Reactivity of Typical Solvolytic Reactions in SDS and TTABr Water-in-Oil Microemulsions

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The kinetics of the solvolysis reactions of diphenylmethyl chloride, 4-nitrophenyl chloroformate, benzoyl chloride, anisoyl chloride, and bis(4-nitrophenyl)carbonate were studied in isooctane/SDS/1-hexanol/water and isooctane/TTABr/1-hexanol/water microemulsions with a constant [1-hexanol]/[surfactant] ratio of 5. The results were interpreted by means of a pseudophase model for (isooctane + hexanol)/(surfactant + hexanol)/water systems, the distribution of hexanol between isooctane and surfactant being calculated from previously published data. The intrinsic rate constant for the reaction in the interfacial pseudophase varied with the water content of the microemulsion droplets in a way that depended on both the nature of the surfactant and the mechanism of the reaction.

Introduction

Three-component water-in-oil (w/o) microemulsions are transparent, thermodynamically stable, isotropic systems consisting of reverse micelles (water droplets surrounded by a monolayer of surfactant) dispersed in a nonpolar bulk solvent.[1,2] The most intensively studied three-component w/o microemulsions have been systems of the form water/AOT/oil, where AOT is sodium bis(2-ethylhexyl)sulfosuccinate.[3] An important property of these systems is the highly structured nature of the water at the interface when the [H_2O]/[surfactant] ratio W is small.[4] For $W \leq 6$, all water molecules are immobilized by strong interactions with the ion pair formed by the polar head of AOT and its counterion. With $W \approx 11$ the ion pairs have dissociated, but all water is still engaged in solvation of the individual anions and cations. Only for $W > 12$ are there water molecules with properties approximating those of the molecules of ordinary bulk water. These alterations in the properties of water can have a significant influence on the kinetics of reactions taking place at the micellar interface.

If a surfactant has a small packing parameter,[5] as is the case of sodium dodecyl sulphate (SDS)[6,7] and alkyl ammonium surfactants,[8] it may only form a stable microemulsion in the presence of a fourth component, the "cosurfactant" (usually an alcohol[7] or a carboxylic acid[9]). Spectroscopic studies of the cosurfactant action of alcohols in oil-in-water microemulsions and direct micelles have shown that the alcohol molecules reduce the surface charge density of the micelle by intercalating among the interfacial surfactant molecules and increasing the separation between their ionic headgroups.[10] Alcohol cosurfactants also influence the kinetics of reactions carried out in o/w microemulsions and direct micelles both by changing the polarity of the intramicellar medium and by diluting the reagents therein.[11,12] Four-component w/o microemulsions have been investigated as regards the influence of alcoholic cosurfactants on the fluidity of the interface and droplet−droplet interaction,[13] but the effects of such cosurfactants on the properties of the micellar water and on the kinetics of reactions carried out in these media have not yet been clarified.

In this work we studied the behavior, in four-component w/o microemulsions, of a series of solvolytic reactions (the solvolyses of diphenylmethyl chloride, 4-nitrophenyl chloroformate, benzoyl chloride, *p*-anisoyl chloride, and bis(4-nitrophenyl)carbonate; see Scheme 1) whose sensitivity to the physical

SCHEME 1
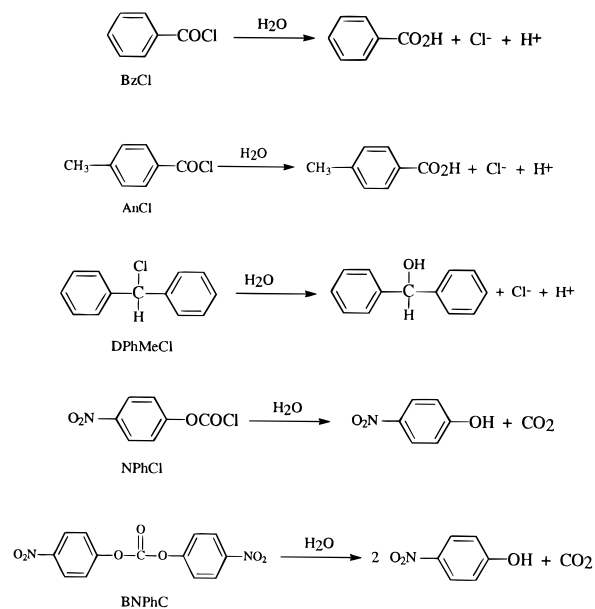
properties of the reaction medium has in the past been used to study the effects of additives on the structure of water[14,15] and whose behavior in water/AOT/isooctane microemulsions we have recently reported.[16] Since all the substrates used are very poorly soluble in water, it may be assumed that in microemulsions they are present only in the nonpolar and interfacial regions and that the solvolysis reactions take place only in the latter. This both simplifies analysis of kinetic data and allows interpretation of results directly in terms of the structure of the interface and interfacial water. The microemulsion systems used were water/SDS/1-hexanol/isooctane, which allowed evaluation of the effects of 1-hexanol by comparison with the earlier results[16] for water/AOT/isooctane (both AOT and SDS being anionic surfactants), and water/TTABr/1-hexanol/isooctane (TTABr = tetradecyltrimethylammonium bromide), which allowed evaluation of the effects of surfactant charge[17] by comparison with the results for water/SDS/1-hexanol/isooctane.

