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Pseudophase Approach to Reactivity in Microemulsions: Quantitative Explanation of the Kinetics of the Nitrosation of Amines by Alkyl Nitrites in AOT/Isooctane/Water Microemulsions[†]

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The kinetics of nitroso group transfer from 2-ethoxyethyl (EEN) and 2-bromoethyl (BEN) nitrite to the secondary amines piperazine (PIP), *N*-methylbenzylamine (NMBA), and morpholine (MOR) in bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane (iC₈)/water microemulsions were determined. They are explained quantitatively in terms of a model in which the reagents are distributed among the aqueous, organic, and AOT film surfactant, with the aqueous pseudophase and the surfactant film as the loci of the reaction.

Introduction

Microemulsions are stable, transparent solutions of water, oil, and surfactant, with or without a cosurfactant. They have been described as consisting of spherical droplets of a disperse phase separated from a continuous phase by a film of surfactant.¹ Because they provide both organic and aqueous environments, microemulsions can simultaneously dissolve both hydrophobic and hydrophilic compounds, each compound being distributed among water, organic solvent, and surfactant film in accordance with its physicochemical nature. One of the microemulsion-forming surfactants receiving much attention in recent years has been sodium bis(2-ethylhexyl) sulfosuccinate (AOT).

Microemulsions have found a growing number of scientific and technological applications: they afford control over the size of synthesised microparticles;² they have numerous applications in the fields of solubilization and extraction;³ and when the surfactant interface is stereoselective for certain reagents, they can be used for stereoselective synthesis.⁴ They have been used to simulate complex biological structures (in particular as regards the behavior of trapped water).^{5,6} In keeping with this proliferating range of applications, there is an increasing interest in studying the details of chemical,^{1a} photochemical,⁷ and enzymocatalytic^{1a,8} processes in microemulsions. In particular, since microemulsions are able, like phase transfer catalysis systems, to enhance reactions between non-hydrosoluble organic substrates and hydrosoluble reagents, the kinetics of numerous reactions in microemulsions have been studied.^{1b,9}

The authors of most of these kinetic studies have not been able to explain the observed kinetic behavior quantitatively except for the simplest case of reactions taking place in the water droplet. However, a previous paper¹⁰ from our laboratory described the application of the pseudophase model that does promise a satisfactory quantitative explanation of reactivity in microemulsions. In that work, the validity of the pseudophase model for reactions occurring exclusively in the surfactant film separating the aqueous and organic pseudophases was supported by successful application of the model to the nitrosation of secondary amines by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) in w/o (water-in-oil) AOT/isooctane/water microemulsions; it was considered that these reactions could not take place

to any significant extent in either the aqueous pseudophase (because of the very low solubility of MNTS in water) or the organic pseudophase (nitrosation reactions being extremely slow in apolar solvents¹¹). We now present results supporting the validity of the pseudophase model for reactions taking place simultaneously in two of the pseudophases of an AOT/isooctane/water microemulsion.

The type of reaction investigated in this work was the nitrosation of amines by alkyl nitrites, a process that has been extensively studied in aqueous media.¹² The amines used—piperazine (PIP), morpholine (MOR), and *N*-methylbenzylamine (NMBA)—were chosen on the basis of their solubilities in the various components of the microemulsions: piperazine is practically insoluble in isooctane, *N*-methylbenzylamine is poorly soluble in water, and morpholine has considerable solubility in both water and isooctane. The alkyl nitrites used, 2-ethoxyethyl nitrite (EEN) and 2-bromoethyl nitrite (BEN), were also chosen on solubility grounds: both are partially soluble in both water and organic solvents, and previous studies¹³ have confirmed that they are taken up to a considerable extent by micelles. We therefore considered that in these experiments the alkyl nitrites would initially be distributed in all three pseudophases, and that it would be the amine that determined where the reaction took place.

Experimental Section

AOT, *N*-methylbenzylamine, and spectroscopic grade isooctane (iC₈) were supplied by Aldrich. AOT was dried for 2 days in a vacuum desiccator and used without further purification. NMBA was purified by distillation. The alkyl nitrites were prepared following standard procedures¹⁴ by reacting sodium nitrite with the corresponding alcohol in an acidic medium, and were stored over molecular sieves in the refrigerator pending use. Heavy water (99.77%) was supplied by CIEMAT. Other reagents were supplied by Merck and were used without further purification.

Reaction kinetics were followed by monitoring changes in absorbance due to appearance of *N*-nitroso compound at 260–280 nm¹⁵ or, when this was not possible, the disappearance of alkyl nitrite at 340–380 nm. Kinetic runs were recorded in Spectronic 3000 Diode Array or Kontron-Uvikon 930 spectrophotometers with cell carriers kept at 25.0 ± 0.1 °C by circulating water from a thermostat.

All reactions were carried out under pseudo-first-order conditions, with the concentration of amine at least 10 times

[†] This paper is dedicated to the Universidad de Santiago de Compostela, in commemoration of the Fifth Centenary of its foundation.

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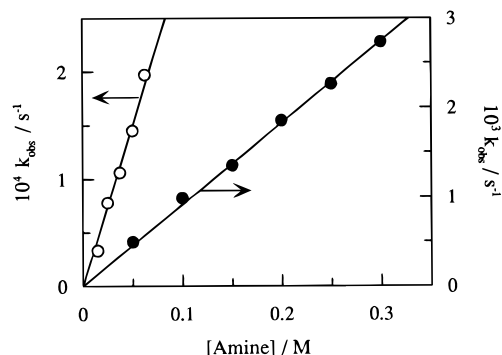
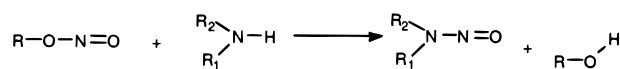


Figure 1. Influence of [amine] on the pseudo-first-order rate constant of the reactions between amines and alkyl nitrites in AOT/iC₈/H₂O microemulsions. (○) NMBA + BEN [RONO] = 3.30×10^{-3} M, [AOT] = 0.6 M, $W = 18$. (●) PIP + EEN; [RONO] = 3.30×10^{-3} M, [AOT] = 0.3 M, $W = 20$.

