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Influence of the Oil on the Properties of Microemulsions as Reaction Media

Luis García-Río,*[a] Ana Godoy,[a] and Pedro Rodríguez-Dafonte[a]

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The influence of the nature of the continuous medium on various properties of a wide range of water-in-oil (w/o) microemulsions was examined. ^{1}H NMR spectroscopy allowed to determine the properties of water in the studied systems and the way they are affected by the solvent to be elucidated. Changes in interfacial polarity were examined from the ^{13}C NMR signals of the surfactant molecule sodium bis(2-ethylhexyl)sulfosuccinate (AOT). Chemical shifts were found to vary with the water content of the microemulsion. The variation of the carbon chemical shift as a function of the water-to-surfactant concentration ratio (W) was used as an indirect measure of polarity changes at the microemulsion interface. The kinetic effects of the microemulsion composition on the solvolysis of anisoyl chloride were studied, and the reagent was found to react with water at the microemulsion interface alone. Based on both kinetic and NMR results, the solvolysis rate constants of anisoyl chloride decrease with increasing penetration of the oil into the interface. Also, the resonance signals for the water H atoms were found to change in parallel with the solvolysis rate constant for anisoyl chloride.

Introduction

Microemulsions are transparent, thermodynamically stable solutions of low viscosity that form spontaneously from mixtures of a surfactant, water, and oil.[1] A water-in-oil (w/o) microemulsion is a solution of water droplets of nanometer size dispersed in a nonpolar solvent with the aid of a surfactant. This type of microemulsion has been widely used as a microreactor for enzymatic reactions, tertiary oil recovery, and nanomaterial production.[2–5] The surfactant most widely used in microemulsions is sodium bis(2-ethylhexyl)sulfosuccinate (AOT). Sulfonate head groups are hydrophilic and tend to point to the microemulsion core, whereas hydrocarbon chains are hydrophobic and spread into the continuous phase. The properties of a microemulsion depend on the type of surfactant used, the water-to-surfactant concentration ratio, W, and the properties of the oil. Microemulsion properties have been widely studied in relation to various surfactant types;[6–11] however, the influence of the nonpolar continuous medium has scarcely been examined, and the few studies on it have led to contradictory conclusions.[12–19]

Temperature-induced dynamic percolation of water-in-oil microemulsions is known to depend on the properties of the bulk solvent.[20] By using *n*-heptane, *n*-octane, and *n*-decane as continuous media, Moulik and co-workers found the percolation temperature to decrease with increasing length of the alkyl chain in the hydrocarbon. In earlier reports,[21–24] the strong attractive interaction between droplets was assumed to be the major factor limiting microemulsion stability. An increase in molar mass of the hydrocarbon oil was found to decrease the density of the continuous phase and facilitate access of the interacting droplets for mass transfer. An increase in droplet radius should also increase the overlap volume between two droplets as they approach each other to form a cluster, thereby increasing the interaction potential and facilitating percolation. While droplet attraction plays a prominent role in percolation, the nature of the droplet interface is also relevant to the process because mass transfer is impossible unless the interface is ruptured in some way.

The characteristics of microemulsion aggregates, and hence their ability to incorporate solutes, can be extremely dependent on the particular external solvent.[25–30] The most extensive comparative study in this context involved AOT/hydrocarbon/water and AOT/benzene/water microemulsions[31] and showed clustering of benzene molecules around AOT head groups to be seemingly more orderly than in saturated alkanes.[32] However, ^{1}H NMR studies[33] have shown AOT/benzene microemulsions to contain some free water, even at low W values. The previous findings are consistent with a specific interaction between the polar head groups in AOT and the more polarizable solvents: chlorobenzene, tetrachloromethane, and benzene. Based on ^{13}C NMR spectroscopic data,[12] benzene and tetrachloromethane were assumed to intercalate between AOT chains; with cyclohexane, however, voids in the surfactant/oil interface were assumed to be occupied by surfactant chains. Solvent penetration was found to decrease in the following sequence: $C_6H_6 > CCl_4 > C_6H_{12}$. Similar conclusions were drawn regarding the solution enthalpies of water.[19]

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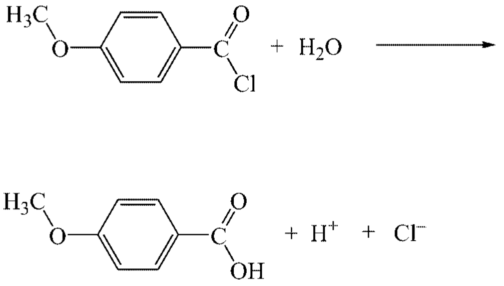
[a] Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela,
15782 Santiago de Compostela

A variety of experimental techniques have confirmed that the bulk solvent influences the size and structure of microemulsions.[34,35] In this work, we conducted a systematic study of the influence of the continuous medium on the properties of AOT-based microemulsions involving various solvents, including alkanes (*n*-heptane, isooctane, and *n*-dodecane), cycloalkanes (cyclopentane, cyclohexane, and cycloheptane), aromatic hydrocarbons (toluene as well as *o*-, *m*- and *p*-xylene), trichloromethane and tetrachloromethane. The microheterogeneous systems were characterized from kinetic and NMR spectroscopic data. ^{1}H NMR and ^{13}C NMR spectroscopy allowed us to elucidate the properties of water[36] and the AOT molecule,[19,37] respectively, in the microemulsions. The latter technique provided information about the local environment of each individual nucleus. The polarity of the interface was determined by using a chemical reaction as a probe; the reaction concerned was the solvolysis of anisoyl chloride (Scheme 1), for which the rate constant is strongly dependent on the solvent polarity. By virtue of its hydrophobic nature, anisoyl chloride can be expected to partition between the continuous medium and the microemulsion interface where the reaction takes place. The influence of the continuous medium on the reaction rate can be used as a measure of the degree of oil penetration into the interface. The use of this reaction as a chemical probe instead of a typical spectroscopic probe has the advantage that the probe is small enough to avoid substantial alteration of the interface.



Scheme 1.

