

# Bromine–AOT Charge-Transfer Complexes and Hydrogen-Bond Donor Ability of Water in AOT–isooctane–H<sub>2</sub>O Reverse Micelles and Water-in-Oil Microemulsions

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Changes, induced by aerosol-OT (sodium bis(2-ethylhexyl) sulfosuccinate, AOT), in the absorption spectrum of bromine, are shown to markedly depend on the nature and the hydration of the AOT-aggregates. A charge-transfer complex (CTC) between bromine and monomeric AOT ( $\lambda_{\text{max}} = 270 \text{ nm}$ ,  $\epsilon_{315} = 1.4 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ , and  $K = 4 \times 10^3 \text{ M}^{-1}$ ) is observed in isooctane, in agreement with a very strong electron donor ability of AOT, attributed to its sulfonate headgroup. In “dry” reverse micelles ( $[\text{AOT}] > \text{cmc}$ ), the constant for the CTC formation  $K = 1.3 \text{ M}^{-1}$  is markedly smaller. In aqueous reverse micelles, the observed  $\epsilon$  decrease ( $\epsilon_{315} = 700 \text{ cm}^{-1} \text{ M}^{-1}$  and  $K = 1.1 \text{ M}^{-1}$  for  $W = [\text{H}_2\text{O}]/[\text{AOT}] = 9$ ) is consistent with a competition between water and bromine in the stabilization of the AOT-head groups. Finally, in water-in-oil (w/o) microemulsions ( $W > 12$ ), the complex disappears. The bromine–tribromide ion equilibrium is also investigated in AOT-w/o microemulsions in the presence of bromide ions. The marked dependence of the equilibrium constant for  $\text{Br}_3^-$  formation on the microemulsion composition ( $W = 12$ ,  $K = 178 \text{ M}^{-1}$ ;  $W \geq 20$ ,  $K = 60 \text{ M}^{-1}$ ; bulk water,  $K = 16 \text{ M}^{-1}$ ) is attributed to a change in the transfer free energy of bromide ion from bulk water to the aqueous pseudophase of the microdroplets ( $\delta\Delta G_{\text{tr}}(\text{Br}^-) = -2.6$  and  $-1.3 \text{ kcal mol}^{-1}$  for  $W = 12$  and  $20$ , respectively). The results are discussed in terms of changes in the hydrogen-bond donor ability and polarity of water in AOT-w/o microemulsions.

## Introduction

The physicochemical properties of AOT, sodium bis(2-ethylhexyl)sulfosuccinate, have been widely investigated because this unique surfactant spontaneously aggregates into reverse micelles and water-in-oil (w/o) microemulsions<sup>1,2</sup> without the need of any cosurfactant. The capacity of its hydrocarbon solutions to dissolve large amounts of water and the possibility of controlling the size of the water pools with  $W$ , the  $[\text{H}_2\text{O}]/[\text{AOT}]$  ratio, have been extensively used in a large variety of applications.<sup>2,3</sup> In this respect, most interest is presently devoted to the properties of water molecules encased in the aqueous nanodroplets. It is now well-established that this water behaves markedly differently from bulk, network-organized water, because of its interactions with the surfactant headgroups.<sup>4</sup>

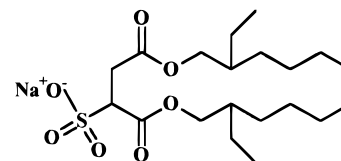
More recently, other kinds of AOT-interactions were pointed out by the formation of strong charge-transfer complexes (CTC) between AOT and iodine or TCNE, tetracyanoethylene, two well-known  $n$ - or  $\pi$ -electron acceptors.<sup>5,6</sup> The AOT-capacity for acting as a  $n$ -donor in electron-donor–acceptor (EDA) complexes was, thus, clearly evidenced. The most surprising result was the large magnitude of the AOT-acceptor interactions since, for example, AOT is able to exchange for naphthalene in naphthalene–TCNE complex.<sup>6</sup> In a previous work on alkene bromination in AOT-reverse micelles and w/o microemulsions,

a reaction which can be viewed as a probe for the HBD (hydrogen-bond donor) ability of the encased water, we found that bromine, a hydrophobic reagent, resides mainly at the interface (bromine partition coefficients between isooctane and water and between isooctane and interface are  $8 \times 10^{-3}$  and  $4$ , respectively) despite the relative polarities of the oily, interfacial and aqueous microphases.<sup>7</sup> This was another indirect evidence for particular bromine–AOT interactions.