SCHEME 1



greater than the concentration of alkyl nitrite. The absorbance–time data were fitted to first-order integrated equations, always with satisfactory coefficients of correlation and residues. The equation derived from the proposed pseudophase model was fitted to the whole set of pseudo-first-order rate constants k_{obs} by means of a nonlinear curve fitting program based on Marquardt's algorithm.¹⁶

Results and Discussion

In water, the reaction between alkyl nitrites and secondary amines consists of nucleophilic attack by the free (unprotonated) amine upon the nitroso group of the alkyl nitrite in a nonsynchronized concerted mechanism with the rupture of the ON–OR bond (Scheme 1).¹² The same mechanism is assumed for the reactions in microemulsions studied in this work. This mechanistic hypothesis is supported by the finding that the pseudo-first-order constant k_{obs} depended linearly on total amine concentration in all the reactions studied (Figure 1). The acid or basic hydrolyses of the alkyl nitrites are all negligible under the experimental conditions used.^{17,18}

Reaction with Piperazine. The influence of the composition of the microemulsion on the rate of nitrosation of PIP by EEN was studied in series of experiments in which [PIP]_{total} was always 5×10^{-2} M, [RONO] was always 3.3×10^{-3} M, the mole ratio $W = [\text{water}]/[\text{AOT}]$ was kept constant within each series but varied from series to series over the range 4–30, and [AOT] was varied within each series (generally from 0.25 to 0.67 M). Properties of the medium with marked effects on reactivity, including polarity, microviscosity, interdroplet mass transfer, and the structure of water, are known to vary significantly over the range of compositions used.

Figure 2 shows the results for $W = 8, 20$, and 30 . For a given W , the pseudo-first-order rate constant was almost unaffected by [AOT]; for a given [AOT] it increased slightly with W . This behavior differs from that observed when the PIP is nitrosated by MNTS in the same media: with MNTS as nitrosating agent, k_{obs} decreases with increasing [AOT] for given W and also decreases with increasing W for given [AOT].¹⁰ The difference is attributable to the reaction with EEN taking place simultaneously in both the AOT film (location of the reaction with MNTS) and the aqueous pseudophase (in which MNTS is insoluble).

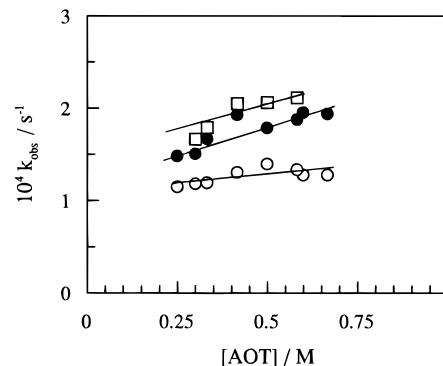
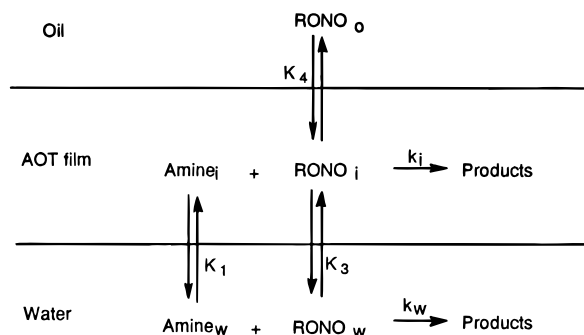


Figure 2. Influence of [AOT] on the pseudo-first-order rate constant of the reaction between PIP and EEN in AOT/iC₈/H₂O microemulsions, for various values of W . [PIP] = 5.00×10^{-2} M, [RONO] = 3.30×10^{-3} M, (○) $W = 8$, (●) $W = 20$, (□) $W = 28$.

SCHEME 2



The pseudophase model for the reaction with EEN and BEN, which treats the microemulsion as a three-layer bulk system and ignores its actual micellar structure, is illustrated in Scheme 2. To avoid having to define the volumes of the pseudophases, the partition coefficients assumed to govern the distribution of the reagents among the three pseudophases are defined in terms of their mole per mole concentrations in the pseudophases:

$$K_1 = \frac{[\text{PIP}]_i}{[\text{PIP}]_w} \quad K_3 = \frac{[\text{RONO}]_i}{[\text{RONO}]_w} \quad K_4 = \frac{[\text{RONO}]_i}{[\text{RONO}]_o} \quad (1)$$

where the subscripts w, o, and i respectively indicate quantities in water, oil, and the surfactant film; square brackets, as usual,¹⁹ indicate concentrations referred to the total volume of microemulsion; and Z is defined, by analogy with W , as the ratio $[\text{iC}_8]/[\text{AOT}]$. With these definitions, the model of Scheme 2 implies that the overall pseudo-first-order rate constant is given by

$$k_{\text{obs}} = k'_i \frac{1}{1 + \frac{W}{K_3} + \frac{Z}{K_4}} + k'_w \frac{W}{K_3} \frac{1}{1 + \frac{W}{K_3} + \frac{Z}{K_4}} \quad (2)$$

where k'_i and k'_w are the pseudo-first-order rate constants in the AOT film and the aqueous pseudophase, respectively; these pseudoconstants are expressed in terms of bimolecular rate constants k_i and k_w as

$$k'_i = k_i \frac{[\text{PIP}]_i}{[\text{AOT}]} \quad k'_w = k_w \frac{[\text{PIP}]_w}{[\text{H}_2\text{O}]} \quad (3)$$

Like the partition coefficients, to avoid having to define the volumes of the pseudophases, k_i and k_w are defined in terms of