Experimental Section

Sodium dodecyl sulfate (SDS) and tetradecyltrimethylammonium bromide (TTABr) were supplied by Sigma and used without further purification. 1-Hexanol and isooctane were

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Aldrich products of the maximum commercially available purity. Deuterated water (99.7% D) was supplied by the Spanish Nuclear Energy Board. Diphenylmethyl chloride (DPhMeCl), 4-nitrophenyl chloroformate (NPhCl), benzoyl chloride (BzCl) and *p*-anisoyl chloride (AnCl) (all from Aldrich), and bis(4-nitrophenyl) carbonate (BNPhC) (from Sigma) were of the maximum commercially available purity. Microemulsions of the desired compositions were prepared from stock water/surfactant/1-hexanol/isooctane microemulsions by addition of appropriate amounts of isooctane and/or water.

The solvolysis reactions were carried out in a Spectronic 3000 diode array or Kontron-Uvikon spectrophotometers fitted with thermostated cell holders (all experiments were carried out at 25 °C) and were followed by monitoring the absorbance at the maximum of the spectrum of the aromatic products (238 nm for DPhMeCl, 340 nm for NPhCl, 288 nm for BzCl, 290 nm for AnCl, and 315 nm for BNPhC). The integrated first-order expression

$$A_t = A_0 + (A_\infty - A_0)\exp(-k_o t) \qquad (1)$$

(where A_0, A_t, and A_∞ are the absorbances at times 0, t and infinity, respectively, and k_o is the observed first-order constant) was fitted to the absorbance−time data by nonlinear regression to avoid the problems associated with the linearization of exponential data.[18]

^{1}H NMR spectra were recorded in a Brucker AMX300 apparatus operating at 300.1 MHz with a coaxial tube of DMSO-d_6 for locking.

Results and Discussion

Incorporation of Alcohol in the Interface. Microemulsions and other types of surfactant aggregates such as monolayers, micelles, and vesicles all have an interfacial region that separates the oil and water regions and is composed of surfactant headgroups, associated counterions and co-ions, and any added polar additives. Determining the compositions of aggregate interfaces is an active area of research because interfacial compositions, not stoichiometric concentrations of components, reflect the balance of forces controlling aggregate structure and stability.[19]

To simplify analysis of the kinetic results, it was assumed that the concentration of the very poorly water-soluble 1-hexanol in the aqueous pseudophase was negligible, and the microemulsion was accordingly treated as an (isooctane + hexanol)/(surfactant + hexanol)/water pseudophase system, the distribution of hexanol between isooctane and surfactant being calculated using the partition coefficient

$$K_2 = ([hex_i][isooctane])/([hex_o][surfactant]) \qquad (2)$$

where [hex_i] and [hex_o] are the bulk concentrations of interfacial and oil-phase hexanol, respectively. K_2 was obtained from the expression

$$K^w_o = K_2/K_1 \qquad (3)$$

where K^w_o is the partition coefficient for the distribution of 1-hexanol in a two-phase water/isooctane system (estimated as $K^w_o = 0.059$ on the grounds that it must be close to the coefficients for octane/water, decane/water, and dodecane/water,[20] and

$$K_1 = ([hex_i][H_2O])/([hex_w][surfactant]) \qquad (4)$$

(where [hex_w] is the bulk concentrations of aqueous-phase

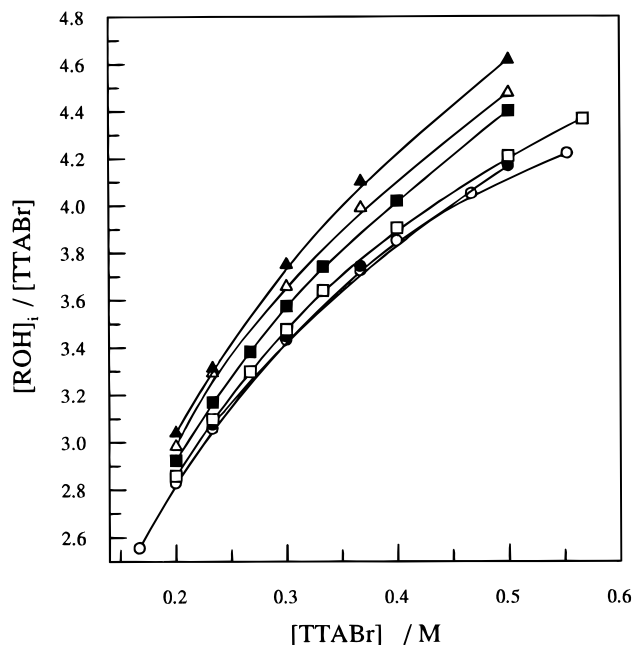**Figure 1.** Dependence of [hex$_i$]/[TTABr] on [TTABr] in isooctane/TTABr/1-hexanol/water w/o microemulsions at 25 °C for [hex]/[TTABr] = 5: (○) $W = 3$; (●) $W = 5$; (□) $W = 10$; (■) $W = 20$; (△) $W = 30$; (▲) $W = 40$.

