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Nitrosation Reactions in Water/AOT/Xylene Microemulsions

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A kinetic study of the nitroso group transfer from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) to the secondary amines piperazine (PIP) and *N*-methylbenzylamine (NMBA) in water/AOT/xylene and water/AOT/isooctane microemulsions was carried out. The water/AOT/xylene system is nonpercolative by effect of the decreased ability of the aromatic continuous medium to penetrate into the microemulsion interphase. The kinetic study was conducted at 50 °C (i.e., above the percolation temperature for water/AOT/isooctane microemulsions). The kinetic parameters for the reactions involved were determined by using the pseudophase model. This model assumes that the reactants partition between the three pseudophases in the microemulsion (viz., water, oil, and the interphase) as a function of their solubility and provides a quantitative explanation for the experimental behavior observed. In all cases, the reaction takes place at the microemulsion interphase. Also, the bimolecular rate constants, k_2^i , differ markedly between the two types of microemulsions. The difference can be ascribed to the differential polarity of the reaction medium. The activation parameters for the reactions of MNTS with PIP and NMBA in water/AOT/isooctane microemulsions were calculated.

Introduction

Microemulsions are thermodynamically stable systems consisting of two immiscible liquids separated and stabilized by a monolayer of surfactant.^{1,2} In recent years, microemulsions have increasingly been used in a wide range of chemical fields from nanoparticle research^{3,4} to cultural heritage conservation.⁵ In this work, however, we focused on their use as chemical nano-reactors.^{6,7} The extensive use of microemulsions as reaction media has been promoted by (a) their similarity to biological membranes (the interfacial properties of microemulsions allow a hydrophobic domain to be brought into contact with a hydrophilic one at the nanoscale level and both polar and nonpolar substances to be dissolved by concentrating reagents of variable solubility)^{8,9} and (b) their kinetic potential as scalable reactors.^{10–13} The ability to have chemical reagents partition between, or concentrate in, different pseudophases in a macroscopically homogeneous system is of high kinetic interest. Also, the water molecules confined in the water pool differ in a number of ways from bulk water. Recently, the solvation dynamics of the confined water molecules in microemulsions have been reported to exhibit a component that is rather slow relative to bulk water.^{14,15}

Microemulsions are highly dynamic structures. Electrical conductivity measurements provide a very useful method for characterizing micellar interactions.^{16,17} The electrical percolation phenomenon has been explained by assuming a mechanism involving the formation of channels through which mass is exchanged between disperse water droplets in the continuous phases (see Scheme 1). It is therefore necessary to have an effective collision between two water droplets in the microemulsion to cause the droplets to fuse together. Subsequently, mass transfer between the water droplets must take place to allow charge to be conducted and the droplets to separate by fission.

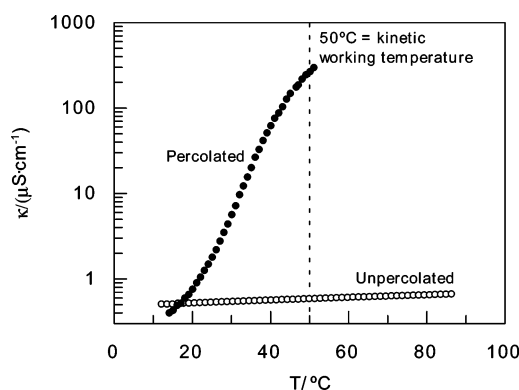


Figure 1. Conductivity vs temperature plot for a water/AOT/isooctane microemulsion (●) and a water/AOT/*o*-xylene microemulsion (○): [AOT] = 0.5 M; $W = 12$.

Percolation phenomena in microemulsions are widely documented.^{18–24} The microemulsions most extensively examined in this respect are of the water-in-oil and water/AOT/isooctane types, which are thermodynamically stable over a wide range of water proportions. The size of these aggregates can be controlled via parameter W ($W = [H_2O]/[AOT]$) as the droplet radius is directly related to W ($r = 1.5W$).²

The influence of an aromatic continuous medium on the percolation temperature has been studied to a comparatively much lesser extent. In this work, we examined the water/AOT/xylene system, using both *o*-, *m*-, and *p*-xylene. This type of microemulsion is nonpercolative²⁵ (see Figure 1) but becomes percolative in the presence of 0.5 M sodium cholate.²⁶ However, the purpose of this work was to conduct a comparative kinetic study on percolative (water/AOT/isooctane) and nonpercolative (water/AOT/xylene) microemulsions. The difference in composition between the two should result in differences in structure and physical properties as the ease with which the oil can penetrate the surfactant layer will vary markedly with the steric hindrance it encounters.⁴⁷ We studied the nitroso group transfer from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) to secondary amines *N*-methylbenzylamine (NMBA) and piper-

