} = \text{Intercept/Slope} \quad (4)$$

The alcohol distribution constants thus obtained for TTABr and SDS microemulsions, *viz.* $(K_{oi}^{\text{ROH}})_{\text{TTABr}} = 35 \pm 1$ and $(K_{oi}^{\text{ROH}})_{\text{SDS}} = 19 \pm 1$, were subsequently used to transform a quaternary microemulsion into a pseudo-ternary one. Alcohols behave highly non-ideally in solution in alkanes due to self-aggregation, however their observed partition coefficients are concentration independent. The reason for this behavior should reside in their incorporation to the microemulsion

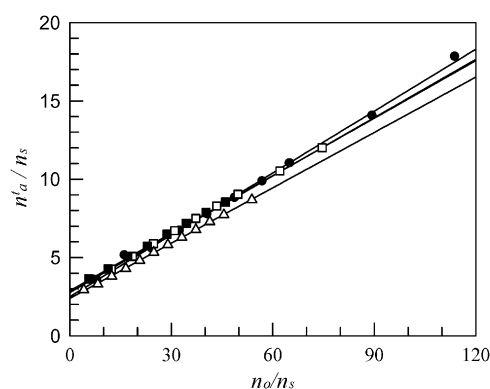


Fig. 2 Plot of n_a^t/n_s vs. n_o/n_s according to eqn (3) for w/o SDS-isooctane-water-hexanol microemulsion systems at 25.0 °C with different SDS concentrations: (●) 0.0037; (□) 0.0049; (■) 0.0054 and (Δ) 0.0073 M.

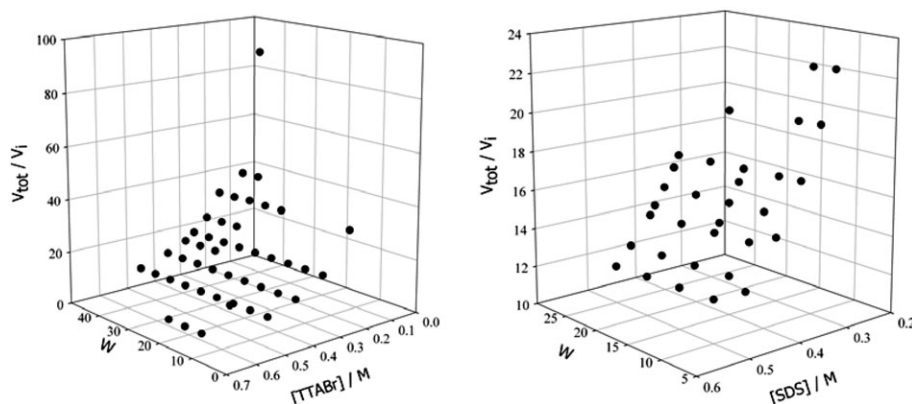


Fig. 3 Influence of W and surfactant concentration upon V_{tot}/V_i : (left) TTABr–hexanol–isooctane–water microemulsions. $[\text{Hexanol}]/[\text{TTABr}] = 4$, (right) SDS–hexanol–isooctane–water microemulsions. $[\text{Hexanol}]/[\text{TTABr}] = 5$.

interface in such a way that the percent of alcohol in the continuous medium is very small.

Variation of the interfacial volume

Transforming a quaternary microemulsion into a pseudo-ternary one entails redefining the composition-related parameters for the system concerned. Since the alcohol can be taken to be a solute at the interface, we used the Stilbs approximation²² under the assumption that the surfactant was the sole component determining the properties of the interface. Therefore, the composition parameter W ($W = [\text{H}_2\text{O}]/[\text{Surfactant}]$) remained unchanged. However, the composition of the continuous medium is altered by the presence of the alcohol, so parameter Z , initially defined as $Z = [\text{Isooctane}]/[\text{Surfactant}]$, was redefined in the following form:

$$Z^* = \frac{[\text{Isooctane}] + [\text{ROH}]_o}{[\text{Surfactant}]} \\ = Z + \frac{Z[\text{ROH}]_{\text{tot}}}{(K_{oi}^{\text{ROH}} + Z)[\text{Surfactant}]} \quad (5)$$

where $[\text{ROH}]_{\text{tot}}$ denotes the total concentration of 1-hexanol added to the microemulsion. In our experimental conditions, $[\text{ROH}]_{\text{tot}}/[\text{TTABr}] = 4$ and $[\text{ROH}]_{\text{tot}}/[\text{SDS}] = 5$.

For this formalism to be applicable, the total number of moles of alcohol that are incorporated into the interface must increase with increasing concentration of surfactant,²³ and hence increasing the interfacial volume. In ternary microemulsions (e.g. AOT–isooctane–water microemulsions), the interfacial volume can be assumed to remain constant. In quaternary microemulsions, however, the incorporation of large amounts of cosurfactant into the interface cause the interfacial volume to change with the surfactant concentration. This situation is similar to that in micellar systems when a high concentration of alcohol is added to the reaction medium.²⁴

The interfacial volume can be assumed to consist of the volumes of surfactant and alcohol incorporated into the interface, namely:

$$V_i = \bar{V}_{\text{Surfactant}}[\text{Surfactant}]_i + \bar{V}_{\text{ROH}}[\text{ROH}]_i \quad (6)$$

$$\frac{V_{\text{tot}}}{V_i} = \frac{1}{\bar{V}_{\text{Surfactant}}[\text{Surfactant}]} + \frac{K_{oi}^{\text{ROH}} + Z}{\bar{V}_{\text{ROH}}K_{oi}^{\text{ROH}}[\text{ROH}]_{\text{tot}}} \quad (7)$$

Because the percentage of trapped water at the interface is lower than 3% of total water and because the small molar volume of water, we can neglect its contribution to the total volume of the interface with an error smaller than 10%. We used a molar volume of surfactant $\bar{V}_{\text{TTABr}} = 0.326 \text{ M}^{-1}$ for TTABr²⁵ and $\bar{V}_{\text{SDS}} = 0.246 \text{ M}^{-1}$ for SDS,^{26–28} which corresponded to the overall volume of the micelles. The molar volume of 1-hexanol, $\bar{V}_{\text{ROH}} = 0.126 \text{ M}^{-1}$, was calculated from its density.

Fig. 3 shows how the relationship V_{tot}/V_i (values calculated according to the eqn (7)) decreases as the surfactant concentration increases. The decrease in V_{tot}/V_i with the TTABr or SDS concentration is a consequence of the alcohol incorporation into the interface and its consequent increase in volume. Hence, the calculated values for V_{tot}/V_i are independent of the W parameter. This behavior is due to the quantity of solubilized alcohol in the aqueous pseudophase of the microemulsion being negligible.

The kinetic results obtained should be explained by taking into account the alcohol incorporation into the interface of the microemulsion and consequently the variation of the volume of the interface with the surfactant concentration and with the molar relationship $[\text{ROH}]_{\text{tot}}/[\text{TTABr}]$.