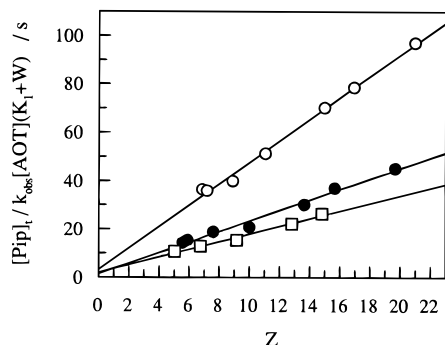


Figure 3. Plots corresponding to eq 6, derived from the pseudophase model for the reaction between PIP and EEN in AOT/iC₈/H₂O microemulsions, for various values of W . $[PIP] = 5.00 \times 10^{-2}$ M, $[RONO] = 3.30 \times 10^{-3}$ M, (○) $W = 8$, (●) $W = 20$, (□) $W = 28$.

mole per mole concentrations in the corresponding phases; then eq 2 becomes

$$k_{\text{obs}} = \frac{k_i}{[AOT]} \frac{[PIP]_T K_1}{K_1 + W} \frac{1}{1 + \frac{W}{K_3} + \frac{Z}{K_4}} + \frac{k_w}{[AOT]} \frac{[PIP]_T W}{(K_1 + W) K_3} \frac{1}{\left(1 + \frac{W}{K_3} + \frac{Z}{K_4}\right)} \quad (4)$$

$$k_{\text{obs}} = \frac{[PIP]_T (k_i K_1 + (k_w W / K_3))}{[AOT] (K_1 + W) \left(1 + \frac{W}{K_3} + \frac{Z}{K_4}\right)} \quad (5)$$

which predicts linear dependence of $[PIP]_T / k_{\text{obs}} [AOT] (K_1 + W)$ on Z :

$$\frac{[PIP]_T}{k_{\text{obs}} [AOT] (K_1 + W)} = \frac{1 + (W / K_3)}{k_i K_1 + \frac{K_w W}{K_3}} + \frac{Z}{K_4 \left(k_i K_1 + \frac{k_w W}{K_3}\right)} \quad (6)$$

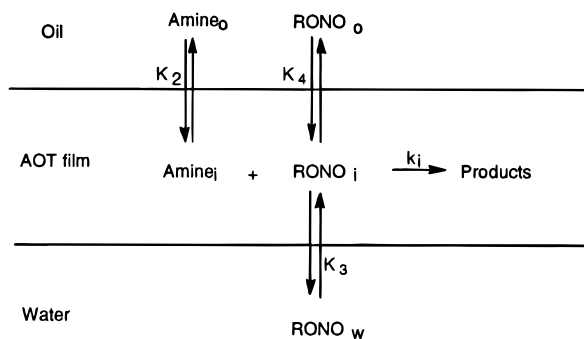
The validity of the proposed model is therefore supported by the actual observance of this linear dependence of k_{obs} on Z predicted by eq 6 (Figure 3).

The parameters k_i , K_3 , and K_4 were estimated by fitting with a multidimensional nonlinear regression program based on Marquardt's algorithm;¹⁶ to keep the number of optimized parameters to a minimum, K_1 was assigned the value of 10 previously found for nitrosation of PIP by MNTS,¹⁰ and k_w was calculated as 1.8 s^{-1} by determining the bimolecular rate constant of the nitrosation of PIP by EEN in water. Table 1 lists the values of k_{obs} and the fitted surface (k_{calc}) for each combination of W , Z , and $[AOT]$. Although in this case, with three parameters to optimize in the equation, there is a significant degree of correlation, the fitting is good (discrepancy was less than 10%). This is confirmed by the agreement of the values with previously reported k_i values of similar reactions in AOT microemulsions¹⁰ and K_3 values for association of alkyl nitrites to SDS direct micelles.^{23a} The optimized values of k_i , K_3 , and K_4 are listed in Table 3.

Analogous results for the reaction of PIP with BEN are likewise listed in Tables 1 and 3.

Reaction with *N*-Methylbenzylamine. The reactions of EEN and BEN with NMBA in AOT/iC₈/water microemulsions were studied by means of series of reactions analogous to those described for their reactions with PIP. In this case, however, k_{obs} values increase significantly with $[AOT]$ for given W , and

SCHEME 3



only slightly with W for given $[AOT]$ (Figure 5 shows the results with BEN); similar behavior is exhibited when NMBA is nitrosated by MNTS in these media.¹⁰

Because of the poor solubility of NMBA in water, the pseudophase model for this reaction would a priori consider simultaneous reactions in the AOT film and the isooctane pseudophase. However, there are two reasons for ignoring the reaction in the isooctane pseudophase: firstly, the reaction rate in isooctane (11) is several orders of magnitude less than those observed in this work; secondly, a significant contribution by the reaction in isooctane, in which k_{obs} exhibits a complex dependence on amine concentration,¹¹ would not be compatible with the linear dependence observed in this work (Figure 6). The pseudophase model adopted for the reaction of NMBA is therefore that shown in Scheme 3.