Results and Discussion

1. Influence of the Oil on the ^{1}H NMR Resonance Signal for the Water H Atoms

The ^{1}H NMR spectrum for the water/AOT/solvent system was used to elucidate the types of water present in the microemulsion: water trapped between the surfactant alkyl chains, water bonded to head groups, free water, and water bonded to the counterion (sodium). The NMR spectroscopic data provided an average value for the four types of water as their rate of exchange is much higher than the NMR time scale. The position of the NMR signal may be of help with a view to estimating the contribution of each type of water to the overall signal.

At low *W* values, most of the water present interacts with Na^+ ions and the polar groups of AOT. Hydration of the anionic head groups in AOT molecules increases the electron density on the H atoms in water molecules and shifts the water signal upfield. As the water content increases, the system contains a gradually larger amount of free water in the microemulsion droplets that are available for hydrogen bonding. This decreases the electron density on the H atoms and shifts the signal for free water downfield (i.e. to higher δ values) relative to bonded water.

As the water content of the microemulsion continues to grow, the number of bonded molecules increases and so does, especially markedly, that of free water. On the other hand, the amount of trapped water at the interface remains constant.[15] As a result, the chemical shift for water changes from $\delta \approx 4.0$ at low *W* values to levels close to that for water ($\delta^{water} \approx 4.8$) for high *W* values.

All solvents exhibited a similar behaviour, but also substantial differences among them. Thus, the solvent molecules that penetrated deeply into the interface established interactions with the head groups of AOT and decreased droplet size.[17] As droplet size decreased, so did the number of free water molecules in the microemulsions. Thus, at a given *W* value, the deeper the oil penetrated into the interface, the lower was the ^{1}H NMR chemical shift for the water molecules. The results shown in Figure 1 (top) suggest that the degree of oil penetration into the interface increased in the following sequence: *n*-heptane < *n*-dodecane ≈ isooctane for aliphatic hydrocarbons and cycloheptane < cyclohexane < cyclopentane [see Figure 1 (centre)] for cyclic hydrocarbons.

These results are consistent with those for the interdroplet attractive interaction in water/AOT/oil microemulsions, which was found to increase with increasing chain length of the oil. An increased molecular mass of the hydrocarbon decreased the density of the continuous phase, thereby facilitating access of the interacting droplets and hence mass transfer. Robinson et al.[38] studied the rate of micellar exchange, k_{ex}, in water/AOT/alkane systems and found it to increase slightly with increasing number of carbon atoms from *n*-pentane to *n*-dodecane; also, they found k_{ex} to be significantly smaller for the corresponding cyclic alkanes (particularly cyclohexane). Binks et al.[39] discussed the extent of oil penetration into the surfactant chain region and found micelle rigidity to increase with decreasing solvent chain length from C_{14} to C_7. Theoretical studies[40] account for the dependence of absorption on alkane chain length. In microemulsions, penetration expands the spontaneous curvature of the surfactant layer to reduce the micelle radius. The limit of penetration of the solvent molecules into the surfactant layer has been estimated to be in the region of 9.5 carbon atoms, above which nonpolar solvent molecules can hardly be expected to penetrate surfactant layers.[17] However, Keh and Valeur[41] have shown that the characteristics of AOT micelles appear not to be altered in

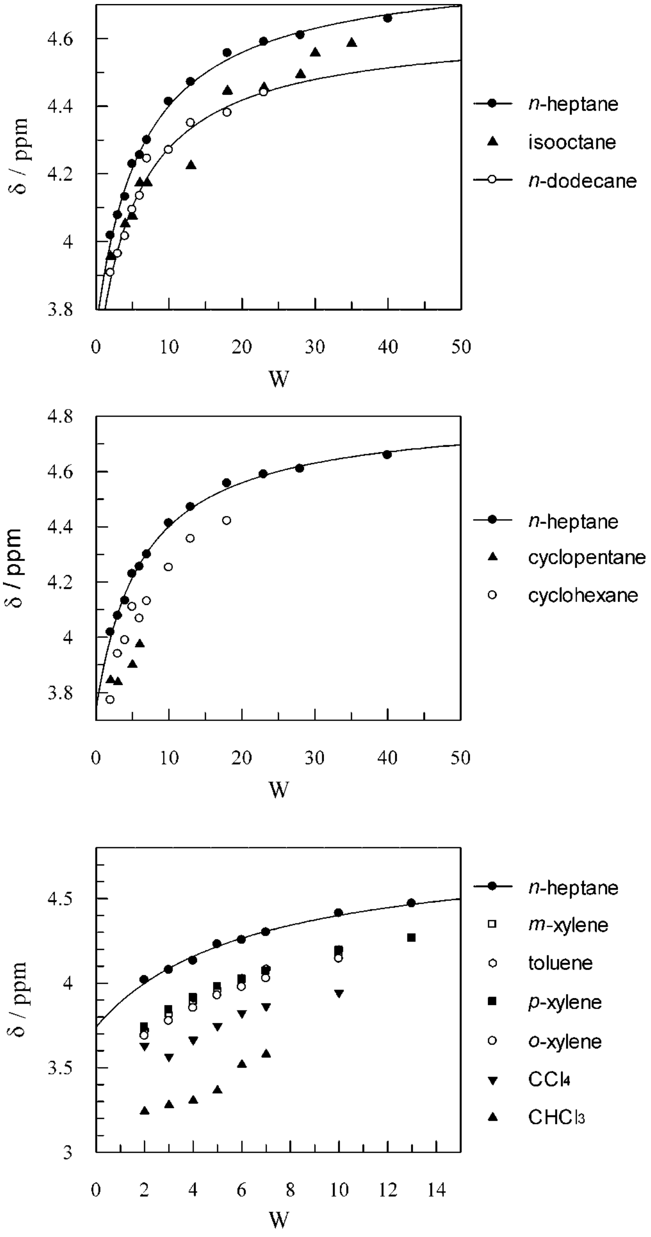


Figure 1. Variation of the chemical shift for the water H atoms as a function of *W* in water/AOT/oil microemulsions at 25.0 °C.