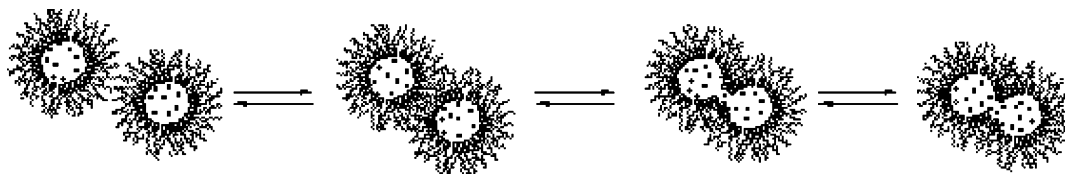
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Scheme 1



zine (PIP), which were chosen on the grounds of their differential solubility in the three microemulsion domains. Because NMBA and MNTS are virtually insoluble in water, they should be present mainly in the continuous aromatic medium. On the other hand, PIP is soluble in water and insoluble in oil. Therefore, the reaction should only take place to an appreciable extent in the surfactant film in both cases.

Experimental Section

AOT was purchased from Aldrich and used without further purification after drying in a vacuum desiccator for 2 days. All other reagents were supplied by Merck or Aldrich and were used as received.

Electrical conductivity measurements were made with a Radiometer CDM3 conductimeter with a 1.0 cm^{-1} cell constant thermostated to within $\pm 0.1\text{ }^{\circ}\text{C}$. The percolation temperature was determined from the variation of the electrical conductivity of the microemulsions with temperature in $0.2\text{ }^{\circ}\text{C}$ steps in the vicinity of the percolation threshold which was in turn calculated from conductivity data (κ/T).

The kinetics of the reaction were followed on a Kontron-Uvikon spectrophotometer equipped with thermostated cell holders and monitored via absorbance changes due to MNTS consumption. Because xylenes exhibit a strong absorption band at ca. 250 nm , the temporal variation of the absorbance had to be recorded at 392 nm . In any case, the concentration of MNTS ($2 \times 10^{-3}\text{ M}$) was always much lower than that of the amine ($[\text{PIP}] = 5 \times 10^{-2}\text{ M}$ and $[\text{NMBA}] = 0.103\text{ M}$). Absorbance–time data pairs were fitted to a first-order integrated rate equation by using linear regression. All correlation coefficients and residuals were quite satisfactory ($r > 0.999$). The *pseudo*-first-order constant is denoted by k_{obs} below.

$$\ln(A_t - A_{\infty}) = \ln(A_0 - A_{\infty}) - k_{\text{obs}}t \quad (1)$$

Results

1. Percolation. The studied system has been experimentally shown to be of the nonpercolative type. The conductivity of a water/AOT/*o*-xylene microemulsion ($[\text{AOT}] = 0.5\text{ M}$, $W = 12$) exhibited no substantial changes over the temperature range $25\text{--}90\text{ }^{\circ}\text{C}$. Figure 1 compares it with the conductivity of a water/AOT/isooctane microemulsion of identical $[\text{AOT}]$ and W . The figure reveals the absence of mass transfer through the formation of channels between droplets above a given temperature. Replacing the alkane with an aromatic molecule in the continuous medium probably hinders percolation to a considerable extent. As noted earlier, the presence of sodium cholate can make a microemulsion percolative. The addition of two amines such as PIP and NMBA has not been found to alter the percolative nature of these microemulsions. On the other hand, the addition of PIP or NMBA to an isooctane-containing microemulsion has been found to increase T_p by $0.4\text{ }^{\circ}\text{C}$.²⁷

2. Reactivity in Water/AOT/*o*-Xylene Microemulsions. The nitroso group transfer between a secondary amine such as NMBA or PIP and MNTS in water and various types of microemulsions is well documented. We first examined the

stability of water/AOT/*o*-xylene systems in the presence of these amines. The water solubility in these microemulsions is lower than that in water/AOT/isooctane microemulsions. In microemulsions where isooctane provides the continuous medium, W can be as large as 80 at a surfactant concentration of 0.5 M . In contrast, W can barely reach 20 at identical surfactant concentrations in water/AOT/*o*-xylene microemulsions at $25\text{ }^{\circ}\text{C}$. Raising the temperature slightly increases the solubility of water in the microemulsion. The kinetics of the nitroso group transfer are first-order in amine concentration (PIP or NMBA) in water/AOT/*o*-xylene microemulsions at different temperatures (see Figure 2). We chose to use a fixed temperature of $50\text{ }^{\circ}\text{C}$ in all kinetic studies. This temperature was well above the percolation temperature for one of the systems (water/AOT/isooctane); meanwhile, for the water/AOT/*o*-xylene system, no channels are formed between droplets, so it is of the nonpercolative type.