With K_3 and K_4 defined as above and K_2 by

$$K_2 = \frac{[NMBA]_i}{[NMBA]_o} Z \quad K_3 = \frac{[RONO]_i}{[RONO]_w} W \quad K_4 = \frac{[RONO]_i}{[RONO]_o} Z \quad (7)$$

calculations analogous to those described for piperazine lead to the expression

$$k_{\text{obs}} = \frac{k_i}{[AOT]} \frac{[NMBA]_T}{1 + \frac{Z}{K_2}} \frac{1}{1 + \frac{W}{K_3} + \frac{Z}{K_4}} \quad (8)$$

However, with the values of K_3 and K_4 obtained from the reaction with PIP (Table 3), and in the working conditions used, W/K_3 is negligible in comparison with $(1 + (Z/K_4))$, so that eq 8 reduces to

$$k_{\text{obs}} = \frac{k_i}{[AOT]} \frac{[NMBA]_T}{1 + \frac{Z}{K_2}} \frac{1}{1 + \frac{Z}{K_4}} \quad (9)$$

which can be rewritten in the form

$$\frac{1}{k_{\text{obs}} [AOT]} = \frac{(K_2 + Z)(K_4 + Z)}{k_i K_2 K_4 [NMBA]_T} \quad (10)$$

Fitting eq 10 to the experimental data with the same nonlinear regression program as described above (with $K_4 = 2.82$ for EEN and $K_4 = 2.64$ for BEN fixed as the value obtained in the experiments with PIP) afforded the values of K_2 and k_i listed in Table 3. The satisfactory fit obtained for experiments with $W > 12$ (Figures 7 and 8) supports the validity of the model employed. The anomalous behavior in systems with $W < 12$, in which the reaction is slower than predicted by the model, is

TABLE 1: Observed First-Order Pseudoconstants k_{obs} for the Reactions of Piperazine with 2-Ethoxyethyl and 2-Bromoethyl Nitrites in AOT/iC₈/H₂O Microemulsions of the Compositions Indicated, with the Values k_{calc} Calculated for Eq 5 after This Equation Was Fitted to the Experimental Data by Nonlinear Regression Analysis^a

W	Z	[AOT]	EEN		BEN		W	Z	[AOT]	EEN		BEN	
			$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$	$k_{\text{calc}}/10^{-4} \text{ s}^{-1}$	$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$	$k_{\text{calc}}/10^{-4} \text{ s}^{-1}$				$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$	$k_{\text{calc}}/10^{-4} \text{ s}^{-1}$	$k_{\text{obs}}/10^{-4} \text{ s}^{-1}$	$k_{\text{calc}}/10^{-4} \text{ s}^{-1}$
4	6.34	0.6667	1.05	1.15			16	10.45	0.4170	1.79	1.55		
4	7.34	0.6000	1.31	1.15			16	14.09	0.3333	1.64	1.52		
4	7.62	0.5830	1.28	1.16			16	16.09	0.3000	1.57	1.51	8.57	9.00
4	9.34	0.5000	1.16	1.16			16	20.09	0.2500	1.42	1.49		
4	11.71	0.4170	1.25	1.17			18	4.80	0.6667	1.94	1.71		
6	6.10	0.6667	1.14	1.24			18	5.83	0.6000	1.96	1.68	10.10	9.67
6	7.10	0.6000	1.40	1.25			18	6.10	0.5830	1.86	1.68		
6	7.41	0.5830	1.28	1.25			18	7.81	0.5000	1.54	1.64		
6	9.14	0.5000	1.28	1.25			18	10.21	0.4170	1.81	1.61		
6	11.52	0.4170	1.25	1.25			18	13.89	0.3333	1.69	1.57		
6	15.18	0.3333	1.15	1.25			18	15.89	0.3000	1.48	1.54		
6	17.18	0.3000	1.20	1.25			18	19.93	0.2500	1.44	1.52		
8	5.86	0.6667	1.27	1.34			20	4.59	0.6667	1.94	1.79		
8	6.90	0.6000	1.27	1.33			20	5.59	0.6000	1.95	1.75		
8	7.20	0.5830	1.33	1.33			20	5.89	0.5830	1.87	1.73		
8	8.70	0.5000	1.39	1.32			20	7.61	0.5000	1.79	1.69	8.96	9.30
8	11.32	0.4170	1.30	1.32			20	10.02	0.4170	1.93	1.67	9.59	9.02
8	15.00	0.3333	1.19	1.30			20	13.67	0.3333	1.66	1.60	10.20	9.81
8	16.97	0.3000	1.18	1.31			20	15.69	0.3000	1.50	1.58		
8	21.00	0.2500	1.15	1.31			20	19.69	0.2500	1.48	1.56		
10	5.68	0.6667			10.50	10.30	22	4.38	0.6667	1.68	1.85	9.40	9.93
10	6.66	0.6000	1.60	1.42			22	5.39	0.6000	1.71	1.80		
10	6.96	0.5830	1.30	1.41			22	5.68	0.5830	2.03	1.80		
10	8.70	0.5000	1.69	1.40	9.88	10.10	22	7.37	0.5000	1.78	1.75		
10	11.08	0.4170	1.27	1.39	10.50	9.98	22	9.78	0.4170	2.03	1.70		
10	14.75	0.3333	1.39	1.37	9.93	9.90	22	13.42	0.3333	1.70	1.67		
10	16.77	0.3000	1.32	1.36	9.33	9.92	22	15.42	0.3000	1.58	1.63		
10	20.74	0.2500	1.23	1.36	9.24	9.72	22	19.45	0.2500	1.65	1.60	8.76	8.38
12	5.46	0.6667	1.30	1.49			22	31.95	0.1667			8.22	8.04
12	6.43	0.6000	1.66	1.50	10.10	9.97	24	5.15	0.6000	1.87	1.88	9.72	9.69
12	6.75	0.5830	1.69	1.48			24	5.44	0.5830	1.98	1.87		
12	8.50	0.5000	1.65	1.45			24	7.17	0.5000	2.01	1.82		
12	10.89	0.4170	1.63	1.44			24	9.58	0.4170	1.75	1.74		
12	14.51	0.3333	1.46	1.43			24	13.24	0.3333	1.78	1.70		
12	16.50	0.3000	1.39	1.42			24	15.15	0.3000	1.61	1.67	8.43	8.43
12	20.58	0.2500	1.23	1.40			26	6.97	0.5000	1.96	1.86		
14	5.22	0.6667	1.42	1.56			26	9.34	0.4170	1.98	1.79		
14	6.23	0.6000	1.79	1.55			26	13.00	0.3333	1.70	1.72		
14	6.59	0.5830	1.69	1.54			26	15.02	0.3000	1.81	1.69		
14	8.29	0.5000	1.65	1.52			28	6.73	0.5000	2.06	1.94		
14	10.65	0.4170	1.61	1.50			28	9.15	0.4170	2.05	1.83	9.14	8.85
14	14.33	0.3333	1.54	1.47			28	12.82	0.3333	1.79	1.75		
14	16.29	0.3000	1.45	1.47			28	14.82	0.3000	1.67	1.72		
14	20.34	0.2500	1.34	1.45			30	6.52	0.5000			8.70	9.34
16	5.01	0.6667	1.53	1.64	9.99	9.99	30	8.91	0.4170	1.97	1.88		
16	6.03	0.6000	1.86	1.62			30	12.58	0.3333	1.77	1.79		
16	6.30	0.5830	1.68	1.61			30	14.55	0.3000	1.69	1.77		
16	8.05	0.5000	1.51	1.57			30	30.65	0.1667			7.68	7.71