In this paper, we report results on bromine–AOT charge-transfer complex in isooctane, its formation and its partition between isooctane and interface, which confirm the  $n$ -donor



ability of AOT. The marked strength of the EDA interactions are attributed to the sulfonate headgroup of AOT, rather than to its ester groups as postulated earlier.<sup>5,6</sup> Moreover, the major role of AOT-aggregation is evidenced by the marked decrease in the constant for the formation of bromine–AOT complexes on going from monomeric AOT species ( $K = 4 \times 10^3 \text{ M}^{-1}$ )



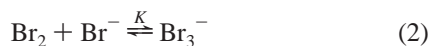
to reverse micelles ( $K = 1 \text{ M}^{-1}$ ). An increase in the water content of the AOT solutions results in a significant decrease

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in the molar absorption coefficient of the bromine-AOT complex which vanishes at  $W$  larger than 12.

The hydrogen-bonding capability of water in AOT-isooctane- $H_2O$  w/o microemulsions is also investigated via the  $W$ -dependence of bromine-tribromide ion equilibrium constant,  $K$  in eq 2.



$K$ , which is known to be mainly controlled by the solvation energy of bromide ion,<sup>8</sup> is 4 times larger in very large water nanodroplets ( $W > 20$ ) than in bulk water, emphasizing the marked differences between microemulsion water and network-organized water.<sup>4</sup>

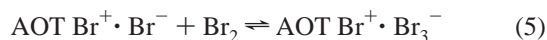
## Results and Discussion

**AOT–Bromine Charge-Transfer Complex.** The absorption spectrum of bromine in isooctane, as in any hydrocarbon,<sup>8</sup> exhibits two characteristic bands at  $\lambda_{max} = 405$  nm ( $\epsilon = 6$  cm<sup>2</sup> mol<sup>−1</sup>) and 238 nm ( $\epsilon = 5 \times 10^4$  cm<sup>2</sup> mol<sup>−1</sup>). When AOT is added in concentrations smaller or markedly larger than its operational cmc,<sup>10</sup> a new absorption band appears<sup>11</sup> at 270 nm (Figures S1 and S2 in Supporting Information). The position of this new band does not depend significantly on the AOT-concentration but its intensity increases markedly with [AOT].

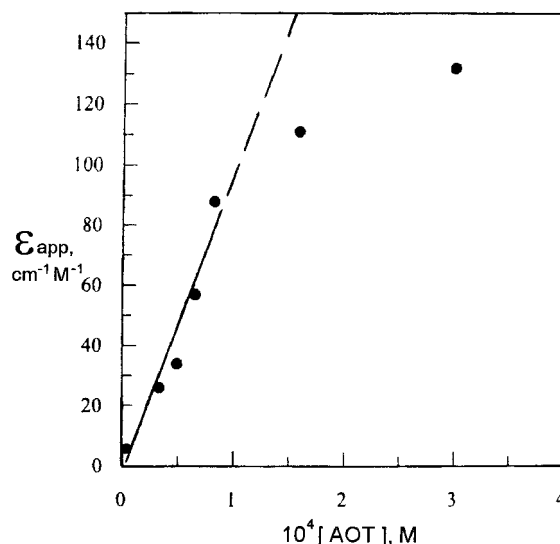
In agreement with many literature data,<sup>5,6,9,12,13</sup> the appearance of the band at 270 nm can be readily attributed to the formation of a charge-transfer complex, CTC, between bromine and AOT. On one hand, similar bands are currently observed when bromine interacts with a variety of  $\pi$ -donors and in particular with benzene<sup>9</sup> ( $\lambda_{max}^{CTC} = 292$  nm in  $CCl_4$ ) and with cyclohexene<sup>14</sup> ( $\lambda_{max}^{CTC} = 285$  nm in hexane). On the other hand, it is now well-known that AOT acts as a  $n$ -donor and forms CTCs with iodine and tetracyanoethylene, two acceptors analogous to bromine.<sup>5,6</sup> Furthermore, it is unlikely that the 270 nm band can be due to tribromide ion,  $Br_3^-$ , which absorbs<sup>8</sup> in the same region (vide infra) and which could arise, as shown in eq 3, via the formation of a 1:2 AOT–bromine complex consecutive to that of the 1:1 complex (eq 1).