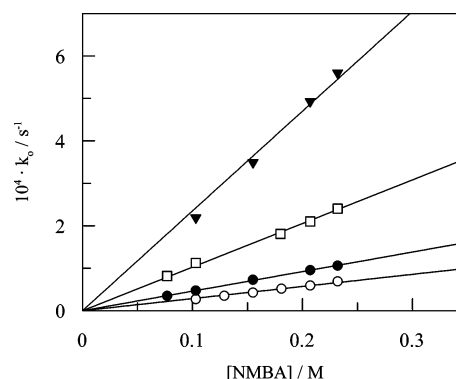


Figure 2. Influence of the concentration of NMBA on its transamination reaction with $2 \times 10^{-3}\text{ M}$ MNTS in water/AOT/*o*-xylene microemulsions ($[\text{AOT}] = 0.5\text{ M}$; $W = 12$) at a variable temperature: (○) $25\text{ }^{\circ}\text{C}$; (●) $30\text{ }^{\circ}\text{C}$; (□) $40\text{ }^{\circ}\text{C}$; (▼) $50\text{ }^{\circ}\text{C}$.

(a) Nitrosation of Piperazine (PIP). The kinetic study of PIP nitrosation was conducted using *o*-xylene as the continuous medium in the microemulsions, variable AOT concentrations from 0.1 to 0.7 M , and W values over the range $7.4\text{--}15.7$. The amine, PIP, and MNTS concentrations were kept constant at 5×10^{-2} and $2 \times 10^{-3}\text{ M}$, respectively, to examine the effect of the medium composition on the nitrosation reaction.

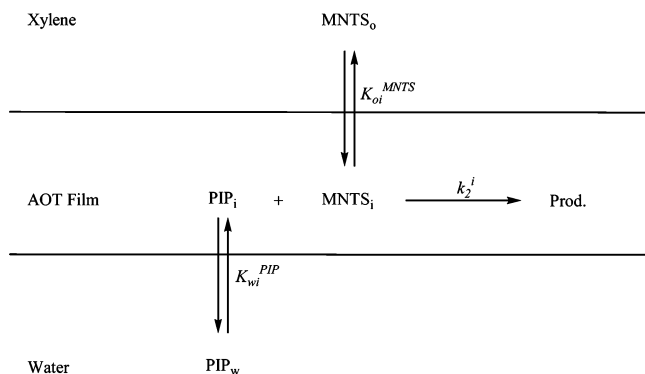
Piperazine is readily soluble in water but insoluble in oil, so it should partition between the aqueous pseudophase and the surfactant film. As a result, the reaction should only take place at the AOT film (see Scheme 2).

If, by analogy with water/AOT/isooctane microemulsions, Z is taken to be the $[\text{Xylene}]/[\text{AOT}]$ ratio, the partition coefficients governing the distribution of the reactants between the pseudophases (viz., xylene and the interphase) can be defined in terms of their mole per mole concentrations in the two pseudophases:

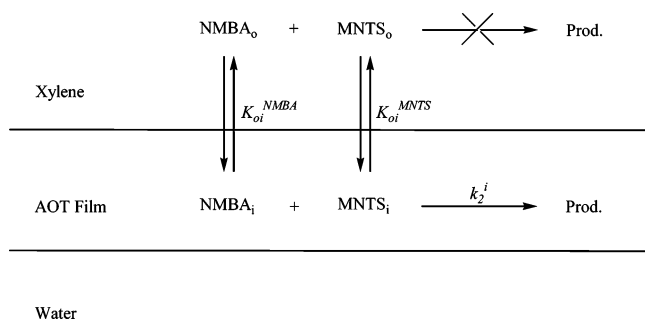
$$K_{\text{wi}}^{\text{PIP}} = \frac{[\text{PIP}]_i}{[\text{PIP}]_w} \quad K_{\text{oi}}^{\text{MNTS}} = \frac{[\text{MNTS}]_i}{[\text{MNTS}]_o} Z \quad (2)$$

where subscripts o, i, and w denote quantities in the oil pseudophase, AOT film, and water, respectively. With these