^a $W = [\text{H}_2\text{O}]/[\text{AOT}]$, $Z = [\text{iC}_8]/[\text{AOT}]$, $[\text{amine}] = 5.00 \times 10^{-2} \text{ M}$, $[\text{RONO}] = 3.30 \times 10^{-3} \text{ M}$.

attributed to the fact that under these conditions a large proportion of water molecules are involved in solvation of AOT head groups, which alters the physicochemical properties of the interface medium (dielectric constant, microviscosity, hydrogen bond network, etc.) in ways that hinder reaction.

Reaction with Morpholine. In experiments on the reaction between morpholine (MOR) and BEN, k_{obs} was virtually independent of [AOT] for fixed W , and decreased slightly with increasing W for fixed [AOT] (Table 2). This behavior, different from that observed for other amines, should be related to the distribution of reagents among the pseudophases. Thus, since MOR is soluble in both isooctane and water, and since the reaction studied is several orders of magnitude slower in isooctane than was observed in the microemulsions used in this work,¹¹ the pseudophase model applied is that shown in Scheme 4. Calculations analogous to those described in the previous

sections lead to the expression

$$k_{\text{obs}} = \frac{k_i}{[\text{AOT}]} \frac{[\text{MOR}]_{\text{T}}}{1 + \frac{W}{K_1} + \frac{Z}{K_2}} \frac{1}{1 + \frac{W}{K_3} + \frac{Z}{K_4}} + \frac{k_w}{[\text{AOT}]} \frac{W[\text{MOR}]_{\text{T}}}{K_1 K_3} \frac{1}{1 + \frac{W}{K_1} + \frac{Z}{K_2}} \frac{1}{1 + \frac{W}{K_3} + \frac{Z}{K_4}} \quad (11)$$

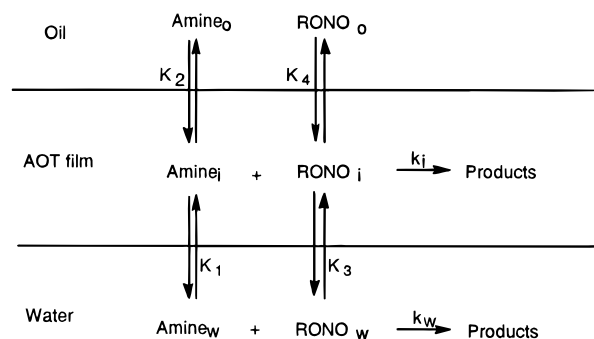
$$k_{\text{obs}} = \frac{[\text{MOR}]_{\text{T}} \left(k_i + \frac{k_w W}{K_1 K_3} \right)}{[\text{AOT}] \left(1 + \frac{W}{K_1} + \frac{Z}{K_2} \right) \left(1 + \frac{W}{K_3} + \frac{Z}{K_4} \right)} \quad (12)$$

Fitting eq 12 to the experimental data for $W > 10$, with K_1 ,

TABLE 2: Observed First-Order Pseudoconstants k_{obs} for the Reactions of Morpholine with 2-Bromoethyl Nitrite in AOT/iC₈/H₂O Microemulsions of the Compositions Indicated, with the Values k_{calc} Calculated for Eq 12 after This Equation Was Fitted to the Experimental Data by Nonlinear Regression Analysis^a