Nucleophilic substitution by bromide ion in benzyl chloride

This reaction was studied in TTABr–1-hexanol–isooctane–water microemulsions at a constant $[\text{1-Hexanol}] : [\text{TTABr}]$ ratio of 4 : 1. The aim was twofold, namely: (a) to construct a kinetic model accounting for the reactivity of benzyl chloride towards Br^- ion irrespective of the microemulsion composition and (b) to use the model to determine the fraction of neutralized charge at the interface of the microemulsion.

Influence of the microemulsion composition. We examined the influence of the microemulsion composition on the observed rate constant, k_{obs} , for the nucleophilic attack of bromide ion on benzyl chloride at a variable surfactant concentration, $[\text{TTABr}]$, from 0.10 to 0.70 M and a constant mole ratio $W = [\text{H}_2\text{O}]/[\text{TTABr}]$. By way of example, Fig. 4 shows selected results. As can be seen, k_{obs} increases on increasing the

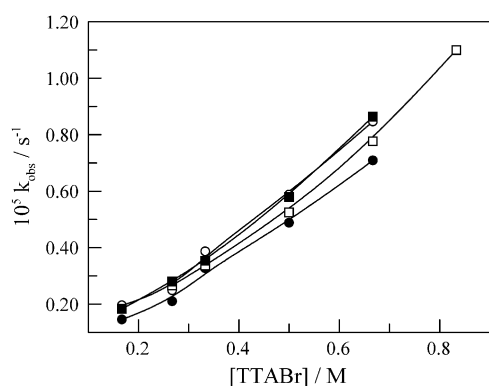
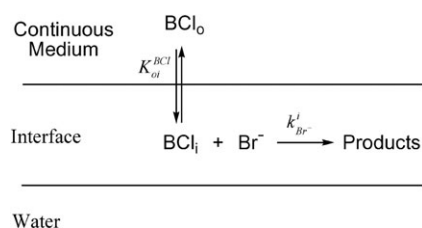


Fig. 4 Influence of the TTABr concentration on k_{obs} in the nucleophilic attack of bromide ion on benzyl chloride in TTABr–1-hexanol–isooctane–water microemulsions at 25.0 °C. $W = (\circ)$ 5, (\bullet) 7, (\square) 10 and (\blacksquare) 15.

surfactant concentration, but was virtually independent of the water content of the microemulsion, W .

The behavior of this system can be interpreted in qualitative terms as a function of the partitioning of benzyl chloride between the continuous medium and the interface. Raising the surfactant concentration increases the amount of benzyl chloride that binds to the interface. The reaction between bromide ions and benzyl chloride can only take place at the microemulsion interface owing to the strongly hydrophobic character of the substrate; also, if the fraction of micellar charge that is neutralized does not change with the water content of the microemulsion, the concentration of bromide ions bound to the interface must be independent of W .

Partitioning of the reactants. The quaternary microemulsion can be simplified to a pseudo-ternary microemulsion (Scheme 2) with isooctane and 1-hexanol as the continuous medium, TTABr and 1-hexanol as the interface, and water as the aqueous medium. Accurately interpreting the kinetic results obtained in the nucleophilic substitution by bromide ion in benzyl chloride entails considering the way the reactants partition among the different pseudo-phases of the microemulsion. Scheme 3 shows the partitioning of benzyl chloride between the continuous medium and the microemulsion interface. The low solubility of this reactant in water allows its partitioning between the aqueous medium and the interface to be assumed negligible.



Scheme 3

The partition constant for benzyl chloride, $K_{\text{oi}}^{\text{BCl}}$, can be defined in classical terms as:

$$K_{\text{oi}}^{\text{BCl}} = \frac{[\text{BCl}_i]}{[\text{BCl}_o]} Z^* \quad (8)$$

where $Z^* = ([\text{Isooctane}] + [1\text{-Hexanol}])/[\text{TTABr}]$; subscripts i and o denote the interface and continuous medium, respectively; and concentrations are referred to the total volume of the microemulsion.

Kinetic model for the reaction in microemulsions. Based on the reactant partitioning of Scheme 3, the interface is the sole microemulsion region where the reactants can come into contact and hence the sole reactive region. The observed rate constant for the reaction will therefore be given by:

$$k_{\text{obs}} = \frac{k_{\text{Br}^-} K_{\text{oi}}^{\text{BCl}}}{(K_{\text{oi}}^{\text{BCl}} + Z^*)} \quad (9)$$

where k'_{Br^-} being is the *pseudo* first-order rate constant at the interface and can be expressed as a bimolecular rate constant at the interface as:²⁹

$$\begin{aligned} k'_{\text{Br}^-} &= k_{\text{Br}^-}^i [\text{Br}^-]_i = k_{\text{Br}^-}^i \frac{V_{\text{T}}}{V_i} [\text{Br}^-] \\ &= k_{\text{Br}^-}^i \frac{V_{\text{T}}}{V_i} \beta [\text{TTABr}] \end{aligned} \quad (10)$$

$[\text{Br}^-]_i$ being the concentration of bromide ion at the interface relative to the interfacial volume, and $[\text{Br}^-]_i$ the concentration of bromide ion referred to the total micro-emulsion volume. In the absence of bromide ions other than those resulting from dissociation of the surfactant, the total concentration of bromide at the interface will be equal to the product of the fraction of neutralized charge at the interface, β , and the total concentration of surfactant. Based on the foregoing, one can derive the following expression for the *pseudo* first-order rate constant:

$$k_{\text{obs}} = \frac{V_{\text{T}}}{V_i} \beta [\text{TTABr}] k_{\text{Br}^-}^i \frac{K_{\text{oi}}^{\text{BCl}}}{(K_{\text{oi}}^{\text{BCl}} + Z^*)} \quad (11)$$

which can be rearranged to:

$$\frac{V_{\text{T}}}{V_i} \frac{[\text{TTABr}]}{k_{\text{obs}}} = \frac{1}{\beta k_{\text{Br}^-}^i} + \frac{1}{\beta k_{\text{Br}^-}^i K_{\text{oi}}^{\text{BCl}}} Z^* \quad (12)$$

This equation predicts a linear relationship between $(V_{\text{T}}[\text{TTABr}])/(V_i k_{\text{obs}})$ and the microemulsion composition parameter, Z^* . By way of example, Fig. 5 illustrates the good fit of the results to eqn (12).

