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Kinetic Model for Reactivity in Quaternary Water-in-Oil Microemulsions

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Abstract: A study was carried out on the nitrosation of piperazine (PIP) and *N*-methylbenzylamine (MeBzAm) by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) in quaternary microemulsions of tetradecyltrimethylammonium bromide (TTABr)/isooctane/alcohol/water, varying the nature and the concentration of the following alcohols: 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol keeping the [1-alcohol]/[TTABr] = 4 relationship constant. In addition a study was carried out on the influence of the alcohol concentration, working with molar relationships [1-hexanol]/[TTABr] = 3, 4 and 5. On the basis of the molar volumes of the alcohol and surfactant and the concentration of alcohol at the interface it was possible to calculate the change in its volume with as varying compositions of the microemulsion. In order to interpret the experimental results a kinetic model was devised which takes into account the distribution of the reactants between the different pseudophases and the change in the volume of the interface. The rate constants at the interface of the microemulsion are lower than in pure water and are independent of the nature of the alcohol used as a cosurfactant and the molar relationship [alcohol]/[TTABr]. This independence indicates that the main role of the cosurfactant is to increase the volume of the interface with the consequent dilution of the reactants.

Keywords: cosurfactant · kinetics · microemulsions · reaction mechanism · reactivity

Introduction

Microemulsions are thermodynamically stable systems that are composed of a surfactant, an organic solvent, and a small amount of water. These systems appear as homogeneous, transparent solutions that can solvate a wide range of hydrophilic and hydrophobic compounds. The formation of microemulsions requires the presence of water, which is solubilized in a polar core, forming the so-called water pool. These structures are then spherical droplets of water dispersed in oil. Their spontaneous curvature arises from the energetically favorable packing configuration of the surfactant molecules at the water/oil interface and depends basically on the molecular geometry of the surfactant molecules. One of the surfactants often used to form microemulsions is sodium bis(2-ethylhexyl)sulfosuccinate (AOT). However, to attain the appropriate packing of amphiphiles at the interface, the addition of other surface-active substances is often required.

Although quaternary microemulsions have not been investigated to the same degree as AOT microemulsions, researchers have probed a range of properties in these systems.[1] For example, the size and shape characteristics of cetyltrimethylammonium bromide microemulsions formed in alkanes with alcohol cosurfactants have been determined through light scattering, pulse field gradient NMR, near-IR spectroscopy, and conductivity.

These cosurfactants (usually medium-chain linear alcohols) partition themselves among the oil, water and the interface domains. Therefore, without a quantitative description of the dependence of the partition equilibrium on the system composition, a full understanding of quaternary microemulsions cannot be attained. For the estimation of the distribution of the cosurfactants between the interfacial and the bulk oil phase, small-angle neutron scattering,[2] conductivity,[3] interfacial tension[2b,4] and small-angle X-ray scattering and dynamic light scattering[2b] methods have been used. The alcohols added have marked effects on the microemulsion properties such as the critical micelle concentration of three-component microemulsions, the degree of counterion binding of microemulsions with composed ionic surfactants, the aggregation number, and the capacity of microemulsions

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to dissolve oil.[5] Alcohol partition or binding constants are estimated by a variety of methods. Much of this work has been carried out in aqueous three-component microemulsions, some in four-component water-in-oil microemulsions.[6] Romsted and Yao[7] have devised a new method based on the product yields from dediazoniation of 4-hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate to estimate the changes in the composition (concentrations of water and alcohol) at the interface of microemulsions consisting of cetyltrimethylammonium bromide, water, hexadecane and an alcohol (1-butanol or 1-hexanol), on varying the composition of the microemulsion. Their results have enabled them to calculate the distribution constants of the 1-butanol and 1-hexanol between the interface and the continuous medium of the microemulsion.

Lang et al.[8] have studied the effect of alcohol chain length on surfactant aggregation number, radius of the droplet water core, intensity of attractive interdroplet interactions, onset of percolation of electrical conductivity and the rate constant for the exchange of material between droplets of quaternary microemulsions made up of water/chlorobenzene/cationic surfactants/1-alcohol. They found that the aggregation number, the radius of the droplet water core and the intensity of attractive interactions decrease when the alcohol chain length increases. The value of the rate constant for exchange of material between droplets at the percolation threshold is independent of the chain length of the alcohol or surfactant. The percolation threshold increases with the alcohol chain length.

The significant capacity of solvation, together with the specific properties of trapped water in the microemulsions has given rise to a huge amount of kinetic studies on these types of reaction media. The greater simplicity of the AOT microemulsions implied that the majority of kinetic studies have been carried out on AOT/alkane/water microemulsions.[9] However, the number of kinetic studies carried out on microemulsions with four components is very small.[10] In fact, we are not aware of any kinetic study to date which has systematically researched the influence of the chain length of the cosurfactant or its concentration on the reactivity in microemulsions.

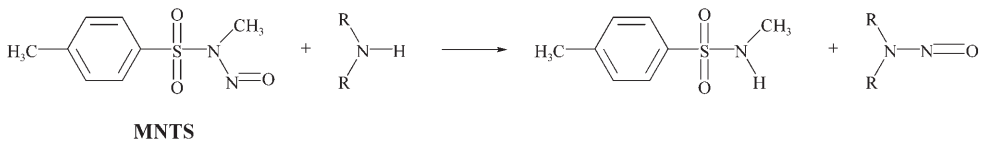
In this article we will describe a systematic study of the influence of a variety of alcohols on a well-characterized reaction in the presence of cationic microemulsions. The fact that reaction kinetics are influenced by the nature of the medium suggests that such studies may throw light on the changes in the microemulsion properties caused by the addition of alcohols. In particular we have studied the influence of the cosurfactant on the reactivity in microemulsions made up of isooctane/tetradecyltrimetylammonium bromide (TTABr)/1-alcohol/water. To this end we have chosen a reaction which is particularly well known to us, namely the nitroso group transfer from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) to secondary amines[11] (Scheme 1). As secondary amines we have used piperazine, and, to a lesser extent, *N*-methylbenzylamine. The choice of these amines is based on their different solubilization properties on AOT/isooctane/water microemulsions.[13] Hence the comparison of the results obtained for quaternary TTABr microemulsions with those previously obtained in ternary AOT microemulsions will enable us to obtain more information about the influence of the cosurfactant on the reactivity of these media. The alcohols used have varied from 1-pentanol to 1-decanol keeping the [1-alcohol]/[TTABr] = 4 relationship constant. In the case of the 1-hexanol we have also worked with the molar relationships [1-alcohol]/[TTABr] = 3, 4 and 5.

Results

The experiments were carried out under the same conditions as those described in previous articles.[12,13] The rate equations obtained for the reactions in microemulsions were in all cases similar to those in water, with first-order terms in MNTS and total amine concentration (figures not shown). The experimental results obtained from studying the influence of the variation of the microemulsion composition on k_{obs} will depend heavily on the way in which the amine is distributed through the pseudophases of the microemulsion, that is, on the hydrophobicity of the amine.