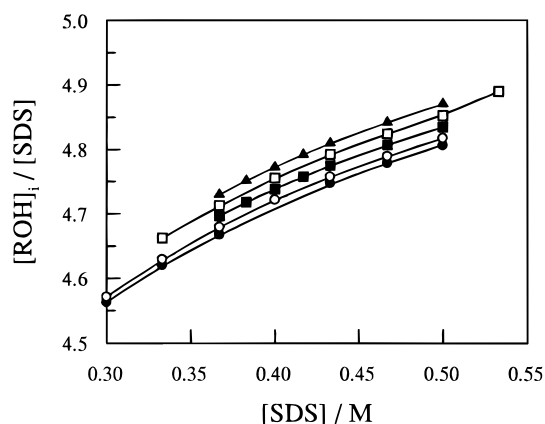**Figure 2.** Dependence of [hex$_i$]/[SDS] on [SDS] in isooctane/SDS/1-hexanol/water w/o microemulsions at 25 °C for [hex]/[SDS] = 5: (●) $W = 7$; (○) $W = 10$; (■) $W = 15$; (□) $W = 20$; (▲) $W = 25$.

hexanol) was taken from published data for direct micelles[21] as $K_1 = 2459$ for SDS systems and $K_1 = 550$ for TTABr systems; these values of K^w_o and K_1 afford K_2 values of $K_2 = 145$ for SDS systems and $K_2 = 32.4$ for TTABr systems. Figures 1 and 2 show how the mole ratio [hex$_i$]/[surfactant] varied with [surfactant] in TTABr and SDS systems, respectively. The fact that the interfacial hexanol content was greater in SDS systems than in TTABr systems is in keeping with a previous report that SDS is more reluctant to form inverse micelles than TTABr.[6d]

Analysis of Kinetic Data. For each substrate, all kinetic experiments were performed using the same concentration of substrate, which was low enough not to perturb micelle structure. For each of various values of W, a series of experiments were carried out in which the surfactant concentration was varied while the [hex]/[surfactant] ratio was kept equal to 5.

Because of their poor solubility in water, it was hypothesized that all the substrates, such as 1-hexanol, would be distributed exclusively between the isooctane pseudophase and the interface and that the reaction with water would accordingly take place only in the latter region (Scheme 2).[22,23]
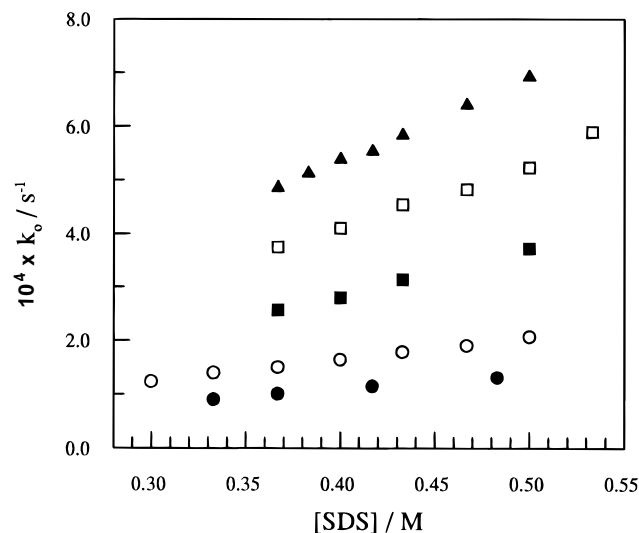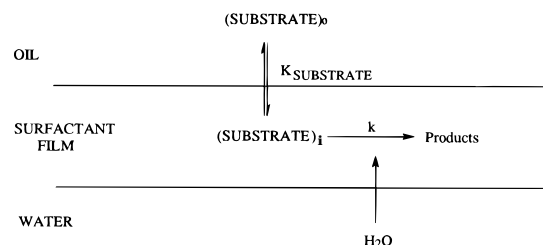
Figure 3. Influence of [SDS] on the first-order pseudoconstant k_o for the solvolysis of benzoyl chloride in isooctane/SDS/1-hexanol/water w/o microemulsions with [hex]/[SDS] = 5 and various values of W = [H$_2$O]/[SDS] at T = 25 °C: ($\bullet$) W = 7; ($\bigcirc$) W = 10; ($\blacksquare$) W = 15; ($\square$) W = 20; ($\blacktriangle$) W = 25.

SCHEME 2

According to Stilbs,[24] the partition coefficient of substrate was defined as

$$K_{sub} = \{[sub_i]([isooctane] + [hex_o])/([sub_o][surfactant])\} \tag{5}$$

(An analogous definition has previously been used successfully in a study of direct micellar systems[12].) These hypotheses lead to the following expression for the first-order pseudoconstant k_o:

$$k_o = kK_{sub}/(K_{sub} + Z^*) \tag{6}$$

where k is the intrinsic rate constant for the reaction in the interfacial region and

$$Z^* = ([isooctane] + [hex_o])/[surfactant] \tag{7}$$

is calculable using eq 2. For each substrate, the adequacy of the above simplifying hypotheses, and of the pseudophase model employed, was tested by verifying whether, in accordance with eq 6, $1/k_o$ depended linearly on Z^* and whether the values of K_{sub} obtained from these plots were independent of W as required by the pseudophase model.