The 270 nm band exists whatever the relative concentration of bromine and AOT and, in particular, when the AOT-concentration is markedly larger than that of bromine, i.e., when bromine is fully bound to AOT in a 1:1 complex (eq 1), so that there is no free bromine to make the formation of the 1:2 complex possible (eq 3). The formation of  $Br_3^-$  through an inner complex (eq 4 and 5), analogous to those observed for iodine complexation



with strong donors such as pyridine<sup>15</sup> or polyacetylene<sup>16</sup> but not with AOT,<sup>5</sup> is also unlikely for bromine since the formation constants for  $Br_3^-$  via eq 3 or 5 are smaller than those for  $I_3^-$  by 1–2 powers of 10.<sup>8</sup> Moreover, the bonding of AOT with the highly electrophilic positive bromine, as in eq 4, would certainly involve the formation of a bromine–AOT chemical bond by substitution of some hydrogen atoms of its hydrocarbon



**Figure 1.** Effect of AOT in concentrations, in M, smaller than its cmc, on  $\epsilon_{app}$ -values of bromine, in cm<sup>2</sup> mol<sup>−1</sup>, in isooctane at 315 nm. (●): experimental data. Full line: calculated values<sup>20</sup> (eq 6, see text).  $[Br_2]_{total} = 2.8 \times 10^{-3}$  M;  $[AOT]_{total} = 3.3 \times 10^{-5}$ ,  $5.00 \times 10^{-5}$ ,  $6.67 \times 10^{-5}$ ,  $8.33 \times 10^{-5}$ ,  $1.67 \times 10^{-4}$  and  $3.3 \times 10^{-4}$  M.

chains, which is not observed. There is no change in the <sup>1</sup>H and <sup>13</sup>C NMR spectra<sup>17</sup> of AOT when a 10-fold excess of bromine is added to AOT in carbon tetrachloride.<sup>18</sup>

Finally, the most straightforward evidence for a very minor role of  $Br_3^-$  in “dry” AOT-isooctane solutions comes from the marked decrease in the intensity of the 270 nm band and its final disappearance by addition of more and more water (vide infra). On the contrary, water should favor  $Br_3^-$  formation via the well-known water–bromine reaction<sup>19</sup> releasing bromide ion and promoting eq 5, which is not observed.

**Formation Constant of Bromine–AOT Charge-Transfer Complex.** The equilibrium constant for the formation of the 1:1 AOT–bromine CTC (eq 1) is obtained from the [AOT]-dependence of the apparent molar absorption coefficient of bromine,  $\epsilon_{app}$ , at constant total bromine concentration (Figure 1).  $\epsilon_{app}$ -values were measured at 315 nm, a wavelength where only CTC absorbs and where the absorbance varies from 0 to 0.4, i.e., in a range in which it is reasonable to assume a linear absorbance–concentration relationship. AOT concentrations are smaller than the operational cmc<sup>10</sup> ( $4 \times 10^{-4}$  M). In experiments in which bromine concentration is significantly large ( $2.8 \times 10^{-3}$  M) as compared to that of AOT ( $\leq 3 \times 10^{-4}$  M), a marked increase in  $\epsilon_{app}$ , from 6 cm<sup>2</sup> mol<sup>−1</sup> when [AOT] = 0 to 132 cm<sup>2</sup> mol<sup>−1</sup> with [AOT] =  $3.3 \times 10^{-4}$  M, is observed showing that the molar absorption coefficient of the complexed bromine is much larger than that of free bromine. However, the quantitative analysis of the data of Figure 1 in terms of  $\epsilon_{AOT-Br_2}^0$  and  $K_1$ -values is not straightforward for two reasons: (i) the impossibility of working at  $[Br_2] \ll [AOT] < 4 \times 10^{-4}$  M, because of the difficulties of maintaining bromine concentration in the range of  $10^{-6}$  M constant, and (ii) the formation of premicellar AOT-aggregates, according to the E-aggregation mechanism<sup>21</sup> which involves the formation of cyclic reverse micelles from linear AOT- $n$ -mers. On one hand, an iterative procedure<sup>20</sup> specifically designed for cases in which the concentrations of the complex and of the free donor are unknown (eq 6) is used, instead of the usual equation relating the experimental  $\epsilon_{app}$ -values to the total donor concentration. On the other hand, only data for  $[AOT]_{total}$  significantly smaller than  $10^{-4}$  M are taken into account in order to avoid a significant