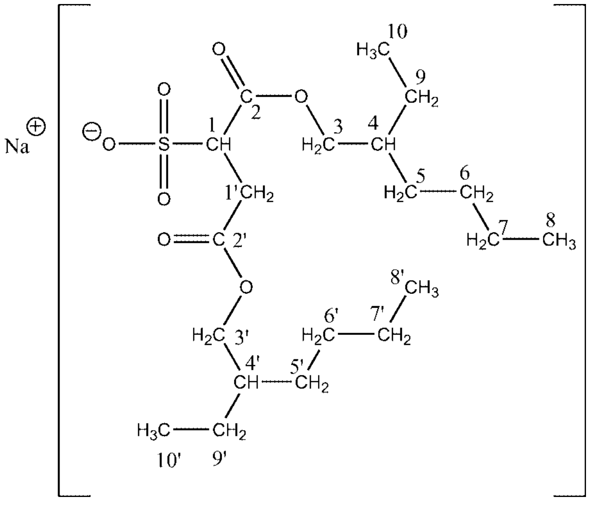
the *n*-alkane series from *n*-hexane to *n*-dodecane, and only slightly altered in various nonpolar solvents. On the other hand, studies based on synchrotron radiation small-angle X-ray scattering spectroscopy have shown that the penetration of solvent molecules into the micelle surfactant layer depends strongly on the length of the linear hydrocarbon chain for *n*-hexane, *n*-heptane, *n*-octane, and isooctane.[17]

Highly polarizable solvents such as benzene, toluene, and tetrachloromethane penetrate into the amphiphilic layer presumably up to the water core boundary. As can be seen from Figure 1 (bottom), the resonance signals for the water H atoms in toluene, *m*-xylene, and *p*-xylene microemulsions are indistinguishable. The *δ* values are all smaller than those for *n*-heptane microemulsions, which is consistent with increasing penetration into the oil. The resonance signals for the water H atoms suggest that penetration is slightly deeper with *o*-xylene than with the other aromatic solvents. Penetration is also more marked in CCl_4 and $CHCl_3$. This results contradict the increased percolation temperature found in xylenes and toluene as the continuous media for AOT-based microemulsions.[20]

2. Influence of the Oil on the ^{13}C NMR Signals for AOT

In characterizing microemulsions, the ^{13}C NMR technique has the advantage that it requires the use of no probe molecule, and hence avoids potential alteration of the target system. Also, the carbon spectrum provides valuable information about the environment of the AOT molecules.[37]

By analyzing the ^{13}C NMR spectrum as a function of the water content of the microemulsion one can assess environmental changes (i.e. changes at the interface) as a function of the microemulsion droplet size. The addition of water has a slight effect on the chemical shifts for the carbon atoms C4, C4′, C10, and C10′ (see Scheme 2 for numbering). The result is always an upfield shift. In any case, the most substantial changes are those in the region of the head group. Thus, C1 is influenced by the hydration of the head group: once completed, δ_{C1} levels off. The carbonyl group at C2′ is highly sensitive to the nature of the local environment. Thus, the chemical shift for C2′ decreases with increasing *W*, which suggests an increased polarity of the medium. Figure 2 shows the variation of the chemical shift with *W*.



Scheme 2.

Maitra et al. examined the aggregational behaviour of AOT in nonpolar solvents and the uses of these systems in various areas.[42] The AOT molecule can occur in two major conformations, namely: *trans* (II) and *gauche* (I) (see Scheme 3). As the water content increases, so does the proportion of the *trans* isomer, leading to an increase in the surfactant–water contact area at the interface. Conformational changes in AOT are a result of polarity changes.

The influence of organic molecules on the properties of the interface can be ascribed to two different effects: (*a*)

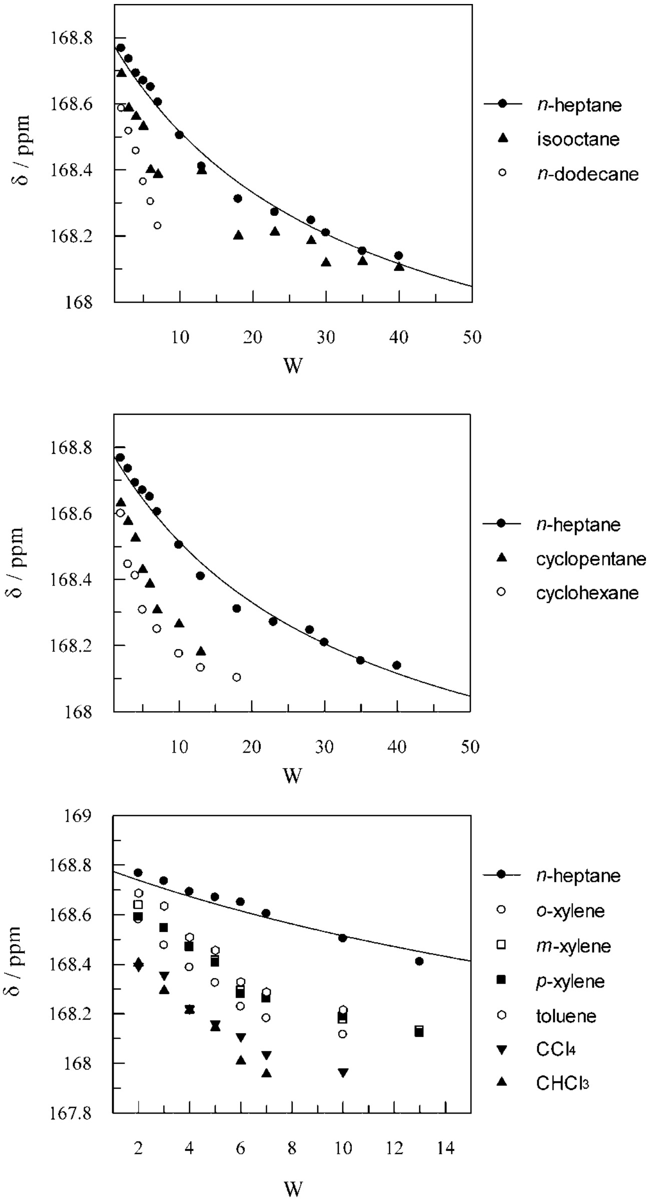


Figure 2. Variation of the chemical shift for the carbon atom in the carbonyl group (*C2′*) as a function of *W* in water/AOT/oil microemulsions at 25.0 °C.