Nitrosation of piperazine: A series of experiments were performed at 25.0 °C and fixed amine concentration and variable TTABr concentration (typically between 0.1 and 0.8 M) with the water/TTABr mol ratio, *W*, fixed at values ranging from $W = 10$ to 45. Two experiments were carried out. In the first experiment the molar relationship remained constant [alcohol]/[TTABr] = 4 regardless of the microemulsion composition. These experiments were carried out using microemulsions in which the length of the chain of the alcohol varied between 1-pentanol and 1-decanol. In the second experiments the influence of the molar relation [alcohol]/[TTABr] on k_{obs} was studied using molar relationships [1-hexanol]/[TTABr] = 3, 4 and 5.

Figure 1 shows an example of observed experimental behavior. In all microemulsions it has been observed that the pseudo-first-order rate constant, k_{obs}, for the nitrosation of



Scheme 1.

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PIP by MNTS, decreases as the TTABr concentration increases and as the water content of the microemulsion increases[13] (increase in W) (see Figure 1). The decrease in k_{obs} as W increases is not very marked, and decreases almost threefold as W increases from 10 to 40. If we compare the influence of [TTABr] on k_{obs} in experiments carried out with $W=10$ and with different alcohols no clear tendency is observable (not shown) although there seems to exist a slight tendency for k_{obs} to decrease as the length of the hydrocarbon chain of the alcohol increases.

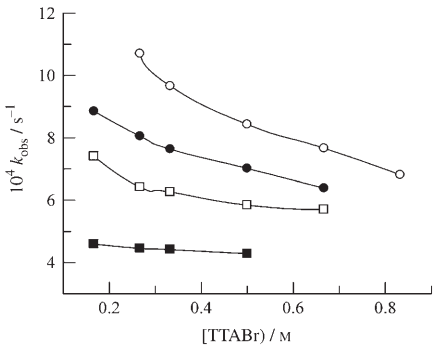

Figure 1. Influence of the TTABr concentration upon k_{obs} for the nitrosation of piperazine by MNTS at constant W in TTABr/1-hexanol/isooctane/water microemulsions. $[ROH]_{tot}/[TTABr]=5$. $[piperazine]_{tot}=5.45\times10^{-2}$ M; (○) $W=10$; (●) $W=15$; (□) $W=20$; (■) $W=40$. Lines are drawn for clarity. $T=25.0$ °C.

Figure 2 shows the variation of k_{obs} with TTABr concentration for experiments carried out at $W=10$ with different molar relationships [1-hexanol]/[TTABr]. It can be seen that the pseudo first-order rate constant, k_{obs}, increases as the concentration of alcohol present in the reaction medium decreases. This variation of k_{obs} with the alcohol content in the medium can be interpreted as being due to the dilution of the reactants. As more alcohol is added to the microemulsion the quantity of alcohol which will be incorporated into the interface increases and, hence, the volume of the interface increases. This increase in volume causes the MNTS and amine to be diluted and therefore k_{obs} decreases. Moreover, incorporation of small molecules into the interfacial region of microemulsions can increase the rigidity[14] of the interface layer affecting the reaction rates.

Nitrosation of *N*-methylbenzylamine: The study of the influence of the microemulsion composition on k_{obs} in the nitrosation of MeBzAm by MNTS has been more limited. Figure 3 shows an example of the experimental behavior observed when studying the influence of TTABr concentration on k_{obs} in series of experiments in which W remained constant. The observed behavior is the opposite of that shown in the nitrosation of PIP by MNTS. Hence, k_{obs} for the nitrosation of MeBzAm by MNTS does indeed increase along with the surfactant concentration and the water content of the microemulsion. The difference between the observed behavior in the nitrosation of PIP and MeBzAm, respectively, must be due to their different hydrophobicity.

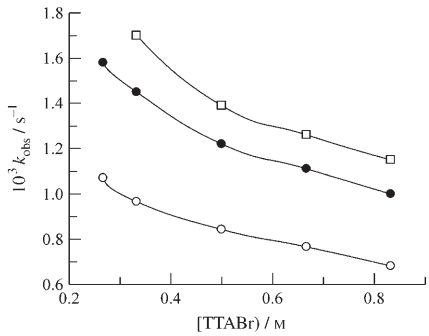

Figure 2. Influence of TTABr concentration upon k_{obs} for the nitrosation of piperazine by MNTS at $W=10$ in TTABr/1-hexanol/isooctane/water microemulsions. $[piperazine]_{tot}=5.45\times10^{-2}$ M; (○) $[ROH]_{tot}/[TTABr]=5$; (●) $[ROH]_{tot}/[TTABr]=4$; (□) $[ROH]_{tot}/[TTABr]=3$. Lines are drawn for clarity. $T=25.0$ °C.

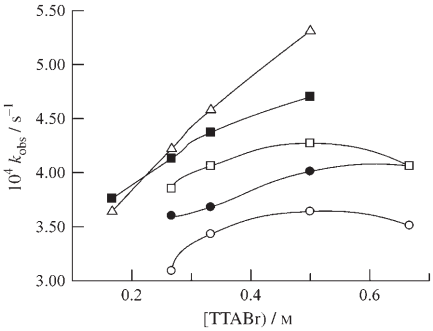

Figure 3. Influence of TTABr concentration upon k_{obs} for the nitrosation of MeBzAm by MNTS at constant W in TTABr/1-pentanol/isooctane/water microemulsions. $[ROH]_{tot}/[TTABr]=4$. $[N\text{-methylbenzylamine}]_{tot}=0.10$ M; (○) $W=10$; (●) $W=15$; (□) $W=20$; (■) $W=30$ and (△) $W=35$. Lines are drawn for clarity. $T=25.0$ °C.

Alcohol distribution in the microemulsion: As mentioned above, it is important to be aware of the distribution of the alcohol between the different pseudophases of the microemulsion. Given that the alcohol acts as a solubilized substance, we can transform the four-component microemulsion into a microemulsion consisting of three pseudocomponents (Figure 4).

As we can see from Figure 2 we neglect the amount of solubilized alcohol in the aqueous phase. This simplification seems correct given the low solubility of the alcohols used

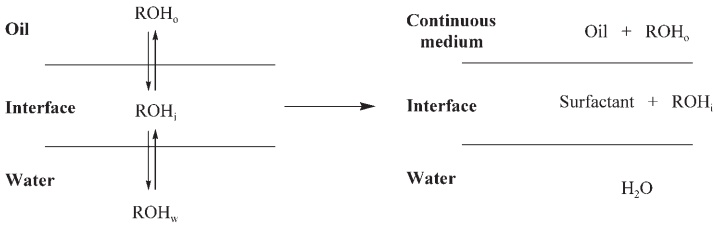

Figure 4.

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in water and the small fraction in volume of the aqueous phase. The distribution constants of the alcohol between the pseudophases of the microemulsion can be defined as:

$$K_{wi}^{ROH} = \frac{[ROH]_i}{[ROH]_w}\frac{[H_2O]}{[TTABr]} = \frac{[ROH]_i}{[ROH]_w}W \quad (1)$$

$$K_{oi}^{ROH} = \frac{[ROH]_i}{[ROH]_o}\frac{[isooctane]}{[TTABr]} = \frac{[ROH]_i}{[ROH]_o}Z \quad (2)$$

where W and Z are the parameters of the microemulsion composition, $W=[H_2O]/[TTABr]$ and $Z=[isooctane]/[TTABr]$.