Scheme 2



Scheme 3



definitions, and on the basis of the model of Scheme 3, the pseudo-first-order rate constant, k_{obs} , will be given by

$$k_{\text{obs}} = k'_i \frac{K_{\text{oi}}^{\text{MNTS}}}{K_{\text{oi}}^{\text{MNTS}} + Z} \quad (3)$$

k'_i being the pseudo-first-order rate constant at the interphase. Such a rate constant can be expressed as a function of the bimolecular rate constant at the interphase, k_2^i :

$$k'_i = k_2^i [\text{PIP}]_i = k_2^i \frac{V_i}{V_i} [\text{PIP}]_i = k_2^i \frac{[\text{PIP}]_i}{\bar{V}_{\text{AOT}}[\text{AOT}]} \quad (4)$$

where $[\text{PIP}]_i$ is the PIP concentration at the microemulsion interphase referred to the volume of the interphase and $[\text{PIP}]_i$ is that referred to the overall volume of the system. The interphase volume is given by that occupied by AOT. Thus, $V_{\text{tot}}/V_i = 1/(\bar{V}_{\text{AOT}}[\text{AOT}])$, where \bar{V}_{AOT} is the molar volume of the surfactant ($\bar{V}_{\text{AOT}} = 0.37 \text{ M}^{-1}$ (ref 28)) and $[\text{AOT}]$ is the total AOT concentration referred to the total microemulsion volume. If the amine concentration at the interphase is expressed as

$$[\text{PIP}]_i = \frac{K_{\text{wi}}^{\text{PIP}}}{K_{\text{wi}}^{\text{PIP}} + W} [\text{PIP}]_T \quad (5)$$

substitution into eq 3 yields

$$k_{\text{obs}} = \frac{k_2^i}{\bar{V}_{\text{AOT}}[\text{AOT}]} \frac{K_{\text{wi}}^{\text{PIP}}}{K_{\text{wi}}^{\text{PIP}} + W} [\text{PIP}]_T \frac{K_{\text{oi}}^{\text{MNTS}}}{K_{\text{oi}}^{\text{MNTS}} + Z} \quad (6)$$

which can be rearranged to

$$\frac{[\text{PIP}]_T}{k_{\text{obs}} \bar{V}_{\text{AOT}}[\text{AOT}]} = \frac{(K_{\text{wi}}^{\text{PIP}} + W)(K_{\text{oi}}^{\text{MNTS}} + Z)}{k_2^i K_{\text{wi}}^{\text{PIP}} K_{\text{oi}}^{\text{MNTS}}} \quad (7)$$

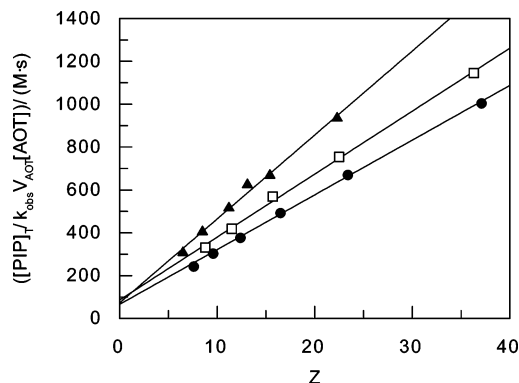


Figure 3. Variation of k_0 with parameter Z for the reaction between MNTS and PIP in water/AOT/*o*-xylene microemulsions: (●) $W = 7.4$; (□) $W = 13.0$; (▲) $W = 14.8$.

The pseudophase model, therefore, provides an expression, eq 7, that relates k_{obs} to the microemulsion composition parameters W and Z .

Equation 7 predicts a linear relationship between $[\text{PIP}]_T / (k_{\text{obs}} \bar{V}_{\text{AOT}}[\text{AOT}])$ and Z at each W value. Figure 3 shows a plot obtained at different W values. As can be seen, the relationship is linear; also, on the basis of eq 7, the ratio of the intercept to the slope will coincide with $K_{\text{oi}}^{\text{MNTS}}$ (i.e., the partition constant of MNTS between *o*-xylene and the surfactant film). From the mean of the results obtained, $K_{\text{oi}}^{\text{MNTS}}$ was calculated to be 2.3. By substituting this value into eq 7, the other kinetic parameters (k_2^i and $K_{\text{wi}}^{\text{PIP}}$) were calculated (see Table 1). The consistency between the experimental and predicted values (see Figure 4) confirms the accuracy of the micellar pseudophase model.