inclusion into the surfactant film and (*b*) replacement of water molecules at the interface. Also, the incorporation of the oil into the surfactant film alters its geometry in two ways: (*i*) the additive acts as a spacer within the surfactant monolayer and increases the effective area of the polar head groups in AOT; and (*ii*) the binding of additives to the surfactant film increases disorder in the interfacial region, thereby decreasing the rigidity of the AOT film and increasing its deformability. The influence of additives on the replacement of water molecules at the interface is probably a result of their ability to displace those in the vicinity of the polar area in the surfactant film. The results of some studies[43] suggest that moderate concentrations of various organic molecules can "open up" the interface and facilitate the penetration of water.

A comparison of the results for *n*-heptane, isooctane, and *n*-dodecane microemulsions reveals that the proportion of *trans* isomer increases with increasing length of the hydrocarbon chain. This is a result of increased penetration of the oil into the interface and hence of an increased distance between AOT molecules (see Scheme 4). The increased interfacial volume results in closer contact between water molecules and AOT head groups, which favours the *trans* conformer. In fact, oil penetration increased in the sequence *n*-heptane < isooctane < *n*-dodecane. Also, the branched nature of the isooctane molecule results in a large molecular volume and hence in substantially low $\delta_{C2'}$ values relative to *n*-heptane microemulsions.

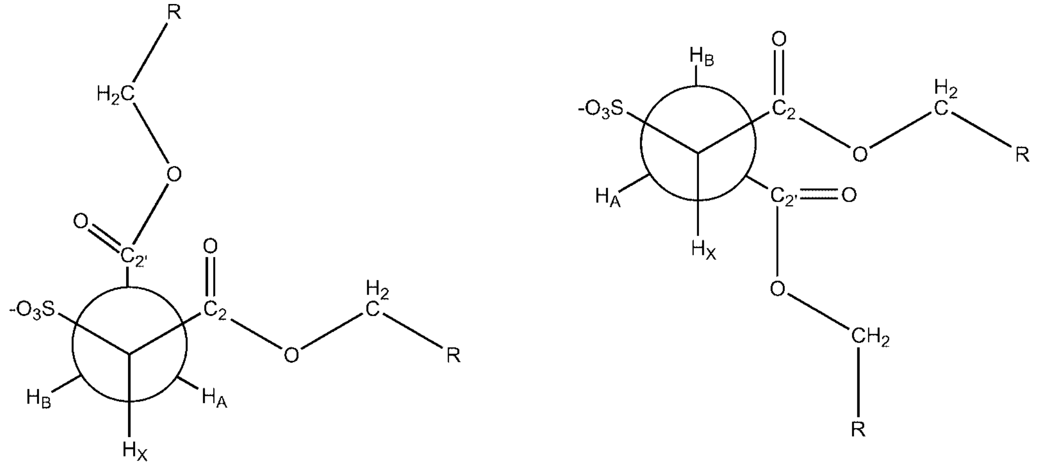
The influence of *W* and the oil on the ^{1}H NMR chemical shifts for the water H atoms and the ^{13}C NMR shifts for the carbon atom C2′ are quite consistent. Thus, increasing penetration of the oil into the interface resulted in increasing separation between AOT molecules, which thus occupied an increased volume and facilitated the penetration of water molecules into the interface. The increased penetration resulted in stronger interactions between AOT head groups and water molecules ($SO_3^-\cdots HOH$), and the stronger interactions shifted δ for the water H atoms upfield as oil penetration increased.

A comparison of the results obtained in cyclohexane and cyclopentane (see Figure 2) as oils reveals an increased prevalence of the *trans* isomer relative to *n*-heptane microemulsions. This is seemingly abnormal, as cyclic hydrocarbons such as cyclopentane and cyclohexane are known to penetrate less deeply into the interface than do linear hydrocarbons. This apparent anomaly is also observed in the ^{1}H NMR spectra for the water H atoms (Figure 1). Thus, the δ values for the H atoms in cyclohexane microemulsions were lower than those in *n*-heptane microemulsions. This can be ascribed to the increased interfacial volume occupied by cyclohexane relative to *n*-heptane.

The solvents most deeply penetrating into the interface, viz. aromatic hydrocarbons and chlorinated hydrocarbons (CCl_4 and $CHCl_3$), interact with the ester group in AOT and increase the population of *trans* isomer. The resulting $\delta_{C2'}$ values were always lower than those obtained in *n*-heptane microemulsions. The results of Figure 2 are consistent with the influence of the oil on the chemical shift for the water H atoms. Thus, all aromatic hydrocarbons exerted a similar effect and halogenated hydrocarbons exhibited increased penetration.

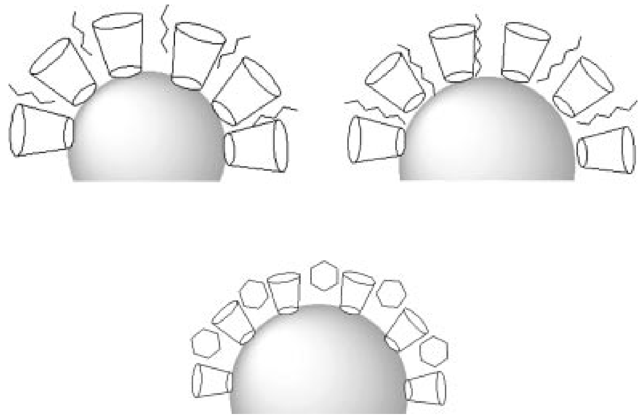
3. Influence of the Oil on the Solvolysis of Anisoyl Chloride (AnCl)

The bulk solvent is known to affect various micellar properties, including the critical micelle concentration,[44] the size of w/o microemulsions,[45] and solvent penetration into the interface.[12] As a result, the properties of water molecules dissolved in the core can be influenced by the nature of the solvent. Velázquez et al.[46] examined the influence of the solvent on the water-entrapped structure. Their IR spectroscopic results suggest that the water structure of AOT mi-



I *gauche* **II** *trans*

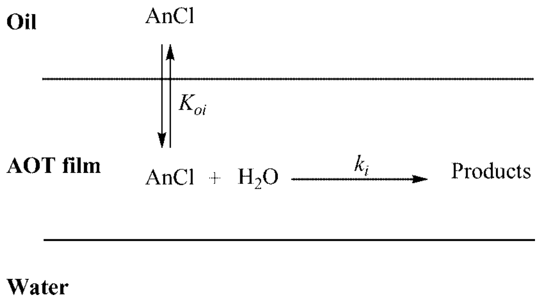
Scheme 3.