Schulman's titration method: For the existence of a stable w/o microemulsion, a critical amount of the cosurfactant has to be present in the oil and at the interface. Other conditions remain 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 (X_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 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 $K=n_a^0/n_0$, the total number of moles of alcohol in the microemulsion system, n_a^t per mole of added surfactant can be represented as:[15]

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

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 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 Equation (3) can yield the values of n_a^i and n_a^o from the intercept and slope if n_a^w is negligible. 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 such as shown in Figure 4:

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

From plots analogous to those of Figure 5 we can get the distribution constants for the different alcohols between the isooctane and the interface of TTABr microemulsions. Values of K_{oi}^{ROH} are shown in Table 1.

Table 1. Values of K_{oi}^{ROH} for alcohol distribution between the continuous medium and the interface of TTABr-based microemulsions.

ROH	K_{oi}^{ROH}	K_{oi}^{ROH}
1-butanol	43[a]	36[b]
1-pentanol	34[a]	31[b]
1-hexanol	35[a]	32[b]
1-heptanol	44[a]	28[b]
1-octanol	48[a]	26[b]
1-decanol	37[a]	23[b]

[a] Obtained by the Schulman's titration method. [b] Extrapolated from aqueous micelles.

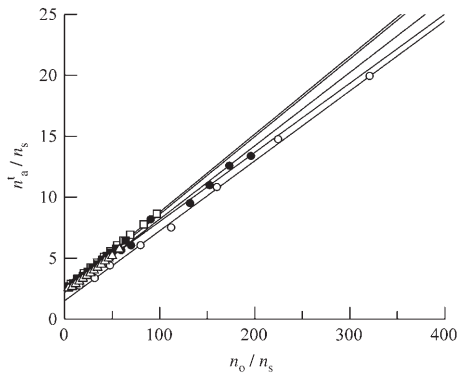

Figure 5. Plot of n_a^t/n_s versus n_0/n_s according to Equation (3) for w/o TTABr/isooctane/water/alcohol microemulsion systems at 25.0 °C with different TTABr concentration: (●) 0.0019 M; (○) 0.0030 M; (△) 0.0043 M; (■) 0.0060 M and (□) 0.0078 M.

Extrapolation from aqueous micelles: The evaluation of the distribution constants is possible on the basis of the values of the association constants of the alcohols to direct micelles (water/tensioactive systems) and the distribution constants of the alcohols between water and isooctane K_o^w.

The values of the distribution constants of the alcohols to direct TTABr micelles are expressed as a molar relationship between the alcohol associated with the micelle and the alcohol present in an aqueous medium,[16] $K_X = X_{ROH}^m/X_{ROH}^w$. These distribution constants of the alcohol can be transformed into the association constants of the alcohol to the micelle, K_S, which is more usual in the kinetic studies, as in $K_S = K_X\bar{v}H_2O$, where $\bar{v}H_2O$ is the molar volume of water. The transformation of K_S, $K_S = [ROH]_m/[ROH]_w$-[surfactant], to the corresponding distribution constant of the alcohol in the microemulsion, K_{wi}^{ROH}, is immediate,

$$K_{wi}^{ROH} = \frac{[ROH]_i}{[ROH]_w}\frac{[H_2O]}{[TTABr]} = K_S[H_2O] \quad (5)$$

where we have considered $[H_2O] = 55.5$ M for direct micellar systems, since in such systems the volume occupied by the surfactant may be negligible. Table 2 shows the calculated values for K_{wi}^{ROH} for the different alcohols used in this study. The values of K_{wi}^{ROH} for the 1-octanol and 1-decanol were obtained by extrapolation on the basis of a linear representation of $\log K_{wi}^{ROH}$ against the number of carbon atoms

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Table 2. Equilibrium constants for the distribution of alcohols between the different pseudophases of the microemulsion.

ROH	K_S/M^{-1}	K_{wi}^{ROH}	K_o^w	$\bar{v}_{ROH}/M^{-1}$
1-butanol	0.90	50	0.72	9.15×10^{-2}
1-pentanol	3.24	180	0.173	0.109
1-hexanol	9.9	550	5.9×10^{-2}	0.126
1-heptanol	38.6	2142	1.3×10^{-2}	0.141
1-octanol	127.8	7096	3.7×10^{-3}	0.157
1-decanol	1523	84528	2.7×10^{-4}	0.191

of the alcohol. This representation was constructed with the values of K_{wi}^{ROH} calculated for 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol (not shown, $R=0.9994$).

On the basis of the values of the distribution constant of the alcohols between water and isooctane, K_o^w, the value of K_{oi}^{ROH} was calculated. The values of K_o^w expressed as a molar relationship between water and isooctane, $K_o^w = X_{ROH}^w/X_{ROH}^o$, can be expressed as:

$$K_o^w = \frac{[ROH]_w}{[ROH]_o}\frac{Z}{W} = \frac{K_{oi}^{ROH}}{K_{wi}^{ROH}} \quad (6)$$

K_o^w values between isooctane and water were estimated considering that they must be in the vicinity of the published values for alcohols distribution between octane/water, decane/water and dodecane/water for 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol.[17] K_o^w values for 1-octanol and 1-decanol were obtained by extrapolation of a representation of ΔG of transfer of the alcohol between water and isooctane against the number of carbon atoms of the alcohol (not shown, $R=0.998$). Table 2 shows the values of K_o^w and Table 1 those of K_{oi}^{ROH} for the different alcohols used in this study.

Discussion

K_{oi}^{ROH} Alcohol distribution constants: It is important to point out two conclusions drawn from the K_{oi}^{ROH} data in Table 1. Firstly, the K_{oi}^{ROH} values obtained by the Schulman's titration method and those extrapolated from aqueous micelles agree quite well. Discrepancies are less than 10% for butanol, pentanol and hexanol and higher for heptanol, octanol and decanol. The differences may be attributed to uncertainties in alcohol binding constants to aqueous micelles for very hydrophobic ones. Importantly the K_{oi}^{ROH} obtained values are close to published values for the incorporation of butanol, pentanol and hexanol from hexane to hexadecyl pyridinium chloride w/o microemulsions: $K_{oi}^{ROH} = 35$, 34 and 48, respectively.[15f] Secondly, the K_{oi}^{ROH} values obtained from the Schulman's titration method show no dependence of K_{oi}^{ROH} on the length of the hydrocarbon chain of the alcohol. This result is consistent with those obtained by small angle neutron scattering measurements[6c] with microemulsions comprising hexadecane/potassium oleate/water, plus several concentrations of 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol. Variation of the alcohol chain length had little apparent effect on microemulsion structure where the volume of the aqueous pseudophase can be taken as a constant.