To compare the xylene and isooctane systems, we carried out a kinetic study in water/AOT/isooctane microemulsions at 50 °C. Kinetic parameters were determined by following the same procedure as used previously. As can be seen from Table 1, the partition equilibrium constant of PIP, $K_{\text{wi}}^{\text{PIP}}$, between water and the AOT film was greater in the *o*-xylene microemulsions. Also, the reaction rate constant at the interphase, k_2^i , was smaller in the surfactant film of the water/AOT/*o*-xylene microemulsions.

(b) Reaction with *N*-Methylbenzylamine (NMBA). The transnitrosation reaction between MNTS and NMBA was studied in a wide range of water/AOT/*o*-xylene microemulsions at 50 °C. The influence of the microemulsion composition on the reaction rate was examined in experiments using each continuous medium, keeping the NMBA and MNTS concentrations ($[\text{NMBA}] = 0.103 \text{ M}$; $[\text{MNTS}] = 2 \times 10^{-3} \text{ M}$) constant, by using W values between 7 and 18 and surfactant concentrations over the range 0.2–0.7 M. As can be seen in Figure 5, k_{obs} increased markedly with increasing surfactant concentration at a constant value of W and more slightly with increase in W at a constant AOT concentration.

The experimental data were processed quantitatively in the light of the micellar pseudophase model. Both NMBA and MNTS are virtually insoluble in water, so the reactants should partition between the continuous medium and surfactant film and be able to react in both pseudophases. However, the reaction between MNTS and NMBA in the continuous medium was found to be very slow and, hence, was discarded. The rate constants of nitrosation processes in alkanes as reaction media are several orders of magnitude higher than the values observed in this work.²⁹ The pseudophase model used is depicted in Scheme 3.

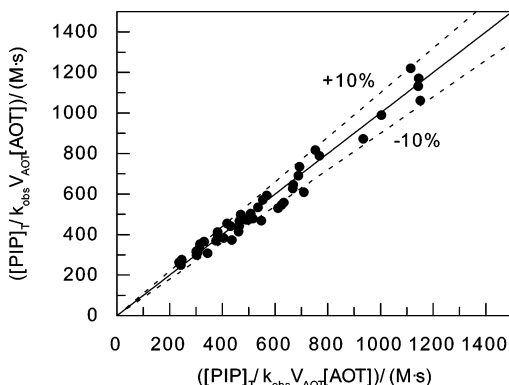


Figure 4. Plot of experimental values against the predictions of eq 7 for the reaction between MNTS and PIP in water/AOT/o-xylene microemulsions.

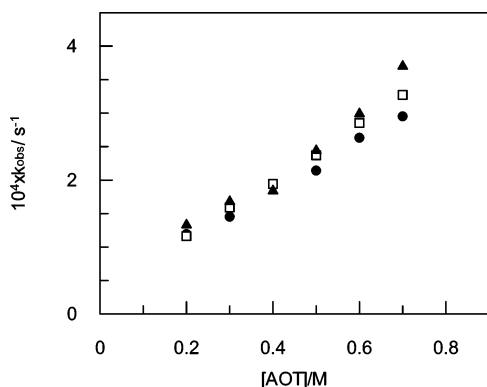


Figure 5. Influence of the AOT concentration on the transnitrosation reaction between NMBA and MNTS in water/AOT/o-xylene microemulsions: [MNTS] = 2×10^{-3} M; (●) $W = 9.3$; (□) $W = 11.1$; (▲) $W = 13.0$.

On the basis of this model, the equilibrium partition constant of NMBA between the AOT film and oil can be expressed as

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

The expression relating k_{obs} to the microemulsion composition,

$$\frac{[NMBA]_t}{k_{obs} \bar{V}_{AOT} [AOT]} = \frac{(K_{oi}^{NMBA} + Z)(K_{oi}^{MNTS} + Z)}{k_2^i K_{oi}^{NMBA} K_{oi}^{MNTS}} \quad (9)$$

was obtained similarly as that for PIP. On the assumption of a constant K_{oi}^{MNTS} —which was previously determined for the reaction with PIP—the kinetic parameters (K_{oi}^{NMBA} and k_2^i) were obtained by fitting the experimental values to this equation (see Figure 6 and Table 1).