Scheme 4.

croemulsions dissolved in cyclohexane and isooctane with variable water contents is quite similar. However, there are significant differences from the water structure of microemulsions in toluene.[47] These results suggest that the water interfacial layer is smaller in AOT microemulsions dissolved in cyclohexane or isooctane than in those dissolved in toluene. This may be a result of toluene penetrating the interfacial layer more readily[12] than isooctane and cyclohexane. Similar preferential penetration by an aromatic solvent has been observed in Triton X-100 microemulsions.[48] The kinetic implications of these changes in the properties of interfacial water with the nature of the oil were examined by studying the solvolysis of anisoyl chloride (AnCl). This reaction involves a dissociation mechanism, and its rate is governed by the solvation capacity of the leaving group (Cl^-), which makes it highly sensitive to the polarity of the medium and hence a suitable probe for the electrophilicity of water in microemulsions.

The experimental results were analysed in the light of the micellar pseudophase model, which assumes a microemulsion to comprise three distinct domains: the aqueous pseudophase, the AOT film, and the solvent.[49] The reactants and products will partition into the microemulsion as a function of their solubility. Anisoyl chloride is virtually insoluble in water, so it will only be present in the continuous medium and the microemulsion interface (see Scheme 5), where the reaction takes place. Figure 3 shows the variation of the solvolysis rate constant with the AOT concentration at constant W values of 18 and 40. As can be seen, k_{obs} increases with increasing AOT concentration as a result of the incorporation of AnCl from the continuous medium



Scheme 5.

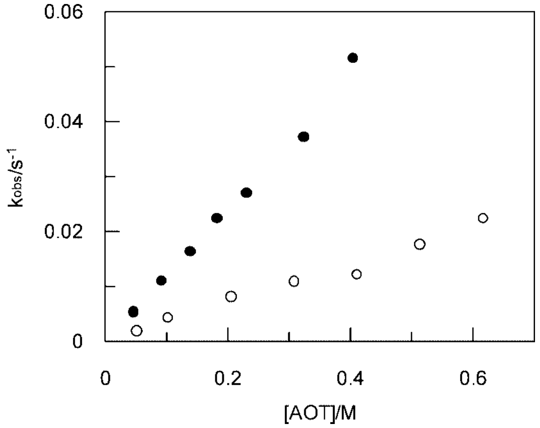


Figure 3. Influence of the AOT concentration on k_{obs} for solvolysis of anisoyl chloride in water/AOT/n-heptane microemulsions at W = 18 (○) and W = 40 (●). T = 25.0 °C.

into the interface. Also, it increased with increasing water content due to an increase in the interfacial polarity.

Application of the pseudophase model (Scheme 5) leads to Equation (1) for the observed rate constant.[50]

$$k_{obs} = \frac{k_i K_{oi}}{K_{oi} + Z} \tag{1}$$

where K_{oi} is the partition constant of AnCl between the continuous medium and the interface, K_{oi} = ([AnCl]$_i$/[AnCl]$_0$)Z, with Z being the [oil]/[AOT] mol ratio. Equation (1) can be rewritten as Equation (2).

$$\frac{1}{k_{obs}} = \frac{1}{k_i} + \frac{Z}{k_i K_{oi}} \tag{2}$$

As can be seen in Figure 4, the experimental data fit equation (2) quite well. The ratio of the slope to the intercept allowed us to determine K_{oi}. Based on the intercepts and slopes of Figure 4, the obtained partition constants were 4.3 ± 1.0 at W = 18 and 5.9 ± 0.8 at W = 40. As found in previous work, K_{oi} should be independent of W.[50] In fact, the partition constant was independent of W in all studied media. The values obtained can be classified into three large groups depending on the nature of the oil, namely: (*a*) cyclic and alicyclic hydrocarbons, (*b*) aromatic hydrocarbons, and (*c*) halogenated hydrocarbons. The K_{oi} values obtained for the oils in group (*a*) (viz. 5.0, 5.9, 7.0, 6.0, 6.2, and 7.0 for *n*-heptane, isooctane, *n*-dodecane, cyclopentane, cyclohexane, and cycloheptane, respectively) show that AnCl partitions in a manner independent of the extent of oil penetration into the interface. The values for the oils in group (*b*) (viz. 2.5, 1.0, 0.9, and 1.2 for toluene, *p*-xylene, *m*-xylene, and *o*-xylene, respectively) were lower than those for the hydrocarbons in the previous group as a result of their increased polarity and hence of the decreased polarity difference between the continuous medium and the microemulsion interface. Finally, the K_{oi} values for CCl_4 and $CHCl_3$ were 5.0 and 2.8, respectively. These partition coefficients are the mean values of those obtained at two independent W values. In all cases, K_{oi} values show that they are W-independent.

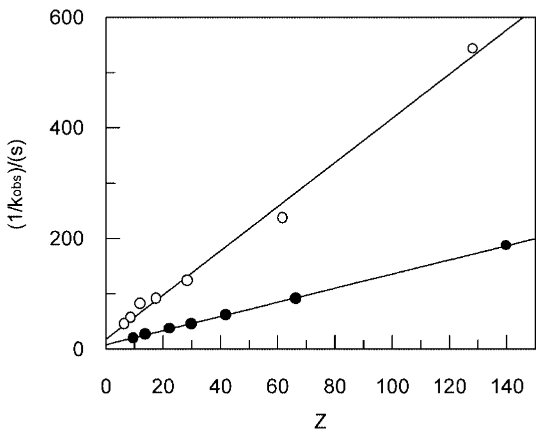


Figure 4. Plot of $1/k_{obs}$ as a function of Z for solvolysis of anisoyl chloride in water/AOT/*n*-heptane microemulsions at W = 18 (○) and W = 40 (●). T = 25.0 °C.