Table 1 lists the slopes and intercepts obtained by fitting the experimental k_{obs} values to eqn (12) at different W values. As can be seen, the intercept was in many cases similar in magnitude to its own error owing to the extrapolation required to obtain it. Based on eqn (12), the slope-to-intercept ratio should be constant and independent of W (Intercept/Slope = $K_{\text{oi}}^{\text{BCl}}$). The results of Table 1 suggest that, in fact, such a ratio remains constant throughout. If all W values are considered, then $K_{\text{oi}}^{\text{BCl}} = 2.1 \pm 0.8$, which is consistent with the results obtained by using the W values 10, 15, 35 and 45 alone (*i.e.* those where the intercept can be accurately determined). If only such W values are considered, then $K_{\text{oi}}^{\text{BCl}} = 2.7 \pm 0.5$. In

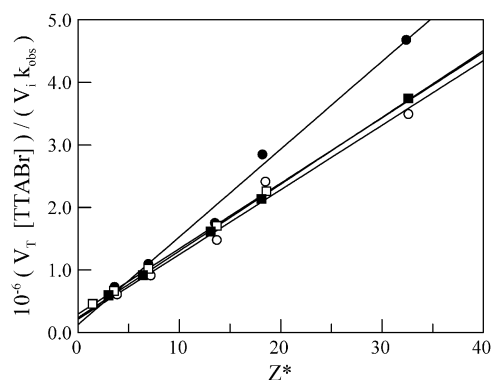


Fig. 5 Fitting of the data in Fig. 4 to eqn (12). $W = (\circ)$ 5, (\bullet) 7, (\square) 10 and (\blacksquare) 15.

what follows, we shall use this value for the partition constant of benzyl chloride between the different phases in the microemulsion.

As can be seen from Fig. 6, the reciprocal of the slopes in Table 1, which were obtained from eqn (12), were W -independent and averaged at $1/\text{Intercept} = (8.7 \pm 0.1) \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. This suggests that the product $\beta K_{\text{oi}}^{\text{BCl}} k_{\text{Br}^-}^{\text{i}}$ is independent of the water content of the microemulsion and hence that so is $\beta k_{\text{Br}^-}^{\text{i}}$, which averaged at $\beta k_{\text{Br}^-}^{\text{i}} = 3.22 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. Therefore, the proposed kinetic model provides an accurate explanation for the kinetic results obtained under rather variable microemulsion compositions. The model satisfactorily explains the reactivity of benzyl chloride irrespective of the particular composition of the microemulsion.

The constancy of $\beta k_{\text{Br}^-}^{\text{i}}$ has two possible implications, namely: (a) both β and $k_{\text{Br}^-}^{\text{i}}$ are W -independent through the studied composition range or (b) their changes cancel each other. Initially, one could expect the fraction of neutralized charge at the interface to increase with decrease in W , which would cause a slight increase in β and a decrease in $k_{\text{Br}^-}^{\text{i}}$. That the rate constants at the interface decrease on decreasing W was previously observed³⁰ and ascribed to a decrease in the ability of interfacial water to solvate the reactants and the transition state upon decreasing the water content of the microemulsion. However, when the rate of the reaction concerned is scarcely sensitive to polarity changes in the medium (e.g. in nitroso group transfers), a single value of the rate constant is obtained at any W value exceeding $W > 5$ –7.³¹

Table 1 Intercepts and slopes obtained by fitting the experimental k_{obs} values for the nucleophilic attack of bromide ion on benzyl chloride in TTABr–1-hexanol–isooctane–water microemulsions to eqn (12)

W	Intercept	Slope
5	$(2 \pm 1) \times 10^5$	$(1.03 \pm 0.09) \times 10^5$
7	$(1 \pm 1) \times 10^5$	$(1.40 \pm 0.08) \times 10^5$
10	$(2.9 \pm 0.1) \times 10^5$	$(1.04 \pm 0.01) \times 10^5$
15	$(2.4 \pm 0.3) \times 10^5$	$(1.07 \pm 0.01) \times 10^5$
20	$(2 \pm 2) \times 10^5$	$(1.3 \pm 0.1) \times 10^5$
30	$(2 \pm 1) \times 10^5$	$(1.07 \pm 0.08) \times 10^5$
35	$(3.5 \pm 0.3) \times 10^5$	$(1.07 \pm 0.03) \times 10^5$
40	$(1 \pm 2) \times 10^5$	$(1.4 \pm 0.1) \times 10^5$
45	$(2.6 \pm 0.9) \times 10^5$	$(1.08 \pm 0.06) \times 10^5$

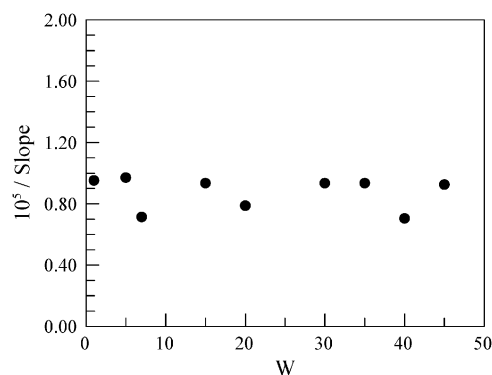


Fig. 6 Variation of the product $\beta K_{\text{oi}}^{\text{BCl}} k_{\text{Br}^-}^{\text{i}}$ as a function of W for the nucleophilic attack of bromide ion on benzyl chloride in TTABr–1-hexanol–isooctane–water microemulsions.

The problem here lies in quantifying the sensitivity of the rate of nucleophilic substitution by bromide ion in benzyl chloride to the solvent polarity. Based on the results of Jaeger *et al.*,³² the rate constant is $k = 3.0 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$ in 25% (v/v) water–ethanol mixtures and $k = 2.9 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$ in 10% (w/w) CTABr–water mixtures at 40.0 °C. These results suggest that the reaction is scarcely sensitive to the polarity of the medium, so $k_{\text{Br}^-}^{\text{i}}$ should possess a unique value irrespective of the particular microemulsion composition provided $5 < W < 45$. If $k_{\text{Br}^-}^{\text{i}}$ is independent of W , then the fraction of neutralized charge at the interface, β , should remain constant throughout the previous range of water content in the microemulsion. This was subsequently confirmed in studying the acid denitrosation of *N*-methyl-*N*-nitroso-*para*-toluenesulfonamide.

The degree of dissociation of the surfactant in aqueous micelles and oil-in-water microemulsions can be readily determined *via* conductivity measurements. Basically, conductivity changes can be related to the degree of dissociation of the surfactant that contributes with ionic components (e.g. sodium ions from SDS) to the aqueous phase. There have been some attempts at determining the degree of dissociation at the interface of SDS–1-butanol–water–toluene microemulsions³³ from conductivity measurements which have provided α values from 0.52 to 0.05.