For comparison with water/AOT/isooctane microemulsions, tests involving the use of the same amine and MNTS concentrations over a wide range of microemulsion compositions were performed at the same temperature (50 °C). Values of W and the AOT concentration were changed over the ranges 11.1–

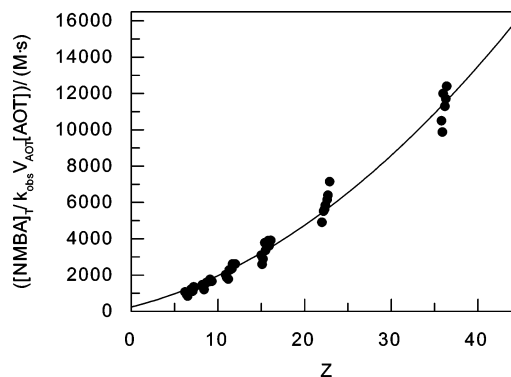


Figure 6. Variation of the rate constant with parameter Z for water/AOT/o-xylene microemulsions. The dashed line corresponds to the fitting of eq 9.

29.6 and 0.1–0.5 M, respectively. Application of the same pseudophase model yielded an identical equation (eq 9), to which the experimental values were fitted in order to obtain the kinetic parameters for the transnitrosation reaction between MNTS and NMBA in water/AOT/isooctane microemulsions at 50 °C (see Table 1). As can be seen, the association constant of NMBA to the surfactant film, K_{oi}^{NMBA} , was similar in the two types of microemulsion. Worth special note is the value of the rate constant, k_2^i , in the xylene microemulsions, which was roughly one-half that in the isooctane microemulsions. This may be a result of the interphase in the former being less polar by effect of the penetration of the continuous medium (xylene) into the surfactant film or of less extensive hydration of AOT in these systems.

The study was completed by examining the reaction of NMBA with MNTS in water/AOT/*m*-xylene and water/AOT/*p*-xylene microemulsions. The choice of this amine was dictated by the fact that, as shown earlier, it partitioned between the AOT film and oil, so it must have been more markedly affected by the structural difference between the two xylene isomers. The pseudophase model used was identical with that depicted in Scheme 3, so the equation relating k_{obs} to parameters W and Z for the microemulsion, eq 9, was also identical. The results are shown in Table 1.

Discussion

1. Water/AOT/Isooctane Microemulsions vs Water/AOT/o-Xylene Microemulsions. The interfacial rate constants obtained from eqs 7 and 9 are listed in Table 1. The k_w/k_2^i ratio is a measure of inhibition of the reaction in a microemulsion by effect of the polarity of the interphase relative to water. The $[(k_w/k_2^i)]^{iso}/[(k_w/k_2^i)]^{xyl}$ ratio allowed us to compare the degree of inhibition resulting from water/AOT/isooctane and water/AOT/o-xylene microemulsions. On the basis of the results, the reaction between MNTS and NMBA was found to be more markedly inhibited in the xylene-containing microemulsions. Thus, the reaction was 2.5 times faster in the isooctane microemulsions than in the o-xylene microemulsions. Also, the

Table 1. Kinetic Parameters Obtained by Fitting the Experimental Data for Water/AOT/Xylene and Water/AOT/Isooctane Microemulsions at 50 °C to Equations 7 and 9

microemulsion	amine	K_{wi}^{PIP}	K_{oi}^{NMBA}	K_{oi}^{MNTS}	k_2^i ($M^{-1} \cdot s^{-1}$)
water/AOT/o-xylene	NMBA		20.1 ± 2.6	2.3	$(4.07 \pm 0.03) \times 10^{-3}$
water/AOT/ <i>m</i> -xylene	NMBA		12.8 ± 2.9	2.3	$(4.44 \pm 0.07) \times 10^{-3}$
water/AOT/ <i>p</i> -xylene	NMBA		12.5 ± 2.6	2.3	$(4.81 \pm 0.07) \times 10^{-3}$
water/AOT/isooctane	NMBA		13.8 ± 2.0	7.7	$(1.03 \pm 0.11) \times 10^{-2}$
water/AOT/o-xylene	PIP	10.6 ± 2.3		2.3	$(2.94 \pm 0.33) \times 10^{-2}$
water/AOT/isooctane	PIP	20.6 ± 2.4		7.7	$(4.48 \pm 0.03) \times 10^{-2}$

Table 2. Kinetic Parameters Obtained by Fitting the Experimental Data for Water/AOT/Isooctane Microemulsions to Equations 7 and 9