K_{oi} allows one to calculate the actual rate constant at the microemulsion interface, using Equation (3).

$$k_i = \frac{(K_{oi} + Z)k_{obs}}{K_{oi}} \tag{3}$$

The value of k_i was calculated from average K_{oi} values in order to minimize potential sources of error arising from uncertainty in the determination of the intercepts of Figure 4. The average K_{oi} values used were 6.2 for cyclic and alicyclic hydrocarbons, 1.4 for aromatic hydrocarbons, 5.0 for CCl_4, and 2.8 for $CHCl_3$. The interfacial rate constants thus obtained at variable W values are shown in Figure 5.

We examined the variation of k_i with the water content of the microemulsion in various continuous media. Anisoyl chloride is a benzoyl chloride bearing an electron-releasing substituent. This facilitates its heterolytic cleavage and the formation of an acylium intermediate via a dissociation pathway. The reaction rate must decrease with decreasing water content in the microemulsion, i.e., with decreasing content in interfacial water, which effects the solvation of the AOT head groups and reduces the ability to solvate the Cl^- leaving group. This relates the interfacial rate constant with the polarity: the higher is the electrophilicity of the water, the higher will be the reaction rate.

Based on the results of Figure 5, the reaction rate in the alicyclic hydrocarbons decreases with increasing penetration of the hydrocarbon. An increased penetration of the oil increases the distance between AOT molecules and facilitates interactions between water molecules at the interface and the surfactant head groups as a result. The interactions decrease the electrophilicity of the water and hence the reaction rate. It should be noted that the rate of this reaction is highly sensitive to the water content in the microemulsion; thus, it decreased by more than 300 times from W = 50 to W = 2 in water/AOT/*n*-heptane microemulsions. On the other hand, it decreased by a factor less than 2 between *n*-heptane, isooctane, and *n*-dodecane microemulsions. A comparison of the *n*-heptane microemulsions with the cyclopentane, cyclohexane, and cycloheptane microemulsions reveals a decreased reaction rate in the cyclic hydrocarbons. This is consistent with the ^{1}H NMR results and with decreased penetration of the oil, but also with an increased volume resulting from the bulkiness of the cyclic hydrocarbons relative to linear ones.

A comparison of the microemulsions formed by the aromatic and halogenated hydrocarbons with the *n*-heptane microemulsions reveals an increased rate in the latter. This is consistent with increased penetration of the oil (an aromatic hydrocarbon) into the interface and hence with stronger interactions between interfacial water and the surfactant head groups. Such interactions hinder solvation of the leaving group in the solvolysis of anisoyl chloride. It should be noted that solvolysis in the microemulsions of halogenated hydrocarbons was faster than expected by virtue of their increased interfacial penetration, as confirmed

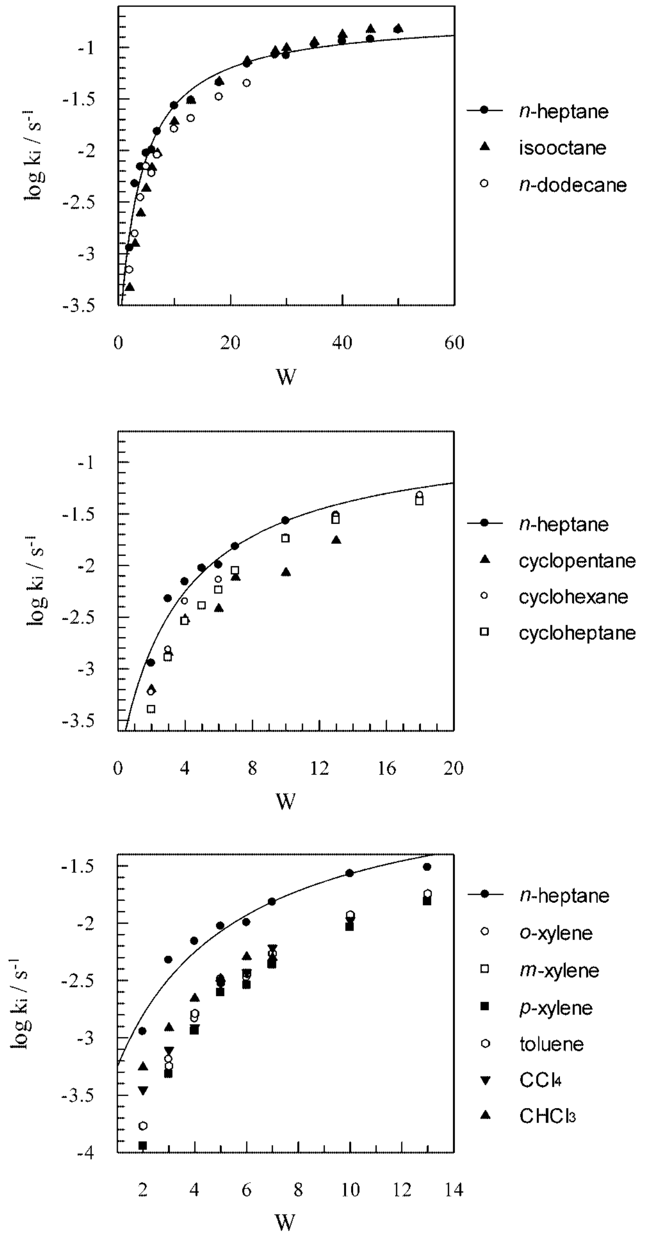


Figure 5. Variation of the solvolysis rate constant for anisoyl chloride as a function of *W* in water/AOT/oil microemulsions at 25.0 °C.

by the ^{1}H NMR and ^{13}C NMR results. The increased penetration relative to aromatic hydrocarbons should have resulted in a decreased reaction rate; however, the results of Figure 5 show that the solvolysis rate was virtually identical in xylene, CCl_4, and $CHCl_3$ microemulsions. This anomaly is a result of the increased polarity of halogenated hydrocarbons relative to *n*-heptane as shown by the values of the polarity parameter $E_T(30)$.[51]

Figure 6 testifies to the good correlation between the solvolysis rate constant for anisoyl chloride and the chemical shifts for the water H atoms. As can be clearly seen, the solvolysis rate in the trichloromethane and tetrachloromethane microemulsions was greater than expected from the chemical shifts for the water H atoms. This was a result of the ability of trichloromethane to stabilize the leaving group in the solvolysis of anisoyl chloride through hydrogen bonding. Note the good correlation for a variety of continuous media including alicyclic, cyclic, and aromatic hydrocarbons spanning a wide range of penetration into the microemulsion interface.