Solvolysis of Benzoyl Chloride. In the experiments with BzCl in SDS microemulsions, the SDS concentration was varied between 0.30 and 0.53 M for each of a number of W values ranging from 7 to 25 (it was not possible to use lower W values because of the reluctance of SDS to form stable reverse micelles without an appreciable quantity of water).[6d] Figure 3 shows that the reaction rate increased significantly with SDS concentration and with W, and Figure 4 shows that plots of $1/k_o$ against Z^* were linear as required by eq 6. In the experiments in
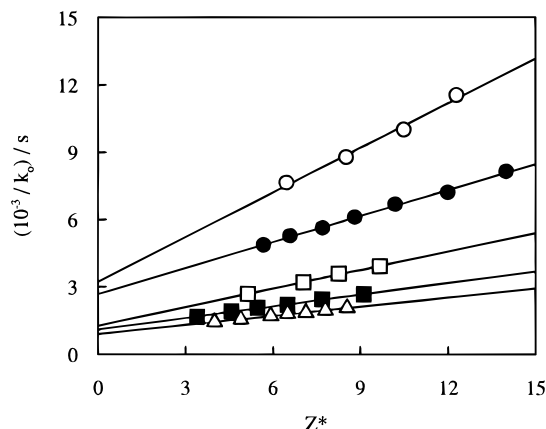

Figure 4. Data of Figure 3 linearized as plots of $1/k_o$ against Z^* in accordance with eqs 6 and 7: ($\triangle$) W = 2.5; ($\blacksquare$) W = 20; ($\square$) W = 15; ($\bullet$) W = 10; ($\bigcirc$) W = 7.

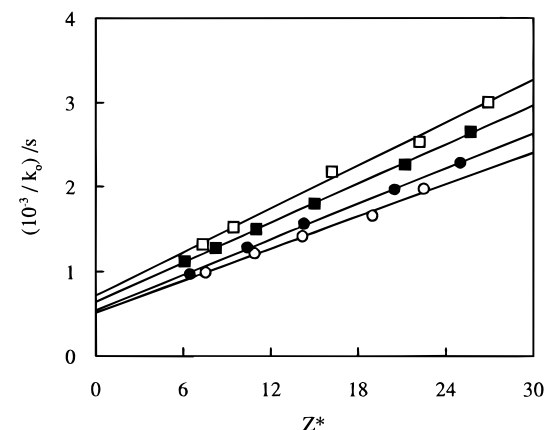**Figure 5.** Influence of Z^* = ([isooctane] + [hex$_o$])/[TTABr] on the reciprocal of the first-order pseudoconstant k_o for the solvolysis of benzoyl chloride in isooctane/TTABr/1-hexanol/water w/o microemulsions with [hex]/[TTABr] = 5 and various values of W = [H$_2$O]/[TTABr] at T = 25 °: ($\bigcirc$) W = 3; ($\square$) W = 5; ($\blacksquare$) W = 15; ($\bullet$) W = 20.

TABLE 1: Partition Coefficients K_{BzCl} and Intrinsic Solvolytic Rate Constants k for Benzoyl Chloride in Isooctane/SDS/1-Hexanol/Water and Isooctane/TTABr/1-Hexanol/Water w/o Microemulsions at 25 °C, Together with Published Values for k in Isooctane/AOT/Water Systems^a

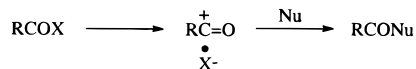|	AOT^b	SDS/1-Hexanol		TTABr/1-Hexanol	
W	k/s^{-1}	k/s^{-1}	K_{BzCl}	k/s^{-1}	K_{BzCl}
3	9.92×10^{-4}			1.94×10^{-3}	8.2
4	8.29×10^{-4}			1.96×10^{-3}	6.0
5	9.03×10^{-4}			1.39×10^{-3}	8.4
7	8.27×10^{-4}	3.10×10^{-4}	4.9	1.17×10^{-3}	11.4
10	9.64×10^{-4}	3.73×10^{-4}	6.9	1.65×10^{-3}	6.5
15	$\simeq 2.8 \times 10^{-3}$	7.76×10^{-4}	4.7	1.56×10^{-3}	8.3
20	$\simeq 3.3 \times 10^{-3}$	9.00×10^{-4}	6.5	1.85×10^{-3}	7.7
25	$\simeq 4.0 \times 10^{-3}$	1.10×10^{-3}	6.8	2.36×10^{-3}	6.6

^{a} [1-hexanol]/[surfactant] = 5. ^{b} *J. Phys. Chem.* **1995**, *99*, 12318.

TTABr microemulsions, the TTABr concentration was varied between 0.17 and 0.50 M for each of a number of W values ranging from 3 to 25; Figure 5 shows the linearity of plots of $1/k_o$ against Z^*. For both surfactants, Table 1 lists the values of k and K_{BzCl} obtained from the $1/k_o$ vs Z^* plots (in both cases, the W-independence of K_{BzCl} supports the validity of the pseudophase model used), together with values of k obtained previously[16] under similar conditions in water/AOT/isooctane microemulsions.