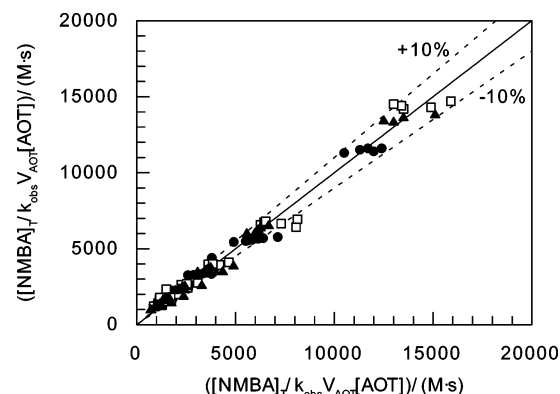
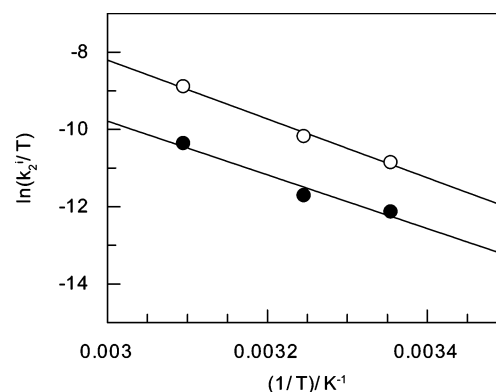
amine	T (°C)	K_{wi}^{PIP}	K_{oi}^{NMBA}	K_{oi}^{MNTS}	k_2^i ($M^{-1}\cdot s^{-1}$)
PIP	25	9.5 ± 0.7		11.0	$(5.81 \pm 0.03) \times 10^{-3}$
PIP ³¹	35	13.1		10.1	1.18×10^{-2}
PIP	50	20.6 ± 2.4		7.7	$(4.48 \pm 0.03) \times 10^{-2}$
NMBA	25		25.0 ± 1.0	11.0	$(1.62 \pm 0.04) \times 10^{-3}$
NMBA ³¹	35		30	10.1	2.55×10^{-3}
NMBA	50		13.8 ± 2.0	7.7	$(1.03 \pm 0.11) \times 10^{-2}$

reaction with PIP was 1.5 times faster in the former than in the latter. The increased inhibitory effect of the xylene microemulsions was a result of the decreased polarity of the reaction medium (viz., the AOT film between the continuous medium and the water). The polarity of the interphase is a function of the amount of water and oil present. Structural evidence suggests that penetration of the continuous medium into the AOT film is easier for the aromatic medium than for isooctane. However, the polarity change induced by an increase in droplet size is slightly more substantial in isooctane microemulsions than in xylene microemulsions. Probably, as W increases, the number of water molecules at the interphase in the isooctane microemulsion also increases and the interphase polarity is slightly higher, as reflected in the kinetic data. Also, the fact that the working temperature used was higher than the percolation temperature for water/AOT/isooctane microemulsions may have altered the polarity of the system.

The equilibrium constants (K_{wi}^{PIP} , K_{oi}^{NMBA} , and K_{oi}^{MNTS}) are suggestive of the way the reactants partition between the three pseudophases in the two reactions. Worth special note is the rather small value of the equilibrium partition constant of MNTS between the continuous medium and the AOT film, K_{oi}^{MNTS} , which may be a result of the increased rigidity of the surfactant film in the water/AOT/xylene microemulsions. In any case, an increase in temperature similarly decreases K_{oi}^{MNTS} for water/AOT/isooctane microemulsions. The equilibrium partition constant between water and PIP, K_{wi}^{PIP} , exhibits a different behavior; thus, an increase in temperature facilitates the migration of PIP to the *pseudo*-reaction phase in water/AOT/isooctane microemulsions (see Table 2). This result also seems to confirm the presence of an amount of water at the interphase that increases as the temperature is raised. In any case, these results should be taken with some reservations as the equilibrium constant values obtained by fitting the experimental values differ less markedly than the rate constants.