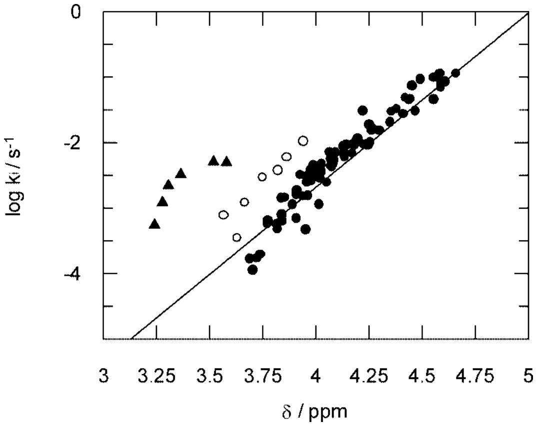


Figure 6. Correlation between the solvolysis rate constants for anisoyl chloride in water/AOT/oil microemulsions and the ^{1}H NMR resonance signals for the water H atoms in (filled circle) microemulsions consisting of *n*-heptane, isooctane, *n*-dodecane, cyclopentane, cyclohexane, cycloheptane, toluene, *o*-xylene, *m*-xylene, or *p*-xylene as oils; (open circle) water/AOT/CCl_4 microemulsions; and (filled triangle) water/AOT/$CHCl_3$ microemulsions.

Conclusions

Nuclear magnetic resonance spectroscopy is an effective tool for studying the influence of the continuous medium on the properties of microemulsions. In this work, ^{1}H NMR spectroscopy allowed the properties of water in microemulsions to be elucidated, and revealed that the amount of free water decreases with increasing penetration of the hydrocarbon. Also, ^{13}C NMR spectroscopy allowed the polarity at the microemulsion interface to be interpreted in the light of the signals for the carbonyl C2′ in AOT; in fact, the polarity was found to increase with increasing penetration of the oil into the interface. This was a result of the volume available for AOT molecules–and hence interactions between water and the surfactant head groups–increasing with increasing penetration of the oil. The kinetic analysis of the solvolysis of anisoyl chloride revealed that the reaction rate decreases with increasing the oil penetration into the interface. This behaviour is a consequence of an increase in the electrophilicity of the interfacial water through interaction with the surfactant head groups.

Experimental Section

AOT was obtained from Aldrich and used without further purification following drying in a vacuum desiccator for two days. All solvents were obtained from Aldrich in the highest commercially available purity. AOT solutions were prepared by direct weighing. Stock solutions containing a 0.5 M concentration of the surfactant in trichloromethane and tetrachloromethane, and 1 M in all other solvents, were used.

NMR spectra were recorded with the aid of a coaxial tube filled with [D$_6$]DMSO to lock on the deuterium signal. The signals of tetramethylsilane were used as ^{1}H NMR references, and those of [D$_6$]DMSO as reference for the ^{13}C NMR spectra. All spectra were recorded with a Bruker AM 500 MHz spectrometer.

Anisoyl chloride was obtained from Aldrich in 99% purity and used to prepare 5×10^{-3} M stock solutions by direct weighing that were used in the kinetic study. The concentration of anisoyl chloride in the microemulsion used was 1.0×10^{-4} M. The reaction was monitored by measuring the UV–Vis absorbance of the products at 295 nm on a Cary 500 Scan UV–Vis–NIR spectrophotometer. Absorbance-time data were fitted to a first-order integral equation in order to obtain the pseudo-first-order rate constant, k_{obs}, with a reproducibility of 5%.

Acknowledgments

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[1] M. P. Pileni, Editor. *Studies in Physical and Theoretical Chemistry 65: Structure and Reactivity in Reverse Micelles*, Elsevier, Amsterdam, **1989**.

[2] N. Krieger, M. A. Taipa, E. H. M. Melo, J. L. Lima-Filho, M. R. Aires-Barros, J. M. S. Cabral, *Appl. Biochem. Biotechnol.* **1997**, *67*, 87–95.

[3] M. P. Pileni, *J. Phys. Chem.* **1993**, *97*, 6961–6973.

[4] F. Debuigne, L. Jeunieau, M. Wiame, J. B. Nagy, *Langmuir* **2000**, *16*, 7605–7611.

[5] P. Walde, Q. Mao, R. Bru, P. L. Luisi, R. Kuboi, *Pure Appl. Chem.* **1992**, *64*, 1771–1775.

[6] E. Caponetti, A. Lizzio, R. Triolo, W. L. Griffith, J. S. Johnson, *Langmuir* **1992**, *8*, 1554–1562.

[7] A. L. Compere, W. L. Griffith, J. S. Johnson Jr, E. Caponetti, D. Chillura-Martino, R. Triolo, *J. Phys. Chem. B* **1997**, *101*, 7139–7146.

[8] S. M. Andrade, S. M. B. Costa, *Photochem. Photobiol. Sci.* **2002**, *1*, 500–506.

[9] T. C. Jao, W. S. Joyce, *Langmuir* **1990**, *6*, 944–948.

[10] P. Menassa, T. Lussier, C. Sandorfy, *Can. J. Chem.* **1986**, *64*, 633–634.