However, the conductivity of w/o microemulsions is closely related to the rate of mass transfer between droplets, a phenomenon that peaks at the onset of electrical percolation. Research into the internal dynamics of w/o microemulsions has largely focused on this intriguing phenomenon, which causes an abrupt increase in electrical conductivity when either the temperature or the volume fraction of the dispersed phase reaches a critical value. Percolation therefore involves a sharp change in electrical conductivity from very low levels typical of small droplets dispersed in a nonconducting continuous medium to values higher by several powers of 10.³⁴ Lang and coworkers^{11d,35} have related electrical percolation to the rate constants governing the exchange of materials between droplets (a process which in turn may have a decisive influence on the rate of fast chemical reactions in w/o microemulsions). Percolation does not occur as the result of the formation of permanent bicontinuous structures in the medium, but rather

of the structure of discrete droplets being preserved. One plausible explanation assumes that the number of collisions between droplets increases sharply in the vicinity of the percolation threshold and leads to the formation of droplet clusters. The opening of interdroplet channels in the clusters facilitates the transport of materials (ions) between droplets and gives rise to the abrupt increase in conductivity observed.

Therefore, the conductivity in microemulsions cannot be related to changes in the number of ionic components. In fact, the addition of salts to an AOT–isooctane–water w/o microemulsion hinders electrical percolation. The absence of correlation between conductivity and the number of ionic components of the system precludes its use to determine the degree of dissociation of the surfactant.

The Poisson–Boltzmann equation has allowed some authors to study the effect of W on the degree of counterion binding, β . Thus, Karpe and Ruckenstein³⁶ found β to decrease with increase in W ; however, β changed by only 7.3% on raising W from $W = 6$ ($\beta \approx 0.86$) to $W = 50$ ($\beta \approx 0.80$). Likewise, the degree of dissociation of ionic microemulsions has been shown to increase with increasing droplet size.³⁷ According to Kozlovich and coworkers,³⁸ the degree of counterion binding of AOT head groups must be greater than 72%. These results are consistent with the sole experimental study to the authors' knowledge available where chemical trapping of bromide ions in microemulsions³⁹ has been used; β for CTAB microemulsions in dodecane/ CHCl_3 was found to be 0.8—which is very similar to the values found in aqueous micelles—at $W > 15$.

If a β value of 0.8, which is the most widely used for direct micellar systems, is adopted, then k_{Br^-} is calculated to be⁴⁰ $k_{\text{Br}^-} = 4.02 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, which is comparable with that obtained by Jaeger *et al.*³² for the reaction in 10% (w/w) CTABr–water mixtures at 40.0 °C (*viz.* $k = 4.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$). As can be seen, the reaction rate is roughly 10 times smaller at the interface of TTABr–1-hexanol–isooctane–water microemulsions than at the interface of aqueous micellar systems; this is consistent with the decreased interfacial polarity of microemulsions relative to simple micellar systems. As shown later on Table 2, a similar behavior was observed in the acid denitrosation of MNTS in single-component SDS micellar systems and in SDS–1-hexanol–isooctane–water microemulsions.

Table 2 Bimolecular rate constant for the nitroso group transfer from MNTS to piperazine (PIP) and *N*-methylbenzylamine (MeBzAm) in various reaction media, and also for the denitrosation of MNTS

Reaction	Reaction medium	$k/\text{M}^{-1} \text{ s}^{-1}$
MNTS + PIP	H_2O^a	2.98×10^{-2}
	AOT–isooctane– H_2O^b	5.33×10^{-3}
	TTABr–1-hexanol–isooctane– H_2O^c	4.69×10^{-3}
MNTS + MeBzAm	H_2O^a	4.10×10^{-2}
	AOT–isooctane– H_2O^b	3.1×10^{-3}
	TTABr–1-hexanol–isooctane– H_2O^c	6.99×10^{-4}
MNTS + H^+	H_2O^d	3.20×10^{-2}
	SDS ^e	3.50×10^{-3}
	SDS–1-hexanol–isooctane– H_2O	7.25×10^{-4}

^a Ref. 45. ^b Ref. 47. ^c Ref. 31b. ^d Ref. 44b. ^e Ref. 49.

Acid denitrosation of *N*-methyl-*N*-nitroso-*para*-toluenesulfonamide in SDS–1-hexanol–isooctane–water microemulsions.

We studied the acid hydrolysis (denitrosation) of MNTS in SDS–1-hexanol–isooctane–water microemulsions at a constant [1-hexanol] : [SDS] ratio of 5 : 1. Kinetic experiments were performed under conditions where HCl was in a very large excess with respect to the *N*-nitroso compound. By way of example, Fig. 7 shows the variation of the *pseudo* first-order observed rate constant, k_{obs} , with the microemulsion composition. Contrary to the nucleophilic attack of bromide ions on benzyl chloride, k_{obs} decreased with increasing concentration of surfactant and was virtually independent of the water content of the microemulsion, W .

These results can be ascribed to a combination of two factors. On the one hand, raising the surfactant concentration increases that of MNTS at the microemulsion interface (the sole region where MNTS and H_3O^+ can come into contact).⁴¹ The increased interfacial concentration of *N*-nitroso compound should result in an increased reaction rate. However, an increase in the concentration of SDS also increases that of unreactive Na^+ ions. Competition between these unreactive counterions and H_3O^+ ions for binding to the microemulsion interface must be the origin of the decrease in rate constant observed as the surfactant concentration is raised. This inhibitory effect of an increased concentration of unreactive counterions has frequently been encountered in micellar systems and interpreted in the light of the *pseudo*-phase ion-exchange formalism.⁸

Providing a quantitative interpretation for the results entails considering the way the reactants partition among the different *pseudo*-phases in the microemulsions (see Scheme 4, where MNTS is assumed to be exclusively present in the continuous medium and the interface, which will thus constitute the sole reactive region in the microemulsion).

The equilibrium constant for MNTS distribution is defined as usual, $K_{\text{oi}}^{\text{MNTS}} = ([\text{MNTS}]_i Z^*)/[\text{MNTS}]_o$, with all concentrations referred to the total volume of the microemulsion, k_{H}^i the bimolecular rate constant for the reaction and the interface, and k_{Na}^{H} the ion-exchange equilibrium constant between protons and the counterions (Na^+). A mass balance assuming

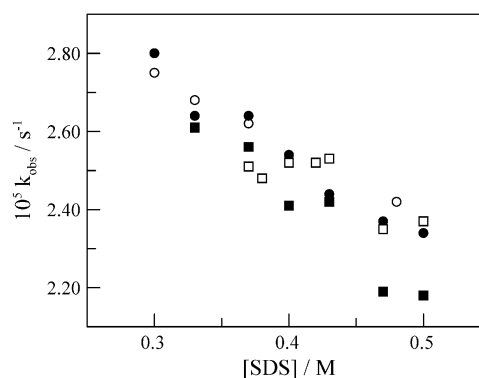
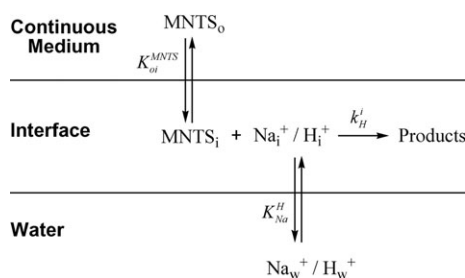


Fig. 7 Influence of the SDS concentration on k_{obs} for the acid denitrosation of MNTS in SDS–1-hexanol–isooctane–water microemulsions at 25.0 °C. $[\text{HCl}] = 6.67 \times 10^{-3} \text{ M}$. $W = (\circ)$ 7, (\bullet) 10, (\square) 15 and (\blacksquare) 20.