2. Water/AOT/*o*-Xylene, Water/AOT/*m*-Xylene, and Water/AOT/*p*-Xylene Microemulsions. Stereochemical changes in the aromatic additive or in the nature of the oil of a microemulsion are known to alter its percolation temperature.^{26,30–32} Thus, Moulik et al.³⁰ found the hydrotropes 2-methoxyphenol, 4-methoxyphenol, 5-methoxyresorcinol, and 3-methoxycatechol to influence the dynamic percolation process. These compounds can either assist percolation by way of bridging a pair of droplets for efficient fusion and ion transfer or delay it through blocking and resisting fusion of the droplets to hinder mass transfer. The position of the hydroxyl groups in the phenolic hydrotrope molecule is the decisive factor for its action on the dynamics of the process. Thus, the monohydroxy compounds resist percolation, whereas the dihydroxy compounds assist it. The percolation efficiency increases in the following sequence: ortho < meta < para. The threshold temperature is directly related to the hydrotrope concentration.

Our purpose was to examine the kinetic implications of changes in the continuous medium of the microemulsion.

**Figure 7.** Plot of experimental vs theoretical data for the transnitrosation reaction between MNTS and NMBA in water/AOT/*o*-xylene (●), water/AOT/*m*-xylene (□), and water/AOT/*p*-xylene (▲) microemulsions.**Figure 8.** Influence of temperature on k_2^i for the reactions of MNTS with PIP (○) and NMBA (●) in water/AOT/isooctane microemulsions.

However, the results (Table 1) revealed the virtual absence of differences between the three xylenes used as continuous media. Figure 7 testifies to the good fit of the experimental data to the equation provided by the pseudophase model for the three types of xylene microemulsions.

3. Activation Parameters. The study was completed with the determination of the activation parameters for the nitroso group transfer reaction from MNTS to the secondary amines NMBA and PIP in water/AOT/isooctane microemulsions. We examined the influence of temperature on the bimolecular rate constant for the two processes and found a linear relationship between $\ln(k/T)$ and $1/T$ in both cases (Figure 8), consistent with the Eyring equation ($r^2 = 0.9928$ and $r^2 = 0.9600$, respectively, for PIP and NMBA). Thus, ΔH^\ddagger was found to be 63.3 ± 5.4 kJ·mol⁻¹ for piperazine and 57.8 ± 11.8 kJ·mol⁻¹ for *N*-methylbenzylamine, and $\Delta S^\ddagger = -75.6 \pm 10.6$ J·mol⁻¹·K⁻¹ for the former and -105.5 ± 43.3 J·mol⁻¹·K⁻¹ for the latter, all in water/AOT/isooctane microemulsions.³³ These values are consistent with those previously obtained in aqueous media³⁴ for the reactions of MNTS with 4-hydroxyproline ($\Delta H^\ddagger = 55.3$ kJ·mol⁻¹, $\Delta S^\ddagger = -81$ J·mol⁻¹·K⁻¹), 3-quinuclidol ($\Delta H^\ddagger = 55.5$ kJ·mol⁻¹, $\Delta S^\ddagger = -87$ J·mol⁻¹·K⁻¹) and azide ion ($\Delta H^\ddagger = 60.2$ kJ·mol⁻¹, $\Delta S^\ddagger = -78$ J·mol⁻¹·K⁻¹), which confirms the accuracy of the pseudophase model in predicting kinetic parameters for microemulsions. The values of thermodynamic parameters for our reactions prove that changes in the rate constant are due to compartmentalization of reactants and changes in the relative concentration in the different pseudophases and that there is no effect upon the chemical mechanism of nitrosation.

Conclusions

Nitroso group transfer from MNTS to secondary amines (NMBA and PIP) in water/AOT/xylene microemulsions can be interpreted in the light of the micellar pseudophase model. The most salient feature of this medium is its nonpercolative nature, which hinders mass transfer in the three pseudophases. Also, the fact that the continuous medium is provided by an aromatic compound hinders penetration of the continuous medium into the surfactant film. Although the way the amine partitions is dictated by its hydrophobicity, the reaction invariably takes place at the interphase between the water droplets and the continuous medium. The ratio between the bimolecular rate constants allowed us to compare the inhibitory effect of water/AOT/isooctane and water/AOT/xylene microemulsions. Thus, the reactions of MNTS with NMBA and PIP were found to be more strongly inhibited in the xylene microemulsions than in the isooctane microemulsions. The increased inhibitory effect of the xylene microemulsions is a result of the decreased polarity at the reaction site (viz., the interphase between the continuous medium and the water). The proposed model accounts highly accurately for the kinetic results obtained in water/AOT/xylene microemulsions. This is the most important conclusion of this work, as it exposes the suitability of the pseudophase model, which is independent of structural connotations and internal dynamics of the system and assumes the water, AOT, and continuous medium to be separate continuous phases.

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