In water, the solvolysis of BzCl takes place via the formation of an acylium ion intermediate (Scheme 3),[25] but in mixtures

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SCHEME 3

$$RCOX \longrightarrow \overset{+}{R}C{=}O \overset{\bullet}{\underset{X^-}{}} \overset{Nu}{\longrightarrow} RCONu$$

of water with less polar solvents there is evidence that the reaction is a concerted process, albeit one in which cleavage of the C−Cl bond has progressed further than formation of the C−OH bond in the transition state.[26] In view of this, the W dependence of k in water/AOT/isooctane microemulsions has been explained[16] in terms of the effects of W on both the polarity of the interfacial medium and the nucleophilicity of interfacial water; the observed fall in k with W at W values greater than 10 is attributed to the decreasing availability of water for solvation of the leaving group, while the W independence of k at W values less than 10 is attributed to the continuing fall in interfacial polarity being offset by an increase in the nucleophilicity of the remaining water molecules, which are increasingly strongly bound to the anionic SDS headgroups.

In the SDS system with $W = 25$ used in this work, k was about 80 times smaller than the rate constant observed in water, $8.6 \times 10^{-2} \text{ s}^{-1}$,[27] and it decreased further with W. As in AOT systems, this decrease can be attributed to an increasing proportion of droplet water content being committed to solvation of the surfactant headgroups and hence being unavailable for solvation of the chloride ion. The fact that the $k-W$ curve did not flatten for SDS systems as it did in AOT systems seems likely to be due simply to the impossibility of using SDS systems with low enough W values. The fact that the values of k are smaller in SDS than in AOT seems unlikely to be due to any difference between SDS and AOT headgroups as to the degree to which they stabilize the transition state. Rather, it is attributable to the hexanol in the interface of the SDS systems being committed to solvation of headgroups and sodium ions, with the result that interfacial polarity is less in SDS than in AOT systems.

In TTABr systems, k remained virtually constant as W decreased. This may be explained as due to the k-reducing effect of decreasing interfacial polarity being offset by the catalytic effect of the alkylammonium salt,[25] which may be attributed to the structure of water being enhanced by the alkyl groups.[15,28] Since decreasing W means increasing TTABr concentration with respect to the aqueous phase, the catalytic effect of TTABr may be expected to increase with falling W. The value of k in all these systems was about 40 times less than in water and about the same as in AOT systems with $W = 15$.

Solvolysis of Anisoyl Chloride. As expected, the solvolysis of AnCl in both SDS and TTABr systems exhibited a linear dependence of $1/k_o$ on Z^*. Figure 6 illustrates this for TTABr systems, and Table 2 lists the corresponding values of K_{AnCl} and k, together with values of k for AOT systems.[16]

The results for AnCl differ from those for BzCl chiefly in that, for AnCl, k fell with W in both SDS and TTABr systems, whereas for BzCl k was practically independent of W in TTABr systems. This difference may be attributed to the greater S_N1 character of the AnCl reaction,[29,30] which makes it more sensitive to reduction in the polarity of interfacial water (when W decreases[31]) and less sensitive to the enhancement of water structure by TTABr (in fact, in water, alkylammonium bromides inhibit rather than catalyze the solvolysis of AnCl[25]). The greater sensitivity of the AnCl reaction to reduced polarity must also be the reason why in SDS systems the AnCl reaction rate fell by a factor of about 15 between $W = 20$ and $W = 7$, as against a factor of only about 3 for BzCl.
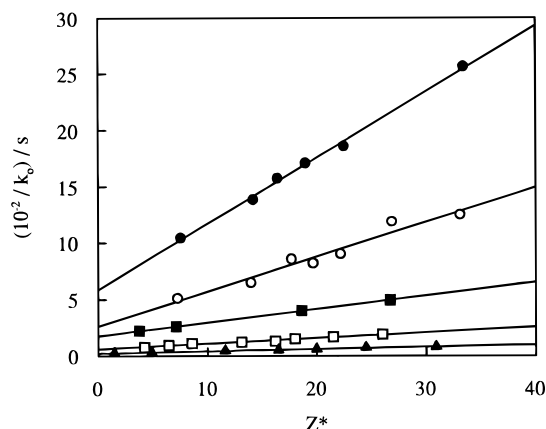

Figure 6. Influence of $Z^* = ([\text{isooctane}] + [\text{hex}_o])/[\text{TTABr}]$ on the reciprocal of the first-order pseudoconstant k_o for the solvolysis of anisoyl chloride in isooctane/TTABr/1-hexanol/water w/o microemulsions with $[\text{hex}]/[\text{TTABr}] = 5$ and various values of $W = [\text{H}_2\text{O}]/[\text{TTABr}]$ at $T = 25 \,°C$: (●) $W = 3$; (○) $W = 5$; (■) $W = 7$; (□) $W = 12$; (▲) $W = 25$.