Scheme 4

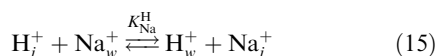
the total MNTS concentration to be the combination of those in the continuous medium and the interface can be used to obtain the following expression for the *pseudo* first-order rate constant:

$$k_{\text{obs}} = \frac{K_{oi}^{\text{MNTS}} k_H'}{(K_{oi}^{\text{MNTS}} + Z^*)} \quad (13)$$

where k_H' is the *pseudo* first-order rate constant at the interface and can be expressed as a bimolecular rate constant at the interface, k_H^i , in such a way that:⁴⁰

$$k_{\text{obs}} = \frac{K_{oi}^{\text{MNTS}} k_H^i [\text{H}^+]_i}{(K_{oi}^{\text{MNTS}} + Z^*)} = \frac{V_T K_{oi}^{\text{MNTS}} k_H^i [\text{H}^+]_i}{V_i (K_{oi}^{\text{MNTS}} + Z^*)} \quad (14)$$

$[\text{H}^+]_i$ being the proton concentration at the interface relative to the interfacial volume and $[\text{H}^+]_i$ that relative to the total volume of the microemulsion. The proton concentration at the interface can be determined by defining the ion-exchange equilibrium constant:



as:

$$K_{Na}^H = \frac{[\text{H}_w^+]_w [\text{Na}_i^+]_i}{[\text{H}_i^+]_i [\text{Na}_w^+]_w} = \frac{[\text{H}_w^+]_w [\text{Na}_i^+]_i}{[\text{H}_i^+]_i [\text{Na}_w^+]_w} \quad (16)$$

where $[\text{H}_w^+]_w$ and $[\text{H}_i^+]_i$ denote concentrations in a phase referred to the phase volume and total microemulsion volume, respectively. Converting values between the two forms entails defining the volume of each phase.

If one assumes the SDS concentrations in the continuous medium and aqueous phase to be negligible (*i.e.* that SDS is entirely present at the interface), the following expression for the fraction of neutralized charge at the interface can be derived:

$$\beta = \frac{[\text{H}_i^+]_i + [\text{Na}_i^+]_i}{[\text{SDS}]} \quad (17)$$

Also, if one assumes Na^+ to be the dominant counterion in the microemulsion droplets,⁴² then, $\beta \cong [\text{Na}_i^+]_i / [\text{SDS}]$. Consequently, a mass balance for the total proton concentration under the assumption that the total concentration of Na^+ will be identical with that of SDS provides the following equation:

$$K_{Na}^H = \frac{([\text{H}^+]_T - [\text{H}^+]_i) \beta [\text{SDS}]}{[\text{H}^+]_i [\text{SDS}] (1 - \beta)} \quad (18)$$

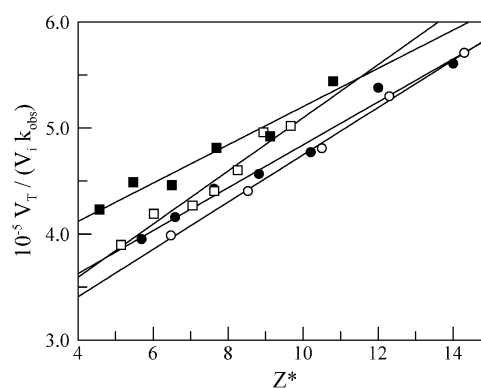


Fig. 8 Fitting of the data of Fig. 4 to eqn (21). $W = (\circ)$ 7, (\bullet) 10, (\square) 15, and (\blacksquare) 20.

and hence:

$$[\text{H}^+]_i = \frac{\beta [\text{H}^+]_T}{\alpha (K_{Na}^H - 1) + 1} \quad (19)$$

where α is the degree of dissociation at the interface ($\alpha + \beta = 1$). Therefore, eqn (13) can be rewritten as the following function of the total proton concentration:

$$k_{\text{obs}} = \frac{V_T}{V_i} k_H^i \frac{K_{oi}^{\text{MNTS}}}{(K_{oi}^{\text{MNTS}} + Z^*)} \frac{\beta [\text{H}^+]_T}{\alpha (K_{Na}^H - 1) + 1} \quad (20)$$

which can in turn be rewritten as:

$$\frac{V_T}{V_i k_{\text{obs}}} = \frac{1}{k_H^i} \frac{\alpha (K_{Na}^H - 1) + 1}{\beta [\text{H}^+]_T} + \frac{1}{k_H^i K_{oi}^{\text{MNTS}}} \frac{\alpha (K_{Na}^H - 1) + 1}{\beta [\text{H}^+]_T} Z^* \quad (21)$$

This equation predicts a linear relationship between the term $V_T / (V_i k_{\text{obs}})$ and Z^* , which is confirmed by the results of Fig. 8. Table 3 lists the slopes and intercepts obtained by plotting $V_T / (V_i k_{\text{obs}})$ as a function of Z^* at variable W values.

The slope/intercept allows one to calculate the partition constant of MNTS between the continuous medium and the interface. As can be seen from the data of Table 3, K_{oi}^{MNTS} was independent of W , which confirms the accuracy of the proposed model. Based on such data, an average K_{oi}^{MNTS} value of $K_{oi}^{\text{MNTS}} = 13 \pm 3$ was obtained that is consistent with previously reported values for AOT and TTABr microemulsions.

As can be seen, the slopes and intercepts obtained from eqn (21) are independent of W (see Fig. 9). Based on the experimental data, the following average values were obtained: $k_H^i \frac{\beta [\text{H}^+]_T}{\alpha (K_{Na}^H - 1) + 1} = (3.9 \pm 0.8) \times 10^{-6}$ and $k_H^i K_{oi}^{\text{MNTS}} \frac{\beta [\text{H}^+]_T}{\alpha (K_{Na}^H - 1) + 1} = (5.0 \pm 0.8) \times 10^{-5}$. The results obtained in the acid denitrosation of MNTS are consistent with those previously found in the nucleophilic attack of bromide ion on benzyl chloride. Determining the slope and intercept in this case requires knowing the ion-exchange equilibrium constant, K_{Na}^H . The most widely accepted value of such a constant for the Na^+/H^+ ion exchange in micellar systems⁴³ is $K_{Na}^H \cong 1$, which allows the previous equations to be simplified to $k_H^i \beta [\text{H}^+]_T = (3.9 \pm 0.8) \times 10^{-6}$ and $k_H^i K_{oi}^{\text{MNTS}} \beta [\text{H}^+]_T = (5.0 \pm 0.8) \times 10^{-5}$.