**TABLE 1: Equilibrium Constants (in M<sup>-1</sup>) for the Formation of Charge-Transfer Complexes between Various Acceptors A, and Donors D**

D	A		
	Br <sub>2</sub>	I <sub>2</sub>	TCNE <sup>a</sup>
benzene	0.10 <sup>b,c</sup>	0.17 <sup>b,d</sup>	0.12 <sup>e</sup>
toluene	0.14 <sup>b,c</sup>	0.25 <sup>b,d</sup>	0.22 <sup>e</sup>
cyclohexene	0.47 <sup>f</sup>		0.03 <sup>e</sup>
di- <i>n</i> -butyl ether		0.44 <sup>b,g</sup>	
AOT	4 × 10 <sup>3</sup> <sup>h</sup>	1.6 × 10 <sup>4</sup> <sup>ij</sup>	2.5 × 10 <sup>3</sup> <sup>ik</sup>

<sup>a</sup> Tetracyanoethylene. <sup>b</sup> In CCl<sub>4</sub>, 25 °C. <sup>c</sup> Reference 9. <sup>d</sup> Reference 22. <sup>e</sup> In CH<sub>2</sub>Cl<sub>2</sub>, 21 °C; reference 23. <sup>f</sup> In dichloroethane, 25 °C; reference 14b. <sup>g</sup> Reference 24. <sup>h</sup> In isooctane, 25 °C; this work. <sup>i</sup> In *n*-hexane, 25 °C. <sup>j</sup> Reference 5. <sup>k</sup> Reference 6.

contribution of premicellar AOT-aggregates.

$$K_1 = \frac{[\text{AOT} \cdot \text{Br}_2]}{[\text{Br}_2][\text{AOT}]_{\text{free}}} \quad (6)$$

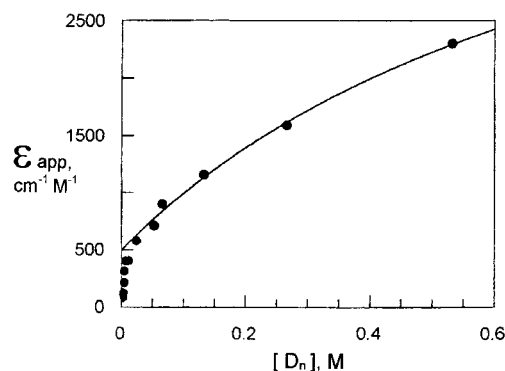
This procedure works fairly well for [AOT]<sub>total</sub> smaller than 10<sup>-4</sup> M and gives the following reasonable values.

$$\epsilon_{\text{AOT} \cdot \text{Br}_2} = (1.4 \pm 0.2) 10^3 \text{ cm}^{-1} \text{ M}^{-1}$$

$$K_1 = (4 \pm 2) 10^3 \text{ M}^{-1}$$

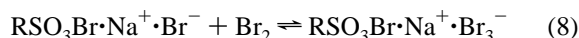
As shown in Figure 1, the agreement between the experimental and calculated  $\epsilon_{\text{app}}$ -values is fairly good, in particular in view of the large experimental error on small  $\epsilon$ -values, 10% about for  $\epsilon_{\text{app}} < 200$ , and 2% only for  $\epsilon_{\text{app}} > 600 \text{ cm}^{-1} \text{ M}^{-1}$ . At the largest [AOT]<sub>total</sub> (1.7 and 3.3 × 10<sup>-4</sup> M), i.e., when [AOT] approaches the cmc, marked deviations corresponding to decreases in  $\epsilon_{\text{AOT} \cdot \text{Br}_2}$  and/or in  $K_1$  are observed. These significant decreases are probably related to the bromine complexation with premicellar AOT-aggregates.<sup>21</sup>