TABLE 2: Partition Coefficients K_{AnCl} and Intrinsic Solvolytic Rate Constants k for Anisoyl Chloride in Isooctane/SDS/1-Hexanol/Water and Isooctane/TTABr/1-Hexanol/Water w/o Microemulsions at 25 °C, Together with Published Values for k in Isooctane/AOT/Water Systems[a]

	AOT[b]	SDS/1-Hexanol		TTABr/1-Hexanol		
W	k/s^{-1}	k/s^{-1}	K_{AnCl}	k/s^{-1}	K_{AnCl}	k^+/k^-
3	7.18×10^{-4}			1.71×10^{-3}	9.9	
4	1.31×10^{-3}					
5	2.64×10^{-3}			3.83×10^{-3}	8.5	
7	7.35×10^{-3}	2.28×10^{-3}	22.4	5.66×10^{-3}	14.8	2.48
10	1.53×10^{-2}	5.74×10^{-3}	19.6	1.07×10^{-2}	12.0	1.86
12	$\simeq 2.0 \times 10^{-2}$			1.63×10^{-2}	12.4	
15	$\simeq 3.0 \times 10^{-2}$	1.65×10^{-2}	12.2	2.16×10^{-2}	13.2	1.31
17	$\simeq 3.7 \times 10^{-2}$			2.39×10^{-2}	12.3	
20	$\simeq 4.5 \times 10^{-2}$	2.23×10^{-2}	24.9	3.32×10^{-2}	10.8	1.51
25	$\simeq 7.0 \times 10^{-2}$	3.53×10^{-2}	12.4	4.24×10^{-2}	12.3	1.20

^{a} [1-hexanol]/[surfactant] = 5. ^{b} *J. Phys. Chem.* **1995**, *99*, 12318.

Although the presence of 0.9 M Me$_4$NBr halves the rate of solvolysis of AnCl in 90:10 trifluoroethanol/water mixtures,[25] the reaction was faster in TTABr systems than in SDS systems. This may be attributed to the exit of the leaving group, Cl$^-$, being more favored by the presence of cationic TTABr headgroups than by that of anionic SDS headgroups. By contrast, Bunton et al.[17] found that in direct micelles the ratio k^+/k^- between the reaction rates in systems with cationic and anionic surfactants was only 0.1. This difference between the behaviors observed in w/o microemulsions and direct micelles may be attributed to a difference in the relative ease of stabilization of the acylium ion and the leaving group. In direct micelles, in which abundant water is available, solvation of the leaving group is fast and easy and the reaction is faster with anionic than with cationic surfactants because the former contribute to stabilization of the acylium ion. In w/o microemulsions, on the other hand, the contribution of the surfactant headgroup to "solvation" of the leaving group outweighs its contribution to stabilization of the acylium ion. This interpretation is in keeping with the finding that, in our experiments, the ratio k^+/k^- increased with decreasing W (Table 2).

Solvolysis of Diphenylmethyl Chloride. It is considered that the mechanism of the solvolysis of DPhMeCl is close to the S_N1 limit,[32] but in certain solvents non-first-order kinetics are observed because the carbocation is sufficiently dissociated to discriminate between the attacking solvent and other nucleophiles that may be present (including the chloride ion).[27,33] To

TABLE 3: Partition Coefficients $K_{DPhMeCl}$ and Intrinsic Solvolytic Rate Constants k for Diphenylmethyl Chloride in Isooctane/SDS/1-Hexanol/Water w/o Microemulsions at 25 °C, Together with Published Values for k in Isooctane/AOT/Water Systems[a]

| | AOT[b] | SDS/1-hexanol | |
W	k/s^{-1}	k/s^{-1}	$K_{DPhMeCl}$
7	9.36×10^{-4}	6.14×10^{-5}	6.9
10	1.35×10^{-3}	2.53×10^{-4}	5.7
15	$\simeq 2.8 \times 10^{-3}$	6.34×10^{-4}	7.1
20	4.66×10^{-3}	8.45×10^{-4}	11.5
25	6.42×10^{-3}	1.68×10^{-3}	5.2

[a] [1-Hexanol]/[surfactant] = 5. [b] *J. Phys. Chem.* **1995**, *99*, 12318.

avoid the extra risk of such complications that would have been occasioned by the use of TTABr, the solvolysis of DPhMeCl was studied only in SDS systems. Table 3 lists the values of k and $K_{DPhMeCl}$ estimated in the same way as for the other substrates, together with reaction rate data for AOT systems.

It has been suggested that in solvents of low polarity the solvolysis of diarylmethyl halides is slowed by internal return within a tight ion pair and that the rate-limiting reaction step may be the attack of the nucleophilic solvent on the ion pair,[34] but to distinguish experimentally between this mechanism and a direct nucleophile−substrate interaction in which the transition state exhibits extensive C−Cl bond breaking would require a means of trapping the ion pair. In any case, the tight ion pair mechanism is certainly not active in the solvolysis of diarylalkyl halides in solvents with low water content, since these latter reactions exhibit common ion effects proving the formation of the free carbocation, which is therefore presumably also formed in dry solvents, albeit with a shorter lifetime.[35] Furthermore, although it might be supposed that the carbocation should be sufficiently stabilized by delocalization of charge for stabilization by external agents to have little effect on the kinetics of the reaction (especially since, in S_N1 reactions, solvation of the leaving group is generally more important than solvation of a bulky, relatively stable carbocation),[36] the fact is that arylalkyl substrates with quite different extents of charge delocalization are similarly affected by the nature of the reaction medium.[37]

In this work, the solvolysis of DPhMeCl was slower in SDS than in AOT systems, which was expected and was attributed, as in the cases of BzCl and AnCl, to the lower polarity caused by the presence of hexanol in the former. Again, since the polarity of interfacial water falls with W, the factor of 27.4 by which the reaction rate in SDS systems fell when the water content was reduced from $W = 20$ to $W = 7$ is in keeping with the reaction of DPhMeCl being more purely S_N1 than those of AnCl and BzCl, for which the corresponding factors were 15.5 and 3.5.