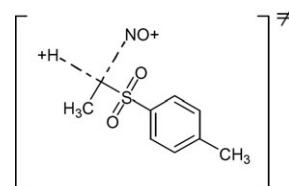
Table 3 Slopes and intercepts of the plots obtained by fitting the experimental k_{obs} values for the acid denitrosation of MNTS in SDS-1-hexanol-isooctane-water microemulsions at 25.0 °C to eqn (21)

W	Intercept	Slope
7	$(2.52 \pm 0.07) \times 10^5$	$(2.23 \pm 0.06) \times 10^4$
10	$(2.8 \pm 0.1) \times 10^5$	$(2.0 \pm 0.1) \times 10^4$
15	$(2.6 \pm 0.2) \times 10^5$	$(2.5 \pm 0.2) \times 10^4$
20	$(3.4 \pm 0.1) \times 10^5$	$(1.8 \pm 0.2) \times 10^4$
25	$(2.0 \pm 0.1) \times 10^5$	$(1.7 \pm 0.2) \times 10^4$

Since the HCl concentration used in the kinetic experiments was $[\text{HCl}] = 6.67 \times 10^{-3} \text{ M}$, $k_{\text{H}}^i\beta = (5.8 \pm 1.2) \times 10^{-4}$ and $k_{\text{H}}^iK_{\text{oi}}^{\text{MNTS}}\beta = (7.5 \pm 1.2) \times 10^{-3}$. Based on the smaller error made in determining slopes, in what follows we shall use $k_{\text{H}}^iK_{\text{oi}}^{\text{MNTS}}\beta = (7.5 \pm 1.2) \times 10^{-3}$. Also, since the partition constant of MNTS between the microemulsion *pseudo*-phases, $K_{\text{oi}}^{\text{MNTS}}$, is 13 ± 3 , then $k_{\text{H}}^i\beta = 5.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$.

As in the previous reaction, the constancy of the product $k_{\text{H}}^i\beta$ with W may have resulted from either β and k_{H}^i being independent of W or their changes (*viz.* an increase in β and a decrease in k_{H}^i with increasing W) cancelling each other. The acid hydrolysis of *N*-methyl-*N*-nitroso-*para*-toluenesulfonamide is a concerted process taking place *via* a transition state such as that shown in Scheme 5. The formation of the N–H bond and cleavage of the N–N bond are simultaneous, but not synchronous.⁴⁴

The reaction is not very sensitive to the solvent polarity. Thus, a comparison of the rate constant in water ($k = 3.20 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) and in 65% (v/v) acetonitrile-water mixtures ($k = 1.12 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) reveals a reduction of only 28 times in the reaction rate. This sensitivity level is similar to that of nitroso group transfers from MNTS to secondary amines. Thus, the nitrosation rate of *N*-methylbenzylamine by MNTS decreases about 25 times from 10 to 66% (v/v) acetonitrile.⁴⁵ Based on previous results,³¹ the rate constants for the nitroso group transfer in AOT-isooctane-water and TTABr-alcohol-isooctane-water microemulsions are independent of W over the range $5 < W < 45$. Since the rate of MNTS denitrosation is similarly sensitive to the polarity of the medium as its rate of transnitrosation, k_{H}^i should also be independent of W in this



Scheme 5

case. This result confirms that the charge fraction that is neutralized at the interface remains constant throughout the same W range.

Therefore, if one accepts that the fraction of neutralized charge at the interface and the rate constant for the acid denitrosation of MNTS are both independent of W , k_{H}^i can be calculated simply by assuming $\beta \cong 0.8$. The k_{H}^i value thus obtained is $k_{\text{H}}^i = 7.25 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, which is 48 times smaller than that in pure water at an ionic strength $I = 0.50 \text{ M}$ (HClO_4) ($k_{\text{H}} = 3.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$). The difference can be ascribed to the decreased polarity of the interface in the microemulsion relative to bulk water.

Comparison of reactivity in various media

Table 2 lists the rate constants obtained for the nitroso group transfer from MNTS to piperazine (PIP) and *N*-methylbenzylamine (MeBzAm), as well as for the acid denitrosation in MNTS, in various reaction media. The nitroso group transfer from alkyl nitrites to amines in water and direct micellar systems has previously been studied.⁴⁶ The reactivity in the micellar phase is known to be lower than in water owing to the decreased polarity of the micellar interface. Thus, the reactivity of 1-phenylethyl nitrite in the micellar phase is lower than with 2-bromoethylnitrite when a particular amine is considered. This can be ascribed to the different sites of average location in both substrates in the micellar interface. The more hydrophilic 2-bromoethylnitrite will be located near the micellar surface, in a strongly hydrated zone, while 1-phenylethyl nitrite will reside in a deeper zone of the Stern layer, the properties of which are quite anisotropic, in a less polar environment.

A similar inhibitory effect is apparent when one compares the rates of nitroso group transfer from MNTS to piperazine and *N*-methylbenzylamine in water, ternary microemulsions⁴⁷ of AOT-isooctane-water and quaternary microemulsions^{13b} of TTABr-1-hexanol-isooctane-water. Thus, the rate constant is about 6 times smaller for piperazine⁴⁸ and 60 times smaller for *N*-methylbenzylamine.

The rate constant for the acid hydrolysis of MNTS in water⁴⁴ is about 10 times greater than that in SDS micelles,⁴⁹ which can be ascribed to a decreased polarity of the micellar interface relative to the aqueous medium. The constant in SDS-1-hexanol-isooctane-water microemulsions is about 45 times smaller than in water. This is consistent with the influence of microemulsions and micelles on the rate of transnitrosation and hydrolysis of MNTS. It should be noted that the results for both the acid denitrosation of MNTS and the nucleophilic attack of bromide ion on benzyl chloride suggest that the microemulsion interface is less polar than in

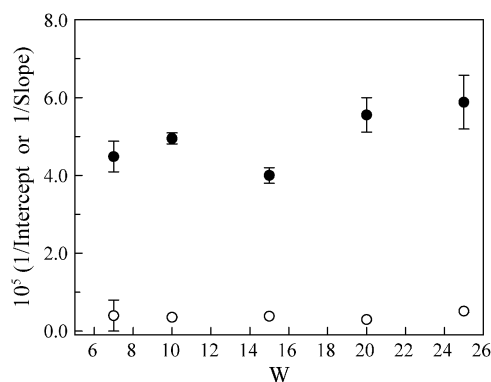


Fig. 9 Variation of the slopes and intercepts of Table 3 with the water content of the microemulsion. (○) $1/\text{Intercept}$; (●) $1/\text{Slope}$.

single-component micellar systems; this is a consequence of the alcohol acting as a cosurfactant and displacing hydration water molecules from the microemulsion interface.