A tendency of K_{oi}^{ROH} to decrease when the number of carbon atoms in the alcohol increases has also been found in experiments by Romsted and Yao[7] when studying product yields from dediazoniation of 4-hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate in microemulsions of cetyltrimethylammonium bromide (CTABr)/water/hexadecane/alcohol (1-butanol or 1-hexanol). Their results indicate that CTABr mixes ideally with both alcohols. The values of K_{oi}^{ROH} for 1-butanol and 1-hexanol are similar, but that for butanol is slightly larger, probably because butanol is less hydrophobic than hexanol and it associates more strongly with the microemulsion interface. This trend has also been observed by others.[6] Constant values of K_{oi}^{ROH} suggest that ROH distributions between the interfacial and oil regions of cationic w/o microemulsions depend primarily on the hydrophobic effect and that both butanol and hexanol mix ideally with CTABr in the microemulsion aggregates. Thus, ROH binding in these microemulsions does not depend upon specific interactions, for example changes in hydration or charge–charge interactions, between ROH and CTABr head groups that would depend upon ROH/CTABr head group ratios in the interfacial region. However, as we mentioned previously results obtained by Moulik and co-workers for alcohol incorporation to the interface of hexadecyl pyridinium chloride/hexane/water/alcohol microemulsions show the opposite behavior.[15f]

The incorporation of alcohols into AOT/heptane/water microemulsions shows a similar behavior to the nature of alcohol.[6b,18] The incorporation of the alcohol increases when the length of the alkyl chain decreases. However, this dependence is small, the partition constants changing by less than a factor of 6 between ethanol and decanol. These results are interpreted in terms of an interfacial localization of the polar head of the alcohols in the interface, with the alkyl chains extended toward the bulk solvent.

On the basis of K_{oi}^{ROH} values (Table 1) it is possible to transfer the four-component microemulsion into one of three pseudo components. In the following discussion we will use the K_{oi}^{ROH} values obtained by the Schulman's titration method in order to avoid any assumption derived from the K_{oi}^{ROH} values extrapolated from aqueous micelles. This transformation means that we must redefine the composition parameters of the system. Given that the alcohol can be considered as a solubilized substance at the interface, we will apply Stilbs' approximation[19] considering that the surfactant, TTABr, is the only component which determines the properties of the interface. Hence, the composition parameter, W, $W = [H_2O]/[TTABr]$, is not modified. However, the composition of the continuous medium is altered by the presence of the alcohol and therefore we will redefine the parameter Z, $Z = [\text{isooctane}]/[TTABr]$, as

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$$Z^* = \frac{[\text{isooctane}] + [\text{ROH}]_o}{[\text{TTABr}]} = Z + \frac{Z\,[\text{ROH}]_{tot}}{(K_{oi}^{ROH} + Z)\,[\text{TTABr}]} \quad (7)$$

where $[\text{ROH}]_{tot}$ refers to the total alcohol concentration added to the microemulsion. In experiments carried out in this study we showed that $[\text{ROH}]_{tot}/[\text{TTABr}] = 4$. The system TTABr/1-hexanol/isooctane/water was also studied, varying the molar relationship $[\text{ROH}]_{tot}/[\text{TTABr}] = 3$, 4 and 5.

Variation of the volume of the interface: In simple three component microemulsions, that is, AOT/isooctane/water, the molar volume of the interface can be considered to remain constant. However, in the presence of cosurfactants its incorporation into the interface causes the molar volume of the interface to be equal to the molar volume of the surfactant plus the molar volume of the bonded alcohol. The application of the formalism developed in the previous section implies that the number of moles of alcohol incorporated into the interface increases along with the concentration of the surfactant.[20] The alcohol incorporation into the interface means that its volume varies along with the composition of the microemulsion. The volume of the interface can be calculated considering it to be equal to the sum of the volumes of the surfactant and the alcohol incorporated into the interface. This approximation is similar to that used in simple micellar systems (water/surfactant).[21]

$$V_i = \bar{V}_{TTABr}\,[\text{TTABr}]_i + \bar{V}_{ROH}\,[\text{ROH}]_i \quad (8)$$

$$\frac{V_{tot}}{V_i} = \frac{1}{\bar{V}_{TTABr}\,[\text{TTABr}]} + \frac{K_{oi}^{ROH} + Z}{\bar{V}_{ROH} K_{oi}^{ROH} [\text{ROH}]_{tot}} \quad (9)$$

As for the molar volume of the surfactant, TTABr, the value of $\bar{V}_{TTABr} = 0.336\,\text{M}^{-1}$ was used, which corresponds with the complete micellar volume of the TTABr micelles.[22] The molar volume of the alcohol, $\bar{v}_{ROH}$, was calculated on the basis of its molecular density and weight (values in Table 2).

Figure 6 shows how the relationship V_{tot}/V_i [values calculated according to the Eq. (9)] decreases as the surfactant concentration increases. The decrease in V_{tot}/V_i with the TTABr 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. Figure 7 shows how V_{tot}/V_i varies with the surfactant concentration for different molar relationships $[\text{ROH}]_{tot}/[\text{TTABr}]$ and at $W = 10$. As the molar relationship $[\text{ROH}]_{tot}/[\text{TTABr}]$ decreases, so does the alcohol concentration incorporated into the interface and hence its volume decreases, increasing the V_{tot}/V_i relationship.

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 $[\text{ROH}]_{tot}/[\text{TTABr}]$.

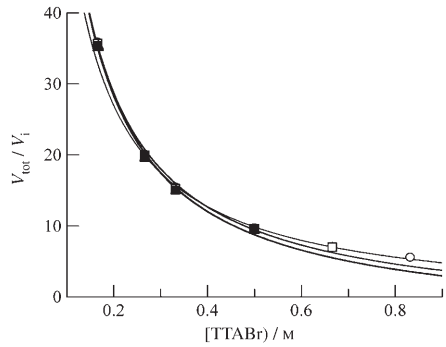

Figure 6. Influence of TTABr concentration upon V_{tot}/V_i at constant W in TTABr/1-hexanol/isooctane/water microemulsions. $[\text{ROH}]_{tot}/[\text{TTABr}] = 5$. (○) $W = 10$; (●) $W = 15$; (□) $W = 20$; (■) $W = 30$; (△) $W = 35$ and (▲) $W = 40$. Lines are drawn for clarity.

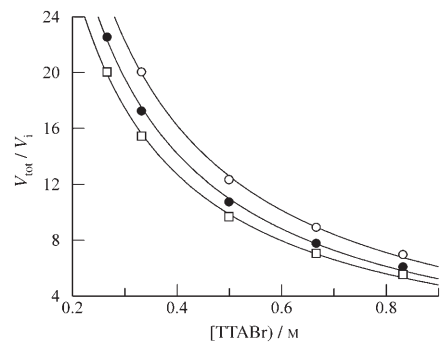

Figure 7. Influence of TTABr concentration upon V_{tot}/V_i at $W = 10$ in TTABr/1-hexanol/isooctane/water microemulsions. (○) $[\text{ROH}]_{tot}/[\text{TTABr}] = 3$; (●) $[\text{ROH}]_{tot}/[\text{TTABr}] = 4$; (□) $[\text{ROH}]_{tot}/[\text{TTABr}] = 5$. Lines are drawn for clarity.

Nitrosation of piperazine: The significant effect of the alcohols on the formation of w/o microemulsions is well documented. For example, the addition of alcohol molecules of appropriate chain length to a ternary system may considerably enlarge the microemulsion range. Alcohols should be considered as cosolvents that are distributed between the pseudophases of the microemulsion, thereby decreasing the effective hydrophilicity of the amphiphile[23,24] and increasing the hydrophilicity of the oil pseudophase. The increase in the hydrophilic character of the continuous medium can alter the distribution equilibrium of the MNTS and amine through the different pseudophases of the microemulsion. Indeed, we have confirmed that piperazine is distributed between the three pseudophases of the microemulsion when an alcohol is used as a cosurfactant.[12] This behavior is different from that observed in AOT/isooctane/water microemulsions[13] and is consistent with the increase in hydrophilicity of the continuous medium. Hence, we can propose a kinetic model (Figure 8) to explain the experimental behavior observed in the nitrosation of piperazine by MNTS.