W	Z	[AOT]	BEN		W	Z	[AOT]	BEN	
			$k_{\text{obs}}/10^{-5} \text{ s}^{-1}$	$k_{\text{calc}}/10^{-5} \text{ s}^{-1}$				$k_{\text{obs}}/10^{-5} \text{ s}^{-1}$	$k_{\text{calc}}/10^{-5} \text{ s}^{-1}$
4	6.34	0.6667	13.0	6.01 ^b	16	16.09	0.3000	6.21	5.70
4	7.62	0.5830	10.8	5.96 ^b	18	6.10	0.5830	6.67	6.52
4	9.34	0.5000	12.3	5.89 ^b	18	7.81	0.5000	7.13	6.31
4	11.71	0.4170	9.08	5.80 ^b	18	10.21	0.4170	6.14	6.09
6	6.10	0.6667	11.7	6.10 ^b	18	13.89	0.3333	5.99	5.82
6	7.41	0.5830	9.09	6.02 ^b	18	15.89	0.3000	6.65	5.71
6	9.14	0.5000	10.8	5.92 ^b	20	5.59	0.6000	7.62	6.69
6	11.52	0.4170	7.72	5.83 ^b	20	5.89	0.5830	6.54	6.63
6	15.18	0.3333	9.24	5.67 ^b	20	7.61	0.5000	6.00	6.39
6	17.18	0.3000	10.1	5.59 ^b	20	10.02	0.4170	5.63	6.13
8	5.86	0.6667	9.86	6.20 ^b	20	13.67	0.3333	6.21	5.86
8	7.20	0.5830	8.86	6.10 ^b	20	15.69	0.3000	5.09	5.73
8	8.70	0.5000	9.13	6.09 ^b	22	5.39	0.6000	7.46	6.80
8	11.32	0.4170	6.83	5.84 ^b	22	5.68	0.5830	6.98	6.74
8	15.00	0.3333	6.86	5.67 ^b	22	7.37	0.5000	6.18	6.49
8	16.97	0.3000	6.66	5.60 ^b	22	9.78	0.4170	6.20	6.21
8	21.00	0.2500	6.34	5.46 ^b	22	13.42	0.3333	5.54	5.91
10	5.68	0.6667	9.41	6.27 ^b	22	15.42	0.3000	5.77	5.79
10	6.96	0.5830	8.42	6.17 ^b	24	5.15	0.6000	7.10	6.95
10	8.70	0.5000	9.05	6.03 ^b	24	5.44	0.5830	6.12	6.89
10	11.08	0.4170	6.74	5.90 ^b	24	7.17	0.5000	7.02	6.57
10	14.75	0.3333	5.97	5.70 ^b	24	9.58	0.4170	6.14	6.26
10	16.77	0.3000	6.94	5.62 ^b	24	13.24	0.3333	5.66	5.94
10	20.74	0.2500	5.92	5.48 ^b	24	15.15	0.3000	5.27	5.84
12	5.46	0.6667	9.01	6.37 ^b	26	4.95	0.6000	7.19	7.07
12	6.75	0.5830	7.75	6.24 ^b	26	5.23	0.5830	5.58	7.02
12	8.50	0.5000	8.15	6.08 ^b	26	6.97	0.5000	5.97	6.66
12	10.89	0.4170	6.55	5.92 ^b	26	9.34	0.4170	6.02	6.35
12	14.51	0.3333	6.23	5.73 ^b	26	13.00	0.3333	5.88	5.99
12	16.50	0.3000	7.64	6.37 ^b	26	15.02	0.3000	5.75	5.85
14	5.22	0.6667	8.48	6.50	28	4.72	0.6000	7.01	7.24
14	6.59	0.5830	7.01	6.29	28	5.03	0.5830	6.55	7.15
14	8.29	0.5000	8.09	6.14	28	6.73	0.5000	6.32	6.78
14	10.65	0.4170	6.00	5.98	28	9.15	0.4170	6.17	6.41
14	14.33	0.3333	6.06	5.76	28	12.82	0.3333	5.09	6.03
14	16.29	0.3000	5.96	5.68	28	14.82	0.3000	5.66	5.88
16	5.01	0.6667	7.66	6.61	30	4.52	0.6000	7.08	7.40
16	6.30	0.5830	6.98	6.43	30	4.81	0.5830	6.39	7.30
16	8.05	0.5000	7.84	6.22	30	6.52	0.5000	6.39	6.89
16	10.45	0.4170	6.00	6.02	30	8.91	0.4170	6.05	6.50
16	14.09	0.3333	6.29	5.80	30	14.55	0.3000	5.39	5.94

^a $W = [\text{H}_2\text{O}]/[\text{AOT}]$, $Z = [\text{iC}_8]/[\text{AOT}]$, $[\text{amine}] = 3.30 \times 10^{-2} \text{ M}$, $[\text{RONO}] = 3.30 \times 10^{-3} \text{ M}$. ^b Data calculated from eq 12 using parameters in Table 3.

SCHEME 4

K_3 , K_4 , and k_w fixed at values obtained as described above (Table 3), yielded the values of k_i and K_2 that are likewise listed in Table 3. The mean discrepancy between the experimental and fitted values of k_{obs} was less than 9% (Table 2); the greater deviation of the data for media with $W < 10$ is attributed to the same cause as in the case of NMBA, to the fact that under these conditions a large proportion of water molecules are involved in solvation of AOT head groups, which alters the physicochemical properties of the interface medium (dielectric constant,

microviscosity, hydrogen bond network, etc.) in ways that hinder reaction.

Additional Remarks. The assumption that the mechanism of these reactions in the microemulsions used in this work is the same as the mechanism obtained in bulk water is supported not only by the arguments sketched at the beginning of the Results and Discussion section, but also by the observation of solvent isotope effects k_H/k_D of respectively 2.0 and 1.6 for the reactions of PIP with EEN (Figure 4) and NMBA with BEN (Figure 6), both these values being similar to the values of about 1.7 typically found for reactions between alkyl nitrites and amines in water.¹² Furthermore, the more precise hypothesis that the reaction mechanism in the interface is the same as in water is supported by comparison of the reactivities of the alkyl nitrites (relative to MNTS or to each other) in the two media: the reactivities of PIP and NMBA with EEN in the interface (k_i or k_2^i in Table 3; for the definition of k_2^i ,^{1,20} see eq 13 below) are, as in water, similar to those reported for their reactions with MNTS under the same conditions;¹⁰ and the reactivity of BEN in the interface is, as in water, about 1 order of magnitude greater than that of EEN. These similarities between the behavior of the alkyl nitrites in water and their behavior in the

TABLE 3: Partition Coefficients and Kinetic Constants Involved in the Fitted Eqs 5, 10, and 12

system	k_w^a/s^{-1}	$k_2/M^{-1} s^{-1}$	k_i/s^{-1}	$k_2^i/M^{-1} s^{-1}$	K_1^b	K_2	K_3	K_4
PIP + EEN	1.80	3.25×10^{-2}	4.39×10^{-3}	1.62×10^{-3}	10		490	2.82
PIP + BEN	19.90	0.36	8.86×10^{-2}	3.28×10^{-2}	10		740	2.65
NMBA + EEN	1.90	3.54×10^{-2}	2.64×10^{-2}	9.77×10^{-4}		18.5	490	2.82 ^c
NMBA + BEN	21.30	0.38	2.55×10^{-2}	9.43×10^{-4}		18.5	740	2.64 ^c
MOR + BEN	2.01	3.62×10^{-2}	4.45×10^{-3}	1.65×10^{-3}	46.9	135	740	2.64 ^c

^a Values obtained assuming that $k_w = k_2/\bar{V}(\text{H}_2\text{O})$. ^b Values taken from the literature.¹⁰ ^c Values obtained from PIP + EEN and PIP + BEN.