Conclusions

Using the *pseudo*-phase formalism to explain the influence of the composition of the microemulsion on the nucleophilic attack of bromide ions on benzyl chloride and the acid denitrosation of *N*-methyl-*N*-nitroso-*para*-toluenesulfonamide allowed us to

(a) Simplify a quaternary microemulsion (TTABr–1-hexanol–isooctane–water or SDS–1-hexanol–isooctane–water) to one consisting of only three components, namely: an aqueous phase, an interface formed by the surfactant and 1-hexanol, and a continuous medium composed of isooctane and 1-hexanol. The incorporation of the alcohol into the interface increases the interfacial volume, which is now the combination of those occupied by the surfactant and alcohol.

(b) Assume the substrate in the nucleophilic attack of bromide ion to benzyl chloride to partition solely between the continuous medium and the interface, and hence that the reaction takes place at the microemulsion interface only. The *pseudo*-phase formalism allowed us to determine the partition constant of the substrate between the continuous medium and the interface, as well as the product of the rate constant and the charge fraction neutralized at the interface ($\beta k_{\text{Br}^-}^i = 3.22 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$). The fact that $\beta k_{\text{Br}^-}^i$ is independent of W suggests that the degree of dissociation of the surfactant at the microemulsion interface is independent of the water content of the microemulsion.

(c) Obtain similar results for the acid denitrosation of MNTS in SDS–1-hexanol–isooctane–water microemulsions. On the assumption that $k_{\text{Na}^+}^{\text{H}} \cong 1$ for the Na^+/H^+ ion-exchange equilibrium, an average $k_{\text{H}\beta}^i$ value of $k_{\text{H}\beta}^i = 5.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ was obtained over the range $7 < W < 25$. This result confirms that the fraction of neutralized charge at the interface is independent of the water content of the microemulsion. Under the assumption that $\beta = 0.8$, a k_{H}^i value was obtained by analogy with micellar systems that is roughly 45 times smaller than in pure water; this is consistent with other results for nitroso group transfers in microemulsions.

Acknowledgements

Financial support from Spain's Ministerio de Ciencia y Tecnología (Project CTQ2005-04779) and Xunta de Galicia (PGIDT03-PXIC20905PN and PGIDT04TMT209003PR) is gratefully acknowledged.

References

- (a) J. K. Thomas, *Chem. Rev.*, 1980, **80**, 283; (b) M. A. López-Quintela, C. Tojo, M. C. Blanco, L. García-Río and J. R. Leis, *Curr. Opin. Colloid Interface Sci.*, 2004, **9**, 264.
- P. Neogi, in *Microemulsions: Structure and Dynamics*, ed. S. E. Friberg and P. Bothorel, CRC Press, Boca Raton, FL, 1987.
- (a) P. L. Luisi, M. Giomini, M. P. Pileni and B. H. Robinson, *Biochim. Biophys. Acta*, 1988, **947**, 209; (b) T. A. Hatton, in *Surfactant Based Processes*, ed. J. F. Scamehorn and J. H. Harwell, Marcel Dekker, Inc., New York, 1989, and references therein.
- E. B. Leodidis and T. A. Hatton, *J. Phys. Chem.*, 1990, **94**, 6400.
- F. Yang and A. J. Russell, *Biotechnol. Bioeng.*, 1994, **43**, 232.
- (a) M. Häger and K. Holmberg, *Chem.–Eur. J.*, 2004, **10**, 5460; (b) N. Ohtani, T. Ohta, Y. Hosoda and T. Yamashita, *Langmuir*, 2004, **20**, 409.
- B. H. Robinson, A. N. Khan-Lodhi and T. Towey, in *Structure and Reactivity in Reversed Micelles*, ed. M. P. Pileni, Elsevier, Amsterdam, 1989.
- (a) J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975; (b) L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5107; (c) L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5113.
- C. A. Bunton and L. S. Romsted, in *Solution Behavior of Surfactants: Theoretical and Applied Aspects*, ed. K. L. Mittal and E. J. Fendler, Plenum, New York, 1982, pp. 975.
- (a) H. F. Eicke, *Top. Curr. Chem.*, 1980, **87**, 85; (b) P. L. Luisi and L. J. Magid, *CRC Crit. Rev. Biochem.*, 1986, **20**, 409; (c) Y. Chevalier and T. Zemb, *Rep. Prog. Phys.*, 1990, **53**, 279; (d) A. Goto, H. Yoshioka, M. Manabe and R. Goto, *Langmuir*, 1995, **11**, 4873; (e) T. K. De and A. Maitra, *Adv. Colloid Interface Sci.*, 1995, **59**, 95, and references therein.
- (a) P. Ekwall, L. Mandell and K. Fontel, *J. Colloid Interface Sci.*, 1969, **29**, 639; (b) M. Seno, K. Sawada, K. Araki, K. Iwamoto and H. Kise, *J. Colloid Interface Sci.*, 1980, **78**, 57; (c) P. D. I. Fletcher, M. F. Galal and B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2053; (d) J. Lang, G. Mascolo, R. Zana and P. L. Luisi, *J. Phys. Chem.*, 1990, **94**, 3069; (e) R. Germani, G. Savelli, G. Cerichelli, G. Mancini, L. Luchetti, P. P. Ponti, N. Spreti and C. A. Bunton, *J. Colloid Interface Sci.*, 1991, **147**, 152.
- (a) P. D. Profio, R. Germani, G. Onori, A. Santucci, G. Savelli and C. A. Bunton, *Langmuir*, 1998, **14**, 768; (b) J. Sunamoto, K. Iwamoto, S. Nagamatsu and H. Kondo, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2469; (c) H. Kondo, I. Miwa and J. Sunamoto, *J. Phys. Chem.*, 1982, **86**, 4826.
- (a) R. Germani, P. P. Ponti, N. Spreti, G. Savelli, A. Cipiciani, G. Cerichelli, C. A. Bunton and V. Si, *J. Colloid Interface Sci.*, 1990, **138**, 443; (b) R. Germani, P. P. Ponti, T. Romeo, G. Savelli, N. Spreti, G. Cerichelli, L. Luchetti, G. Mancini and C. A. Bunton, *J. Phys. Org. Chem.*, 1989, **2**, 553.
- (a) R. Zana, *Adv. Colloid Interface Sci.*, 1995, **57**, 1; (b) J. Van Nieuwkoop and G. Snoei, *J. Colloid Interface Sci.*, 1985, **103**, 417.
- A. Jain and R. P. B. Singh, *J. Colloid Interface Sci.*, 1981, **81**, 536.
- R. Zana, S. Yiv, C. Strazielle and P. Lianos, *J. Colloid Interface Sci.*, 1981, **80**, 208.
- P. Mukerjee, *J. Phys. Chem.*, 1962, **66**, 1733.
- M. Dollet, J. Juillard and R. Zana, *J. Solution Chem.*, 1980, **9**, 827.
- G. Palazzo, F. Lopez, M. Giustini, G. Colafemmina and A. Ceglie, *J. Phys. Chem. B*, 2003, **107**, 1924.
- J. E. Bowcott and J. H. Schulman, *Z. Elektrochem.*, 1955, **59**, 283.
- (a) W. Gerbacia and H. L. Rosano, *J. Colloid Interface Sci.*, 1973, **44**, 242; (b) V. K. Bansal, D. O. Shah and J. P. O'Conel, *J. Colloid Interface Sci.*, 1980, **75**, 462; (c) K. S. Birdi, *Colloid Polym. Sci.*, 1982, **26**, 628; (d) H. N. Singh, S. Swarup, R. P. Singh and S. M. Saleem, *Ber. Bunsen-Ges. Phys. Chem.*, 1983, **87**, 1115; (e) S. P. Moulik, L. G. Digout, W. M. Aylward and R. Palepu, *Langmuir*, 2000, **16**, 3101; (f) S. K. Hait and S. P. Moulik, *Langmuir*, 2002, **18**, 6736; (g) M. Giustini, S. Murgia and G. Palazzo, *Langmuir*, 2004, **20**, 7381.
- P. Stilbs, *J. Colloid Interface Sci.*, 1982, **87**, 385.
- L. García-Río, J. R. Leis and C. Reigosa, *J. Phys. Chem. B*, 1997, **101**, 5514.
- C. Bravo, J. R. Leis and M. E. Peña, *J. Phys. Chem.*, 1992, **96**, 1957.
- (a) A. K. Yatsimirski, K. Martinek and I. V. Berezin, *Tetrahedron*, 1971, **27**, 2855; (b) S. Backlund, B. Bergenstahl, O. Molander and T. Warnheim, *J. Colloid Interface Sci.*, 1989, **131**, 393; (c) E. Kudryashov, T. Kapustina, S. Morrissey, V. Buckin and K. Dawson, *J. Colloid Interface Sci.*, 1998, **203**, 59; (d) G. González-Gaitano, A. Crespo and G. Tardajos, *J. Phys. Chem. B*, 2000, **104**, 1869; (e) A. Lainez, P. Burgo, E. Junquera and E. Aicart, *Langmuir*, 2004, **20**, 5745.