Solvolysis of 4-Nitrophenyl Chloroformate. In water, the mechanism of the solvolysis of NPhCl is similar to that of addition to the carbonyl group of carbonate esters or acid anhydrides in which the rate-limiting process is a nucleophilic addition.[27] In w/o AOT microemulsions, the reaction rate increases as W falls because of the increasing nucleophilicity of the interfacial water,[38] which is caused by increasingly strong hydrogen-bonding interaction with the AOT headgroups.[16]

Table 4 lists the values of k and K_{NPhCl} determined in SDS and TTABr systems in this work, together with the earlier k results for AOT systems.

The absence, in SDS systems, of the increase in k with decreasing W that is exhibited by the reaction in AOT systems is attributed simply to the impossibility of preparing stable SDS microemulsions with low enough W for the nucleophilicity of the interfacial water to be markedly increased by interaction

TABLE 4: Partition Coefficients K_{NPhCl} and Intrinsic Solvolytic Rate Constants k for 4-Nitrophenyl Chloroformate in Isooctane/SDS/1-Hexanol/Water and Isooctane/TTABr/1-Hexanol/Water w/o Microemulsions at 25 °C, Together with Published Values for k in Isooctane/AOT/Water Systems[a]

| | AOT[b] | SDS/1-Hexanol | | TTABr/1-Hexanol | |
W	k/s^{-1}	k/s^{-1}	K_{NPhCl}	k/s^{-1}	K_{NPhCl}
3	4.76×10^{-2}			6.16×10^{-2}	11.7
4	3.24×10^{-2}			6.17×10^{-2}	14.1
5	2.93×10^{-2}			6.55×10^{-2}	13.2
7	2.32×10^{-2}	5.36×10^{-2}	3.1	6.82×10^{-2}	12.7
10	1.96×10^{-2}	4.79×10^{-2}	4.1	7.80×10^{-2}	11.1
15	$\simeq 1.7 \times 10^{-2}$	5.53×10^{-2}	3.4	6.85×10^{-2}	14.5
20	$\simeq 1.5 \times 10^{-2}$	5.36×10^{-2}	3.6	6.84×10^{-2}	13.5
25	$\simeq 1.5 \times 10^{-2}$	4.86×10^{-2}	4.3	7.08×10^{-2}	12.2

[a] [1-hexanol]/[surfactant] = 5. [b] *J. Phys. Chem.* **1995**, *99*, 12318.
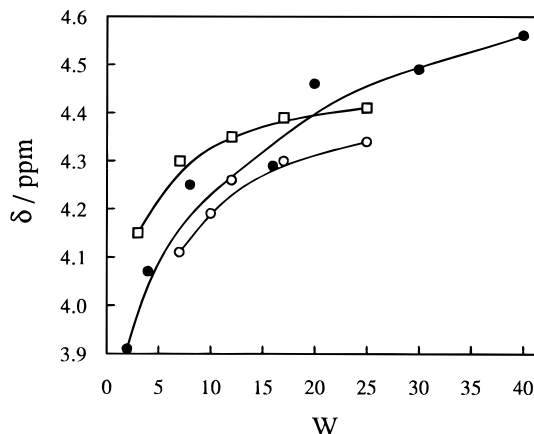
Figure 7. Influence of $W = $ [H$_2$O]/[surfactant] on the ^{1}H NMR chemical shift of the protons of water in isooctane/SDS/1-hexanol/water, isooctane/TTABr/1-hexanol/water, and isooctane/AOT/water w/o microemulsions: (●) AOT; (○) SDS; (□) TTABr.

with the surfactant headgroups. The possibility that there might be a difference in kind between water−surfactant interactions in AOT and SDS systems was ruled out by investigating the W dependence of the ^{1}H NMR signals of the water in isooctane/SDS/1-hexanol/water and isooctane/TTABr/1-hexanol/water microemulsions and by comparing them with published data for AOT/(isooctane or cyclohexane)/water systems.[39] The parallelism between the $\delta-W$ curves for SDS and AOT systems (Figure 7) suggests that there is no radical dissimilarity between the water−headgroup interactions in these microemulsions. In both cases, the marked shift to higher field as W decreases indicates that the predominant effect of the sodium counterion, the concentration of which increases with decreasing W, is to shield the H$_2$O protons by breaking hydrogen bonds rather than to deshield them by polarizing the water molecule.[40] That the upfield shift is much smaller in TTABr systems than in AOT and SDS systems seems likely to be a result of the "structure-enhancing" property of tetraalkylammonium salts.[28]

In TTABr systems, the rate constant k was slightly greater than in water, which is attributed to the enhancement of the nucleophilicity of interfacial water by the "structure-enhancing" surfactant, and hardly varied with W. The latter behavior is attributed, as in the case of BzCl, to the enhancement of nucleophilicity increasing with effective surfactant concentration as W fell, and so offsetting the k-reducing effect of decreasing interfacial polarity.