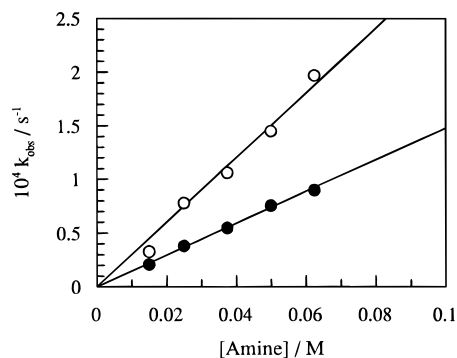


Figure 4. Influence of [amine] on the pseudo-first-order rate constant of the reaction between PIP and EEN in AOT/iC₈/H₂O microemulsions. [RONO] = 3.30×10^{-3} M, [AOT] = 0.3 M, $W = 20$, (○) microemulsions prepared with water, (●) microemulsions prepared with D₂O.

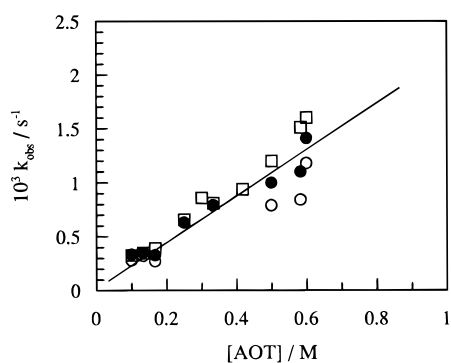


Figure 5. Influence of [AOT] on the pseudo-first-order rate constant of the reaction between NMBA and BEN in AOT/iC₈/H₂O microemulsions, for various values of W . [NMBA] = 0.1 M, [RONO] = 3.30×10^{-3} M, (○) $W = 18$, (●) $W = 26$, (□) $W = 30$.

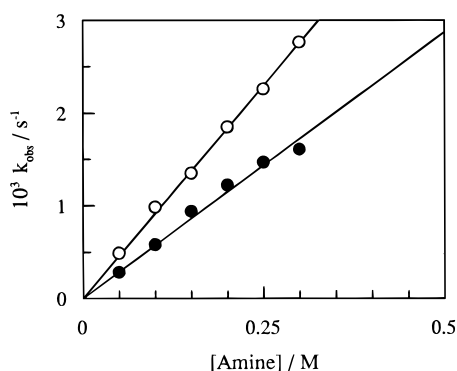


Figure 6. Influence of [amine] on the pseudo-first-order rate constant of the reaction between NMBA and BEN in AOT/iC₈/H₂O microemulsions. [RONO] = 3.30×10^{-3} M, [AOT] = 0.6 M, $W = 18$, (○) microemulsions prepared with water, (●) microemulsions prepared with D₂O.

interface support the notion that the reaction mechanism is the same in both media.

Nature of the Reaction Mechanism. The solvent isotope effects reported above are in keeping with the reaction mechanism consisting, in both water and our microemulsions, of

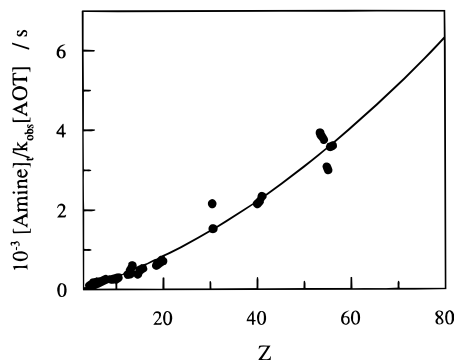


Figure 7. Fitting of experimental data for the reaction between NMBA and BEN in AOT/iC₈/H₂O microemulsions to eq 10. [NMBA] = 0.1 M, [RONO] = 3.30×10^{-3} M.

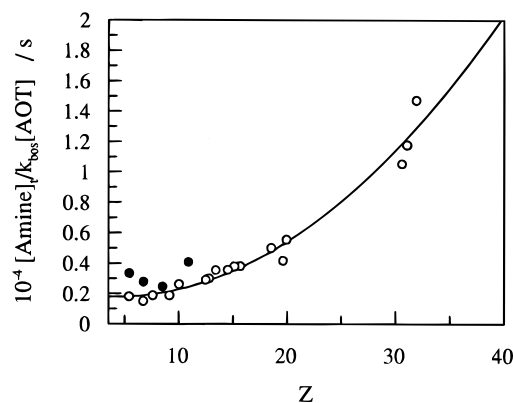


Figure 8. Fitting of eq 10, of experimental data for the reaction between NMBA and EEN in AOT/iC₈/H₂O microemulsions. [NMBA] = 0.15 M, [RONO] = 3.30×10^{-3} M, (○) $W > 12$, (●) $W < 12$.

nucleophilic attack by the unprotonated amine on the nitroso group of the alkyl nitrite, in nonsynchronized concerted mechanism with the rupture of the ON–OR bond. It is thought that this process requires the accumulation of large negative charge on the alkoxide oxygen atom in the transition state (this would explain why BEN is more reactive than EEN, since electron-withdrawing substituents favor the required charge distribution) so as to ensure strong solvation of the alkoxide group. The existence of strong solvation of the alkoxide group (testified to by the large negative entropy of activation reported for the reaction of PIP with EEN in water, $-113.37 \text{ J mol}^{-1} \text{ K}^{-1}$)²¹ raises the possibility that the existence of the departing alkoxide group may be concerted with its protonation. However, this would imply the loss of an OH[−] group from the reaction complex, which in turn would imply a solvent isotope effect as high as 2.08 according to established theory for reactions with late transition states, the fractionation factor for the triply solvated OH[−] ion being 0.48.²² Hence the solvent isotope effects of around 1.8 that are actually observed suggest that concerted protonation of the alkoxide group is unnecessary for the reaction to proceed.