[11] O. A. El Seoud, M. J. Da Silva, L. P. Barbur, A. Martins, *J. Chem. Soc., Perkin Trans. 2* **1978**, 331–335.

[12] C. A. Martin, L. J. Magid, *J. Phys. Chem.* **1981**, *85*, 3938–3944.

[13] L. J. Magid, K. Konno, C. A. Martin, *J. Phys. Chem.* **1981**, *85*, 1434–1439.

[14] N. M. Correa, E. N. Durantini, J. J. Silber, *J. Colloid Interface Sci.* **1998**, *208*, 96–103.

[15] G.-W. Zhou, G.-Z. Li, W.-J. Chen, *Langmuir* **2002**, *18*, 4566–4571.

[16] P. R. Majhi, S. P. Moulik, *J. Phys. Chem. B* **1999**, *103*, 5977–5983.

[17] M. Hirai, R. Kawai-Hirai, M. Sanada, H. Iwase, S. Mitsuya, *J. Phys. Chem. B* **1999**, *103*, 9658–9662.

[18] S. K. Hait, A. Sanyal, S. P. Moulik, *J. Phys. Chem. B* **2002**, *106*, 12642–12650.

[19] A. Goto, H. Yoshioka, H. Kishimoto, T. Fujita, *Langmuir* **1992**, *8*, 441–445.

[20] S. Ray, S. Paul, S. P. Moulik, *J. Colloid Interface Sci.* **1996**, *183*, 6–12.

[21] M. J. Hou, M. Kim, D. O. Shah, *J. Colloid Interface Sci.* **1988**, *123*, 398–412.

[22] A. Jada, J. Lang, R. Zana, *J. Phys. Chem.* **1989**, *93*, 10–12.

[23] A. Jada, J. Lang, R. Zana, *J. Phys. Chem.* **1990**, *94*, 381–387.

[24] P. Alexandridis, J. F. Holzwarth, T. A. Hatton, *J. Phys. Chem.* **1995**, *99*, 8222–8232.

[25] E. Abuin, E. Lissi, R. Duarte, J. J. Silber, M. A. Biasutti, *Langmuir* **2002**, *18*, 8340–8344.

[26] N. M. Correa, E. N. Durantini, J. J. Silber, *J. Colloid Interface Sci.* **2001**, *240*, 573–580.

[27] R. D. Falcone, N. M. Correa, M. A. Biasutti, J. J. Silber, *Langmuir* **2000**, *16*, 3070–3076.

[28] P. Lopez-Cornejo, S. M. B. Costa, *Langmuir* **1998**, *14*, 2042–2049.

[29] R. D. Falcone, N. M. Correa, M. A. Biasutti, J. J. Silber, *Molecules* **2000**, *5*, 553–554.

[30] N. Z. Atay, B. H. Robinson, *Langmuir* **1999**, *15*, 5056–5064.

[31] N. M. Correa, M. A. Biasutti, J. J. Silber, *J. Colloid Interface Sci.* **1995**, *172*, 71–76.

[32] K. Mukherjee, S. P. Moulik, D. C. Mukherjee, *Langmuir* **1993**, *9*, 1727–1730.

[33] F. Heatley, *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 343–354.

[34] R. A. Day, B. H. Robinson, J. H. R. Clarke, J. V. Doherty, *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 132–139.

[35] M. Ueda, Z. A. Schelly, *Langmuir* **1988**, *4*, 653–655.

[36] a) A. N. Maitra, H. F. Eicke, *J. Phys. Chem.* **1981**, *85*, 2687–2691; b) A. Maitra, *J. Phys. Chem.* **1984**, *88*, 5122–5125; c) A. Llor, P. Rigny, *J. Am. Chem. Soc.* **1986**, *108*, 7533–7541; d) M. Wong, J. K. Thomas, T. Nowak, *J. Am. Chem. Soc.* **1977**, *99*, 4730–4736.

[37] a) M. Ueno, H. Kishimoto, Y. Kyogoku, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1776–1779; b) M. Ueno, H. Kishimoto, Y. Kyogoku, *J. Colloid Interface Sci.* **1978**, *63*, 113–119; c) M. Ueno, H. Kishimoto, *J. Phys. Chem.* **1983**, *87*, 850–856.

[38] P. D. I. Fletcher, A. M. Howe, B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 985–1006.

[39] B. P. Binks, H. Kellay, J. Meunier, *Europhys. Lett.* **1991**, *16*, 53–58.

[40] D. W. R. Gruen, D. A. Haydon, *Pure Appl. Chem.* **1980**, *52*, 1229–1240.

[41] E. Keh, B. Valeur, *J. Colloid Interface Sci.* **1981**, *79*, 465–478.

[42] T. K. De, A. Maitra, *Adv. Colloid Interface Sci.* **1995**, *59*, 95–193.

[43] Y. S. Kang, H. J. D. McManus, L. Kevan, *J. Phys. Chem.* **1992**, *96*, 10055–10060.

[44] S. Muto, K. Meguro, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1316–1320.

[45] M. Zulauf, H. F. Eicke, *J. Phys. Chem.* **1979**, *83*, 480–486.

[46] C. Gonzalez-Blanco, L. J. Rodriguez, M. M. Velásquez, *J. Colloid Interface Sci.* **1999**, *211*, 380–386.

[47] C. Gonzalez-Blanco, L. J. Rodríguez, M. M. Velázquez, *Langmuir* **1997**, *13*, 1938–1945.

[48] D. M. Zhu, X. Wu, Z. A. Schelly, *J. Phys. Chem.* **1992**, *96*, 7121–7126.

[49] L. García-Río, J. R. Leis, M. E. Peña, E. Iglesias, *J. Phys. Chem.* **1993**, *97*, 3437–3442.

[50] a) L. García-Río, J. R. Leis, *Chem. Commun.* **2000**, 455–456; b) L. García-Río, J. R. Leis, J. A. Moreira, *J. Am. Chem. Soc.* **2000**, *122*, 10325–10334; c) L. García-Río, J. R. Leis, J. C. Mejuto, *Langmuir* **2003**, *19*, 3190–3197.

[51] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley-VCH, Weinheim, **2003**.

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