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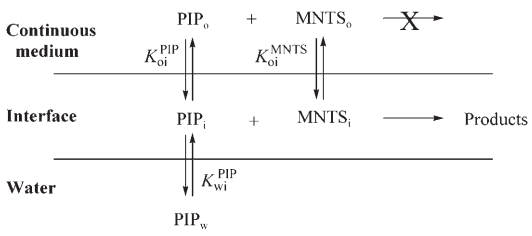

Figure 8.

According to the kinetic model put forward the piperazine will be distributed between the three pseudophases of the microemulsion. Its concentration in each pseudophase can be calculated on the basis of the corresponding distribution constants.

$$K_{wi}^{PIP} = \frac{[PIP]_i}{[PIP]_w} W \qquad K_{oi}^{PIP} = \frac{[PIP]_i}{[PIP]_w} Z^* \tag{10}$$

where $[PIP]_w$, $[PIP]_i$ and $[PIP]_o$ are the amine concentrations in the aqueous pseudophase, interface and continuous medium respectively, with reference to the total volume of the microemulsion. The composition parameter of the microemulsion Z^*, $Z^* = ([\text{isooctane}]+[ROH]_o)/[TTABr]$, has been introduced to reduce the four component microemulsion to one of three pseudo components. The minimal solubility of MNTS in an aqueous medium suggests that MNTS is only found distributed between the interface and the continuous medium. Its distribution constant, K_{oi}^{MNTS}, is defined in the same way as that of the amines, $K_{oi}^{MNTS} = ([MNTS]_i Z^*)/[MNTS]_o$. The rate constant k_2^i corresponds to the bimolecular rate constant for the nitrosation of piperazine by MNTS at the interface of the microemulsion. Given that the kinetic model, which will be set out below, includes the volume of the interface, the rate constant k_2^i will be a bimolecular rate constant with units $M^{-1}s^{-1}$.

From the proposed kinetic model it can be observed that the reactants will be in contact at the interface and in the continuous medium, in such a way that two possible reactive zones will exist in the microemulsion. However, the rate of the nitroso group transfer reactions from alkyl nitrites or *N*-methyl-*N*-nitrosobenzenesulfonamides to amines considerably decreases along with the polarity of the medium,[25] allowing the mechanism of the reaction to be modified. This behavior means that we can disregard the possibility that the reaction may take place in the continuous phase.[26]

Table 3. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-pentanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-pentanol	4	275±12	24±1	11.1
15	1-pentanol	4	325±43	38±4	8.5
20	1-pentanol	4	398±44	51±4	7.8
30	1-pentanol	4	499±38	88±2	5.6

Table 4. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-hexanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-hexanol	3	391±7	37±1	106
15	1-hexanol	3	434±45	53±5	8.2
20	1-hexanol	3	597±59	88±5	6.8
25	1-hexanol	3	577±47	101±10	5.7
30	1-hexanol	3	647±32	118±9	5.5
40	1-hexanol	3	701±41	139±7	5.0
50	1-hexanol	3	906±57	204±9	4.4

Table 5. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-hexanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-hexanol	4	291±3.3	26.1±0.3	11.17
15	1-hexanol	4	394±15.2	42.5±0.8	9.25
20	1-hexanol	4	435±25.3	60.9±1.4	7.15
30	1-hexanol	4	575±28.4	86.6±1.5	6.63
35	1-hexanol	4	620±43.2	101±2.4	6.12
40	1-hexanol	4	637±59.4	109±3.4	5.84
45	1-hexanol	4	614±94.8	125±5.6	4.93

Table 6. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-hexanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-hexanol	5	420±7	34.6±0.7	12.1
15	1-hexanol	5	456±26	55±2	8.3
20	1-hexanol	5	524±8	67±1	7.8
30	1-hexanol	5	593±29	108±2	5.5
35	1-hexanol	5	753±69	115±4	6.5
40	1-hexanol	5	775±89	144±7	5.4

Table 7. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-heptanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-heptanol	4	303±8	27.4±0.8	11.1
15	1-heptanol	4	400±26	39±2	10.2
20	1-heptanol	4	453±21	59±2	7.67
30	1-heptanol	4	553±7	84±1	6.56
35	1-heptanol	4	615±65	99±7	6.21
40	1-heptanol	4	594±14	114±4	5.21

Bearing this in mind, and on the basis of the kinetic model of Figure 9, we can obtain the following expression for k_{obs}.

$$k_{obs} = k_2^i \frac{V_{tot}}{V_i} \frac{K_{oi}^{MNTS}}{(K_{oi}^{MNTS} + Z^*)} \frac{K_{oi}^{PIP} K_{wi}^{PIP} [PIP]_{tot}}{(K_{oi}^{PIP} K_{wi}^{PIP} + K_{oi}^{PIP} W + K_{wi}^{PIP} Z^*)} \tag{11}$$

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Table 8. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-octanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-octanol	4	313±9	24.6±0.9	12.7
15	1-octanol	4	388±10	37±3	10.6
20	1-octanol	4	435±64	50±3	8.6
25	1-octanol	4	561±84	68±2	8.2
30	1-octanol	4	528±83	81±2	6.5
35	1-octanol	4	570±59	94±4	6.0
40	1-octanol	4	643±72	117±5	5.5

Table 9. Slopes and intercepts at the origin obtained upon fitting $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^* [Eq. (12)] to the experimental kinetic data for the reactions of piperazine with MNTS in water/TTABr/1-decanol/isooctane microemulsions at 25 °C.

W	ROH	$[ROH]_{tot}/[TTABr]$	Intercept	Slope	Int/Slp
10	1-decanol	4	310±67	27±2	11.5
15	1-decanol	4	371±71	49±3	7.5
20	1-decanol	4	464±71	63±2	7.4
25	1-decanol	4	533±37	9±3	5.9

Equation (11) can be rewritten as:[27]

$$\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}} = \left(\frac{1}{k_2^i} + \frac{W}{k_2^i K_{wi}^{PIP}}\right) + \left(\frac{1}{k_2^i K_{oi}^{PIP}} + \frac{1}{k_2^i K_{oi}^{MNTS}} + \frac{W}{k_2^i K_{oi}^{MNTS} K_{wi}^{PIP}}\right) Z^* \quad (12)$$

This Equation predicts the existence of a linear dependency between $\frac{V_{tot}}{V_i}\frac{[PIP]_{tot}}{k_{obs}}$ versus Z^*. The results shown as an example in Figure 9 for nitrosation of piperazine by MNTS in microemulsions of TTABr/1-hexanol/isooctane/water, maintaining a relationship of [1-hexanol]/[TTABr] = 5, entirely fulfill the behavior pattern predicted by Equation (12).