Partition Coefficients. The partition coefficients of the reagents are listed in Table 3. Those of the amines, K_1 and K_2 , are consistent with those measured in two-phase iC₈/water

systems.¹⁰ Those of the alkyl nitrites, K_3 and K_4 , show BEN to be more hydrophobic than EEN, as in micellar systems.^{13,23}

Anomalous Behavior with $W < 12$. The reactions with NMBA and MOR were slower than predicted when carried out in media with $W < 12$; similarly anomalous behavior has previously been reported for the nitrosation of these amines by MNTS in microemulsions with low W .¹⁰ We attribute these anomalies to the scarcity of water molecules in such media, in which a large proportion of the water is engaged in solvating AOT head groups. Numerous studies have shown that the dielectric constant of the interface decreases with decreasing W when W is less than 10–15,²⁴ and electron solvation experiments,²⁵ $^1\text{H-NMR}$ studies,²⁶ and studies of solvolysis in microemulsions²⁷ suggest that other kinetically relevant properties of water (solvating power, nucleophilicity, electrophilicity, etc.) also undergo significant alteration in microemulsions with low W . This implies that for media with W less than a certain threshold, the kinetic constant k_i depends on the amount of available water at the interphase and is therefore a function of the composition of the microemulsion.

Percolation. The conditions used in some of the experiments carried out in this work were such that electric percolation may have taken place, i.e., interdroplet mass transport made possible by the fleeting formation of interdroplet channels during droplet–droplet collisions.²⁸ Percolation is facilitated by the presence of amines.²⁹ This phenomenon is not taken into account by the pseudophase model. However, our results for the reactions studied in this work are valid regardless of the occurrence of percolation, because these reactions are chemically controlled and have half-lives very much longer than those of the interdroplet mass transport phenomena.³⁰ To check this, we carried out the reaction between PIP and EEN both in the absence and in the presence of 1,3-dimethylurea (DMU), which drastically lowers the percolation threshold of AOT/iC₈/water microemulsions;²⁹ under conditions in which percolation occurs in the presence of DMU but not in its absence, the slope $k_{2,\text{app}}$ of a plot of k_{obs} against [PIP] was effectively the same in the absence of DMU ($3.01 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) as in its presence ($2.97 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$). Nor did percolation alter the mechanism of the reaction, to judge from the solvent isotope effects of 1.76 and 2.0 observed in experiments with heavy water in respectively the presence and absence of DMU. Such kinetic and mechanistic independence of percolation has previously been reported for the hydrolysis of 4-nitrophenyl chloroformate in microemulsions.²⁷

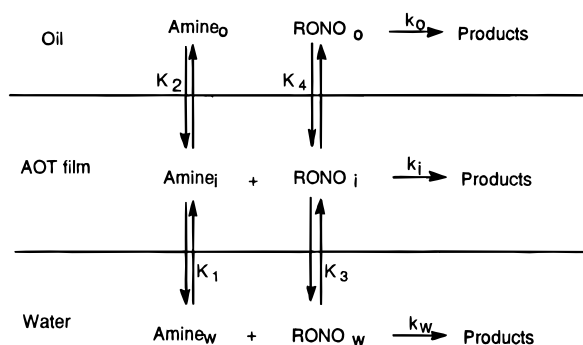
Comparison with Reaction Rates in Water. For comparison of reactivities in the AOT interface with the corresponding reactivities in bulk water, the k_i of Table 3 (defined in terms of mole per mole concentrations and expressed in s^{-1}) must be converted to conventional reaction rates expressed in $\text{M}^{-1} \text{ s}^{-1}$. This requires knowledge of the molar volume of AOT under the conditions obtaining at the interface in our microemulsions, which is far from easy to ascertain with confidence since it implies precise definition and knowledge of the volume of the interface. In the interests of comparability with our results on nitrosation by MNTS in microemulsions,¹⁰ in this work we have adopted the same criterion as in our earlier paper: we assume the molar volume of AOT in the interface, \bar{V} , to be given by its density, and we accordingly define a “conventional” bimolecular rate constant, k_2^i for the reaction at the interface by

$$k_2^i = k_i \bar{V} \quad (13)$$

where under our conditions $\bar{V} = 0.37 \text{ M}^{-1}$.

Comparison of k_2^i and corresponding k_2 in Table 3 shows that the reactions studied proceed much more slowly in the

SCHEME 5



interphase due to the polarity of the interface, like the polarity of the interface of normal micelles,³¹ is less than that of bulk water.

The General Model. The pseudophase models used in this work are all particular cases of the general model shown in Scheme 5. This general model does not seem to be readily verifiable by means of its full application to a single reaction, since most reactions exhibit the same sort of limitations as have led to the use of reduced models in the present work: insolubility of one or more reagents in one of the pseudophases and great disparity (by several orders of magnitude) between the reaction rates in different pseudophases. It is nevertheless useful to have at hand the expression of k_{obs} implied by the general model:

$$k_{\text{obs}} = \frac{[\text{amine}]_T}{[\text{AOT}]} \frac{k_i + \frac{k_w W}{K_1 K_3} + \frac{k_o Z}{K_2 K_4}}{\left(1 + \frac{W}{K_1} + \frac{Z}{K_2}\right) \left(1 + \frac{W}{K_3} + \frac{Z}{K_4}\right)} \quad (14)$$

Appropriate simplification of this one expression yields the expression for k_{obs} for any reduced model, including all those used in this work.

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