Solvolysis of Bis(4-nitrophenyl) Carbonate. The solvolysis of BNPhC was only studied in TTABr systems by using BNPhC concentrations of about 4×10^{-5} M and varying the TTABr concentration over the range 0.17−0.67 M for each value of

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TABLE 5: Partition Coefficients K_{BNPhC} and Intrinsic Solvolytic Rate Constants (k_H and k_D) for Bis(4-Nitrophenyl) Carbonate in Isooctane/TTABr/1-Hexanol/Water (H_2O and D_2O, Respectively) w/o Microemulsions at 25 °C[a]

	H_2O		D_2O		
W	k_H/s^{-1}	K_{BNPhC}	k_D/s^{-1}	K_{BNPhC}	k_H/k_D
3	6.84×10^{-5}	34.1	4.38×10^{-5}	36.4	1.56
4	7.52×10^{-5}	86.5	4.80×10^{-5}	47.9	1.57
5	9.28×10^{-5}	60.4	5.77×10^{-5}	45.4	1.61
7	1.23×10^{-4}	48.6	6.82×10^{-5}	43.9	1.80
10	1.38×10^{-4}	50.4	6.94×10^{-5}	41.2	1.99
15	1.66×10^{-4}	48.7	7.38×10^{-5}	39.9	2.25
20	1.72×10^{-4}	43.2	7.63×10^{-5}	40.2	2.25
25	1.74×10^{-4}	42.5	7.95×10^{-5}	36.6	2.19
30	1.95×10^{-4}	33.9	7.91×10^{-5}	36.8	2.46
40	1.99×10^{-4}	37.1	7.56×10^{-5}	39.4	2.63

[a] [1-hexanol]/[surfactant] = 5.
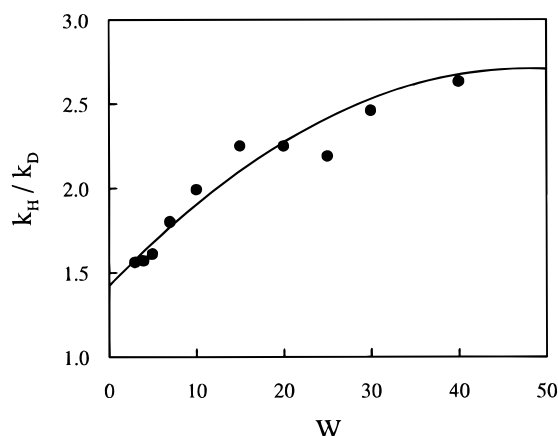
Figure 8. Influence of W = [H_2O]/[TTABr] on the solvent isotope effect k_H/k_D for the solvolysis of bis(4-nitrophenyl) carbonate in isooctane/TTABr/1-hexanol/water w/o microemulsions at 25 °C.

SCHEME 4
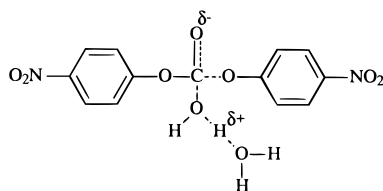
W. Table 5 lists the values of k and K_{BNPhC} obtained for both isooctane/TTABr/1-hexanol/H_2O and isooctane/TTABr/1-hexanol/D_2O systems, together with the k_H/k_D ratio.

The solvolysis of BNPhC involves two molecules of water, one of which acts as an attacking nucleophile and the other as a catalytic base that removes a proton from the former (Scheme 4).[41] In w/o AOT microemulsions,[16] a slight decrease in k with decreasing W is attributed to the decreasing availability of water for catalysis (reflected by a decrease in the solvent isotope effect) and the decrease in the basicity of such water as is available,[39] predominating over the k-increasing increase in the nucleophilicity of interfacial water as W falls. With the cationic surfactant used in the present work, both the nucleophilicity and the polarity of interfacial water must fall with W. In keeping with this, in TTABr systems k falls by a factor of 2.9 as W falls from 30 to 3, as against a factor of only 2.2 for AOT systems (Table 5). The fact that, as W falls from 30 to 3, the k_H/k_D ratio falls by only a factor of 1.6 in TTABr systems (Table 5 and Figure 8), as against 2.4 in AOT systems, may likewise be attributed to the different effects of W on the nucleophilicity of water in the two kinds of system, since the increasingly

nucleophilic water of AOT systems will have less need of catalytic assistance.

Conclusions

We have used a method for estimating the distribution of hexanol between isooctane and surfactant. To simplify, it was assumed that the concentration of the very poorly water-soluble 1-hexanol in the aqueous pseudophase was negligible, and the microemulsion was accordingly treated as an (isooctane + hexanol)/(surfactant + hexanol)/water system.

The alcohol required as cosurfactant to stabilize w/o microemulsions based on SDS and TTABr reduces interfacial polarity and thereby also tends to reduce the reaction rates of solvolysis reactions taking place at the interface. As W falls, the nucleophilicity of interfacial water is probably increased in SDS systems by increasing the interaction with headgroups, and in TTABr systems by the structure-enhancing properties of the alkylammonium salt, whose effective concentration increases with falling W. The W dependence of the intrinsic rate constant for solvolysis at the interface depends on the solvolytic mechanism.

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