This Equation predicts the existence of a linear dependency between the relationship intercept/slope with $1/W$ according to Equation (13):

$$\frac{\text{intercept}}{\text{slope}} = K_{oi}^{MNTS} + K_{oi}^{MNTS} K_{wi}^{PIP} \frac{1}{W} \quad (13)$$

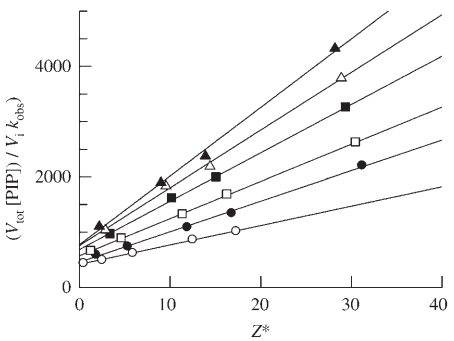

Figure 9. Linearization of the data of Figure 1 in accordance with Equation (12) (see text) for nitrosation of piperazine by MNTS in TTABr/1-hexanol/isooctane/water microemulsions. [1-hexanol]/[TTABr] = 5. ○ W = 10; (●) W = 15; (□) W = 20; (■) W = 30; (△) W = 35 and (▲) W = 40.

Tables 3–9 show the values of the intercepts and slopes obtained by applying Equation (12) in the nitrosation of PIP by MNTS in TTABr microemulsions stabilized by different alcohols.[12] Figure 10 shows how well Equation (13) is fulfilled for the nitrosation of PIP by MNTS in TTABr/1-hexanol/isooctane/water microemulsions where the relationship [1-hexanol]/[TTABr] = 5 has remained constant.

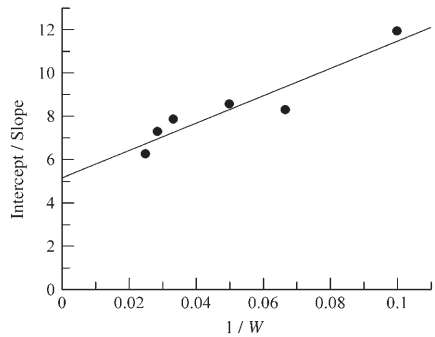

Figure 10. Variation of the relationship intercept/slope of the data of Figure 7, Table 6, in accordance with Equation (13) (see text).

The kinetic model represented in Figure 8 [Eq. (12)] predicts the existence of a linear dependency between the intercepts of Figure 9 (data in Table 6) and W according to Equation (14):

$$\text{intercept} = \frac{1}{k_2^i} + \frac{W}{k_2^i K_{wi}^{PIP}} \quad (14)$$

Figure 11 shows by way of example that the values of the intercepts of Table 6 (Figure 9) comply with the behavior pattern predicted by the kinetic model of Figure 8, Equation (14), for the nitrosation of piperazine by MNTS in TTABr/1-hexanol/isooctane/water microemulsions, in which the relationship [1-hexanol]/[TTABr] = 5 remains constant.

Likewise, on the basis of the kinetic model, Equation (12), the existence of a linear dependence can be observed between the intercepts of the representations of Figure 9 (data

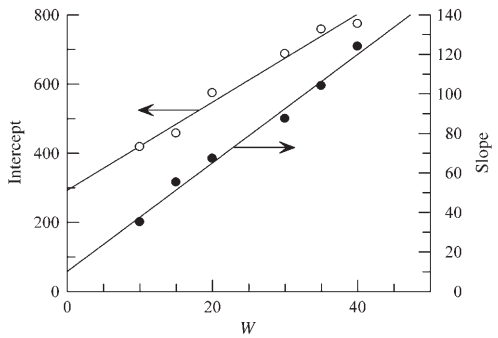

Figure 11. Variation of the *intercepts* and *slopes* of Figure 7 in accordance with Equations (14) and (15), Table 6, (see text).

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in Table 6) and W, in accordance with the following Equation.

$$\text{slope} = \left(\frac{1}{k_2^{\mathrm{i}} K_{\mathrm{oi}}^{\mathrm{PIP}}} + \frac{1}{k_2^{\mathrm{i}} K_{\mathrm{oi}}^{\mathrm{MNTS}}}\right) + \frac{W}{k_2^{\mathrm{i}} K_{\mathrm{oi}}^{\mathrm{MNTS}} K_{\mathrm{oi}}^{\mathrm{PIP}}} \approx \frac{1}{k_2^{\mathrm{i}} K_{\mathrm{oi}}^{\mathrm{MNTS}}} + \frac{W}{k_2^{\mathrm{i}} K_{\mathrm{oi}}^{\mathrm{MNTS}} K_{\mathrm{wi}}^{\mathrm{PIP}}} \quad (15)$$

Figure 11 also shows that Equation (15) is fulfilled for the nitrosation of PIP by MNTS in TTABr/1-hexanol/isooctane/water microemulsions confirming, therefore, the validity of the kinetic model developed in Figure 8.

To obtain the values of the distribution constants of the amine, $K_{\mathrm{wi}}^{\mathrm{PIP}}$, and of the MNTS, $K_{\mathrm{oi}}^{\mathrm{MNTS}}$, as well as the rate constant for the reaction at the interface, k_2^{i}, we have followed the following scheme. The relationship between the slopes of Equations (14) and (15) gives $K_{\mathrm{oi}}^{\mathrm{MNTS}}$. On the basis of the slope of Equation (13) and the value of $K_{\mathrm{oi}}^{\mathrm{MNTS}}$ we can obtain the distribution constant of the amine between the aqueous pseudophase and the interface, $K_{\mathrm{wi}}^{\mathrm{PIP}}$. From the slope of Equation (15) and with the known values of $K_{\mathrm{oi}}^{\mathrm{MNTS}}$ and $K_{\mathrm{wi}}^{\mathrm{PIP}}$ we can obtain the bimolecular rate constant for the reaction in the interface, k_2^{i}. Table 10 shows the values of $K_{\mathrm{oi}}^{\mathrm{MNTS}}$, $K_{\mathrm{wi}}^{\mathrm{PIP}}$ and k_2^{i} obtained for the different systems studied as the length of the hydrocarbon chain of the alcohol varies and as the molar relationship [1-hexanol]$_{\mathrm{tot}}$/[TTABr] varies. In all cases the results obtained are consistent with the kinetic model proposed in Figure 8 and with the transformation of a quaternary microemulsion into one of three pseudo components where a variation in the volume is produced in the interface as the composition of the microemulsion varies.

Table 10. Kinetic parameters and partition coefficients estimated by fitting Equations (12)–(15) to the experimental kinetic data for the reaction of PIP with MNTS in water/TTABr/alcohol/isooctane and in AOT/isooctane/water microemulsions at 25 °C.

ROH	$[\mathrm{ROH}]_{\mathrm{tot}}$/[TTABr]	$K_{\mathrm{oi}}^{\mathrm{MNTS}}$	$K_{\mathrm{wi}}^{\mathrm{PIP}}$	k_2^{i}/M^{-1}s^{-1}
1-pentanol	4	3.5	22.4	3.93×10^{-3}
1-hexanol	3	3.0	25.0	3.39×10^{-3}
1-hexanol	4	3.6	21.3	4.79×10^{-3}
1-hexanol	5	3.5	23.9	3.40×10^{-3}
1-heptanol	4	3.5	22.6	4.42×10^{-3}
1-octanol	4	3.4	28.0	3.45×10^{-3}
1-decanol	4	3.8	23.4	2.81×10^{-3}
AOT/isooctane/water microemulsion		11	9.5	5.33×10^{-3}

Nitrosation of *N*-methylbenzylamine: The minimal solubility of *N*-methylbenzylamine in water means that it is found in the continuous medium and the interface of the microemulsion, as shown in Figure 12.