- 26 G. Roux-Desgaranges, S. Bordere and A. H. Roux, *J. Colloid Interface Sci.*, 1994, **162**, 284.
- 27 R. De Lisi, A. Inglese, S. Milioto and A. Pellerito, *J. Colloid Interface Sci.*, 1996, **180**, 174.
- 28 (a) D. Attwood, V. Mosquera, M. García, J. Rodríguez and M. J. Suárez, *J. Colloid Interface Sci.*, 1993, **157**, 168; (b) M. D. Bakshi, R. Crisantino, R. De Lisi and S. Milioto, *J. Phys. Chem.*, 1993, **97**, 6914.
- 29 Because k_{Br^-} encompasses the reaction volume, it has $M^{-1} s^{-1}$ units.
- 30 L. García-Río, J. R. Leis and E. Iglesias, *J. Phys. Chem.*, 1995, **99**, 12318.
- 31 (a) L. García-Río and J. R. Leis, *J. Phys. Chem. B*, 2000, **104**, 6618; (b) L. García-Río and P. Hervella, *Chem.-Eur. J.*, 2006, **12**, 8284.
- 32 (a) C. A. Martin, P. M. McCrann, G. H. Angelos and D. A. Jaeger, *Tetrahedron Lett.*, 1982, **23**, 4651; (b) C. A. Martin, P. M. McCrann, M. D. Ward, G. H. Angelos and D. A. Jaeger, *J. Org. Chem.*, 1984, **49**, 4392.
- 33 R. Da Rocha Pereira, D. Zanette and F. Nome, *J. Phys. Chem.*, 1990, **94**, 356.
- 34 L. García-Río, J. R. Leis, J. C. Mejuto, M. E. Peña and E. Iglesias, *Langmuir*, 1994, **10**, 1676, and references therein.
- 35 (a) A. Jada, J. Lang and R. Zana, *J. Phys. Chem.*, 1989, **93**, 10; (b) A. Jada, J. Lang, R. Zana, R. Makhloufi, E. Hirsch and S. J. Candau, *J. Phys. Chem.*, 1990, **94**, 387.
- 36 P. Karpe and E. Ruckenstein, *J. Colloid Interface Sci.*, 1990, **137**, 408.
- 37 (a) H.-K. Tsao, Y.-J. Sheng and C.-Y. David Lu, *J. Chem. Phys.*, 2000, **113**, 10304; (b) J.-P. Hsu, J.-M. Jiang and S. Tseng, *J. Phys. Chem. B*, 2003, **107**, 14429.
- 38 N. Kozlovich, A. Puzenko, Y. Alexandrov and Y. Feldman, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1998, **58**, 2179.
- 39 I. M. Cuccovia, L. G. Dias, F. A. Maximiano and H. Chaimovich, *Langmuir*, 2001, **17**, 1060.
- 40 Because the expression for k_{Br^-} encompasses the reaction volume, it has $M^{-1} s^{-1}$ units.
- 41 The sparse solubility of MNTS in water results in a negligible rate of acid hydrolysis in the aqueous *pseudo*-phase. This was previously observed in the nitroso group transfer from MNTS to amines in ternary (ref. 47) and quaternary microemulsions (ref. 31).
- 42 In the most unfavourable case, $[SDS] = 0.3 M$ and $[HCl] = 6.67 \times 10^{-3} M$.
- 43 For SDS micelles, $k_{Na}^H \cong 1$ (see, for example, C. A. Bunton, K. Ohmenzetter and L. Sepúlveda, *J. Phys. Chem.*, 1977, **81**, 2000).
- 44 (a) D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1838; (b) L. García-Río, J. R. Leis, J. A. Moreira and F. Norberto, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1613.
- 45 L. García-Río, E. Iglesias, J. R. Leis, M. E. Peña and A. Rios, *J. Chem. Soc., Perkin Trans. 2*, 1993, 29.
- 46 E. Iglesias, A. Fernández, L. García-Río and J. R. Leis, *Langmuir*, 1995, **11**, 1917, and references therein.
- 47 L. García-Río, J. R. Leis, M. E. Peña and E. Iglesias, *J. Phys. Chem.*, 1993, **97**, 3437.
- 48 The small inhibitory effect observed in the nitrosation of piperazine may have resulted partly from the statistical advantage of possessing two equivalent nitrosable positions in an environment of limited mobility such as the microemulsion interface. The effect on the nitrosation of MeBzAm (*viz.* a decrease of approximately 60 times in the rate constant relative to water) was similar to that previously observed in the nitrosation of amines by alkyl nitrites (see ref. 46).
- 49 (a) C. Bravo, P. Hervés, J. R. Leis and M. E. Peña, *J. Phys. Chem.*, 1990, **94**, 8816; (b) L. García-Río, J. R. Leis, M. E. Peña and E. Iglesias, *J. Phys. Chem.*, 1992, **96**, 7820.