The observed rate constants for reaction of MNTS with *N*-methylbenzylamine (and other amines) in pure isooctane[25] are several orders of magnitude slower than the rate constants observed in the microemulsions, showing that, as in the case of piperazine, in w/o microemulsions the reaction effectively takes place only at the interface, so that the reaction rate in the continuous medium is considered negligible compared with the reaction at the interface.[26]

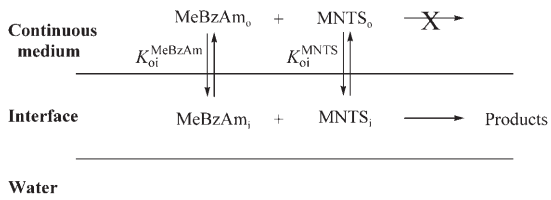

Figure 12.

From Figure 12 and applying a similar methodology to that developed for the nitrosation of piperazine we can obtain rate Equation (16):

$$k_{\mathrm{obs}} = k_2^{\mathrm{i}} \frac{V_{\mathrm{tot}}}{V_{\mathrm{i}}} \frac{K_{\mathrm{oi}}^{\mathrm{MNTS}}}{(K_{\mathrm{oi}}^{\mathrm{MNTS}} + Z^*)} \frac{K_{\mathrm{oi}}^{\mathrm{MeBzAm}}[\mathrm{MeBzAm}]_{\mathrm{tot}}}{(K_{\mathrm{oi}}^{\mathrm{MeBzAm}} + Z^*)} \quad (16)$$

This Equation can be transformed into:

$$\frac{V_{\mathrm{tot}}}{V_{\mathrm{i}}} \frac{[\mathrm{MeBzAm}]_{\mathrm{tot}}}{k_{\mathrm{obs}}} = \frac{(K_{\mathrm{oi}}^{\mathrm{MNTS}} + Z^*)(K_{\mathrm{oi}}^{\mathrm{MeBzAm}} + Z^*)}{k_2^{\mathrm{i}} K_{\mathrm{oi}}^{\mathrm{MNTS}} K_{\mathrm{oi}}^{\mathrm{MeBzAm}}} \quad (17)$$

The application of Equation (17) predicts the existence of a linear and quadratic dependence of $\frac{V_{\mathrm{tot}}}{V_{\mathrm{i}}} \frac{[\mathrm{MeBzAm}]_{\mathrm{tot}}}{k_{\mathrm{obs}}}$ versus Z^* independently of the values of W. As way of example Figure 13 shows the fulfillment of the Equation (17) for the nitrosation of MeBzAm in TTABr/1-pentanol/isooctane/water microemulsions for values of W between 10 and 45 and values of [TTABr] between 0.1 and 0.7, confirming the validity of the proposed kinetic model.

To fit Equation (17) to the experimental results we took as a constant the value of $K_{\mathrm{oi}}^{\mathrm{MNTS}}$ previously obtained in the

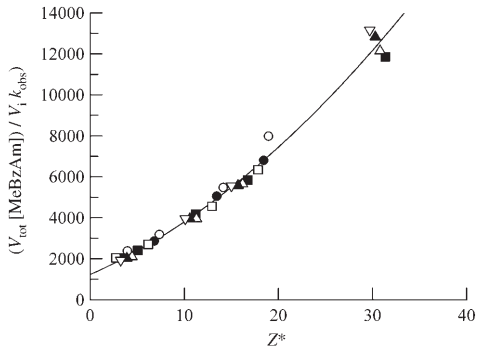

Figure 13. Plot of $\frac{V_{\mathrm{tot}}}{V_{\mathrm{i}}} \frac{[\mathrm{PIP}]_{\mathrm{tot}}}{k_{\mathrm{obs}}}$ versus Z^* for nitrosation of *N*-methylbenzylamine by MNTS in TTABr/1-pentanol/isooctane/water microemulsions. [1-pentanol]/[TTABr] = 4. The solid line is the theoretical line predicted by Equation (17) (parameters in Table 11). [*N*-methylbenzylamine] = 0.10 M. (○) W = 10; (●) W = 15; (□) W = 20; (■) W = 30; (△) W = 35; (▲) W = 40 and (▽) W = 45.

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nitrosation of piperazine (values of K_{oi}^{MNTS} in Table 10). Values of the distribution constants of the amine, K_{oi}^{MeBzAM}, and those of the bimolecular rate constants at the interface of the microemulsions, k_2^i, (values in Table 11) can be obtained for TTABr-based microemulsions stabilized by 1-pentanol, 1-hexanol and 1-heptanol.

Table 11. Kinetic parameters and partition coefficients estimated by fitting Equation (15) to the experimental kinetic data for the reaction of MeBzAm with MNTS in water/TTABr/alcohol/isooctane and in AOT/isooctane/water microemulsions at 25 °C.

ROH	[ROH]/[TTABr]	K_{oi}^{MNTS}	K_{oi}^{MeBzAM}	k_2^i/M^{-1}s^{-1}
1-pentanol	4	3.7	62.4	8.14×10^{-4}
1-hexanol	4	3.5	103	6.99×10^{-4}
1-heptanol	4	3.9	100	8.50×10^{-4}
AOT/isooctane/water microemulsion		11	25.6	3.10×10^{-3}

Comparison of results: Tables 10 and 11 show the values of K_{oi}^{MNTS}, K_{wi}^{PIP}, K_{oi}^{MeBzAM} and k_2^i obtained for the nitrosation of piperazine and *N*-methylbenzylamine in the different microemulsions used. The values of Table 10 show that the distribution constants of the amine, K_{wi}^{PIP}, and of the nitrosating agent, K_{oi}^{MNTS}, obtained in the nitrosation of PIP are independent of the nature of the alcohol used as a cosurfactant and of the molar relationship [1-hexanol]/[TTABr]. The values of K_{wi}^{PIP} are in the vicinity of 23 in all cases. If we analyze the variation of the distribution constant of the nitrosating agent, K_{oi}^{MNTS}, a similar behavior pattern is observed. A mean value of K_{oi}^{MNTS} can be obtained, of around 3.5 for all the microemulsions. It is worth noting that none of the kinetic parameters depend to any significant extent on the presence of alcohol, which must therefore affect the experimental rate constant solely by increasing the reaction volume, that is, by diluting the reactants at the interface of the microemulsion.

From the point of view of reactivity it is more interesting to study the variation of the rate constant of nitrosation of piperazine by MNTS at the interface of the microemulsions, k_2^i. This reaction has been thoroughly researched in water in our laboratory and we have obtained a value of the bimolecular rate constant in pure water of $k_2 = 2.98\times10^{-2}$ M^{-1}s^{-1}. The values obtained at the interface of the microemulsion, k_2^i, are always lower than the value obtained in pure water, and an eight-fold decrease can be observed in the rate constant. The state of water within tertiary, AOT, microemulsions and the influence of *W* on the micellar properties have been investigated using many techniques.[28] CTABr has been known for several years to be capable of forming microemulsions in various solvents such as *n*-hexanol, chloroform and dichloromethane.[29] There is infrared[30] and ^{1}H NMR spectral[29e,31] evidence for a change of the properties of water in these cationic reverse micelles with an increase in *W*. Likewise recent studies carried out in our laboratory on solvolytic processes in TTABr and SDS microemulsions[20] have shown that the polarity of the interface is always substantially less than that of pure water. This reduction of the polarity of the interface with regard to that of pure water is the factor responsible for the decrease in k_2^i with regard to the bimolecular rate constant in water, k_2.

Table 10 shows the values for the parameters K_{oi}^{MNTS}, K_{wi}^{PIP} and k_2^i obtained when studying this reaction in AOT/isooctane/water microemulsions.[13] The values of the distribution constants of the amine and the MNTS are not comparable between the AOT and TTABr microemulsions since surfactants of a different nature are being dealt with. However, it should be possible to establish a comparison between the values of the rate constant for the reaction at the interface. From k_2^i values obtained in the quaternary microemulsions with the different alcohols and different molar relationships [alcohol]/[TTABr] allows us to obtain a mean value of $k_2^i = 3.74\times10^{-3}$ M^{-1}s^{-1}. This value is very close to that obtained in the AOT microemulsions, $k_2^i = 5.33\times10^{-3}$ M^{-1}s^{-1}, although slightly lower. This slight reduction could be due to the distribution of the alcohol between the pseudophases making the interface of the microemulsion more hydrophobic.

Table 11 shows the values of K_{oi}^{MNTS}, K_{oi}^{MeBzAM} and k_2^i obtained for the nitrosation of *N*-methylbenzylamine by MNTS in quaternary microemulsions of TTABr and tertiary ones of AOT/isooctane/water. K_{oi}^{MNTS} values remained constant and equal to those obtained in the nitrosation of PIP by MNTS. Neither the values of K_{oi}^{MeBzAM} nor those of k_2^i show any dependence on the nature of the alcohol used as a cosurfactant. The values of k_2^i are approximately 50 times lower than the value of the bimolecular rate constant obtained in pure water, $k_2 = 4.10\times10^{-2}$ M^{-1}s^{-1}. As in the nitrosation of piperazine, this reduction is considered to be due to the reduction of polarity in the interface. It is important to point out that in the nitrosation of the piperazine an eight-fold reduction is observable in k_2^i with regard to the value of k_2 obtained in pure water, while in the nitrosation of *N*-methylbenzylamine this reduction is approximately fifty-fold. This difference could be a consequence of the fact that the piperazine has two positions in which nitrosation can take place, which constitutes a statistical advantage for the nitrosating process. This advantage must be more important at the interface of the microemulsion than in pure water due to the high microviscosity of the interface of the microemulsions.[32] This high microviscosity gives rise to a lower degree of mobility of the reactants and hence the steric impediments or the statistical advantages of the reaction will be more significant than in pure water.

It is also important to point out the difference observed in k_2^i when we compare microemulsions of three components (AOT/isooctane/water) and those of four components (TTABr/alcohol/isooctane/water). The incorporation of the alcohol at the interface of the latter displaces water molecules and thus increases its hydrophobicity. This increase could be responsible for the reaction rate being less at the interface of TTABr microemulsions than in AOT microemulsions, $(k_2^i)^{AOT}/(k_2^i)^{TTABr} \approx 3.9$ and 1.42 for nitrosation of MeBzAm and PIP respectively.

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Conclusions

The presence of the cosurfactant not only modifies the properties of the interface but also increases the hydrophilic character of the continuous medium. This change in the properties can cause a distribution of the reactants between the pseudophases of the microemulsion, which is different from that observed in microemulsions of three components. There follows a summary of the main conclusions of this study.

We quantified the distribution of the cosurfactant through the different pseudophases of the microemulsion on the basis of the Schulman's titration method and by using the association constants of the alcohols to simple micellar systems (water/surfactant) and the distribution constants of the alcohols between water and isooctane. The calculated results are compatible with those experimentally obtained for the composition of the interface of the microemulsion.

The incorporation of the alcohol into the interface of the microemulsion causes an increase in the volume of the interface with the consequent dilution of the MNTS and amine. The volume of the interface was calculated on the basis of the molar volumes of the surfactant and the alcohol incorporated into the interface considering that an ideal mixture is formed where the volumes are additives. The variation in the volume of the interface was introduced into the kinetic model proposed to explain the experimental behavior.

The application of a kinetic model developed on the basis of the formalism of the micellar pseudophase enabled us to obtain the values of the distribution constants of the reactants between the different pseudophases of the microemulsion and the values of the rate constants of the reaction at the interface, k_2^i. The values of k_2^i are in all cases lower than those obtained in pure water, which has been interpreted as a consequence of the reduction in polarity of the interface in comparison with that of pure water. The values of the distribution constants of the reactants and the rate constants, k_2^i, are independent of the length of the hydrocarbon chain of the alcohol used as a cosurfactant and the molar relationship [alcohol]/[TTABr], indicating that the main effect of the cosurfactant is the increase in volume of the interface with the consequent dilution of the reactants. The values of k_2^i obtained in TTABr/alcohol/isooctane/water microemulsions are always lower than those obtained in AOT/isooctane/water microemulsions. This result is considered to be due to the incorporation of the alcohol into the interface of the microemulsion displacing the water molecules and thus increasing its hydrophobic character.

Experimental Section

Tetradecyltrimethylammonium bromide (TTABr) was supplied by Sigma and used without further purification. Alcohols and isooctane were Aldrich products of the highest degree of purity available commercially. Piperazine (PIP) (Merck) was used without further purification. *N*-Methylbenzylamine (MeBzAm) (Aldrich) was distilled under argon and used shortly afterwards. *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) was supplied by Merck.

Microemulsions of the desired compositions were prepared from stock water/surfactant/isooctane/alcohol microemulsions by addition of appropriate amounts of isooctane and/or water. During the experiments the molar relationship [alcohol]/[TTABr] remained constant and equal to 4 and the nature of the alcohol varied. Likewise the influence of the changes in the molar relationship was studied [1-hexanol]/[TTABr] making it equal to 3, 4 and 5. Densities were measured with a pycnometer.

The transnitrosation reactions were carried out using a Varian Cary 500 Scan UV/Vis-NIR spectrophotometer fitted with thermostated cell holders (all experiments were carried out at 25.0°C). Kinetic measurements were carried out following the disappearance of the absorbance at 260 nm due to MNTS consumption for nitrosation of PIP and the initial MNTS concentration was 1.91×10^{-4} M. In the case of *N*-methylbenzylamine, its high molar absorptivity precluded us from studying the reaction at 260 nm; it was therefore necessary to follow the reaction at 392 nm using an initial MNTS concentration of 2.0×10^{-3} M. In all cases MNTS was in deficit against amine concentration. The kinetic data always fitted the first order integrated rate Equation satisfactorily ($R>0.999$); in what follows, k_{obs} denotes the pseudo first order rate constant.

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