The calculated  $K_1$ -value agrees fairly well with those previously measured for other AOT-complexes shown in Table 1. In particular, the trend of  $K$ -values is consistent with the relative acceptor abilities of bromine, iodine, and TCNE. Nevertheless, the large  $K$ -values for AOT-complexes, in the range of 10<sup>3</sup> M<sup>-1</sup>, contrast markedly with those obtained with other *n*- or  $\pi$ -donors. Among the many data on halogen-CTCs available in the literature, the strongest complexes analogous to those between AOT and halogens are observed when the donors are polyoxygenated ethers<sup>24</sup> with  $K$ -values in the range of 10<sup>2</sup> M<sup>-1</sup>. It has been claimed<sup>5</sup> that AOT may act as a *n*-donor through the free electron pairs on the carbonyl groups of its ester functions. This assumption is not reasonable since, to the best of our knowledge, no CTC complex with esters has been reported previously. Moreover, in our hands, bromine–diethyl succinate mixtures in hexane do not exhibit any charge-transfer band in their UV–vis absorption spectra, showing unambiguously that the AOT–ester functions are not involved in the charge-transfer process of AOT. Therefore, the electron donation from AOT should occur via the sulfonate group, the negative charge of which could explain the unusually strong AOT-charge-transfer complexes. This assumption is supported by the very large interactions between iodine and metal acetylacetonates<sup>25</sup> which, as AOT, can be considered as very tight ion-pairs in apolar solvents. With these latter species, the  $K$ -values for the formation of their molecular complexes are in the 10<sup>3</sup> M<sup>-1</sup> range, i.e., analogous to those obtained for AOT complexes. However, this interaction mechanism (eq 7 and 8) raises again the question of the existence of a AOT·Br<sub>2</sub> inner complex, the bromide ion



**Figure 2.** Effect of AOT in concentrations ([Dn] = [AOT] – cmc, in M) larger than its cmc, on  $\epsilon_{\text{app}}$ -values of bromine, in cm<sup>-1</sup> M<sup>-1</sup>, in isooctane at 315 nm. (●): experimental data. Full line: calculated values (eq 9, see text). [Br<sub>2</sub>]<sub>total</sub> = 3.2 × 10<sup>-3</sup> M; [AOT]<sub>total</sub> from 5 × 10<sup>-4</sup> to 0.53 M.

of which would be stabilized by



formation of Br<sub>3</sub><sup>-</sup> resulting from the reaction with a second bromine molecule. This occurrence is definitely ruled out in experiments with [AOT] ≫ [Br<sub>2</sub>] (Figure 2) although not totally in those with [AOT] ≪ [Br<sub>2</sub>] (Figure 1). Nevertheless, the dissociation of the outer complex (eq 1) into an inner complex (eq 7) is unlikely. This conclusion agrees, in particular, with the fact that TCNE, a donor which cannot readily undergo heterolytic dissociation and which is not expected to form inner complex as in eq 7, interacts with AOT as strongly as bromine (Table 1).

**AOT–Bromine Charge-Transfer Complex in “Dry” Reverse Micelles.** A marked increase in the intensity of the 270 nm band is observed at constant bromine concentration when the AOT concentration increases in a range largely above its cmc (Figure S2). The very large  $\epsilon_{\text{app}}$ -values (Figure 2), much larger than that of free bromine, afford unambiguous evidence for strongly absorbing bromine complexes since, for example,  $\epsilon_{\text{app}}$  is as large as 175 cm<sup>-1</sup> M<sup>-1</sup> when [AOT]/[Br<sub>2</sub>] is 0.2 only and reaches 2300 cm<sup>-1</sup> M<sup>-1</sup> when [AOT], 0.53 M, is 17 times larger than [Br<sub>2</sub>]. With these high [AOT], surfactant micellization occurs so that two different microphases, isooctane and micellar pseudophases, are currently postulated.<sup>2,3</sup> Bromine can, therefore, interact with monomeric C1<sup>o</sup> or linearly aggregated,<sup>21</sup> C1<sup>o</sup>, AOT molecules, and also with the AOT micellar aggregates, leading to a bromine-AOT complex, C2<sup>i</sup>, of unknown stoichiometry. Moreover, the complex C1<sup>o</sup> can also participate to the micellization process. These mechanisms are summed up in Scheme 1 where superscripts <sup>o</sup> and <sup>i</sup> refer to species in the isooctane and micellar pseudophases, respectively. From the usual expressions of the overall absorbance and of the formation constants  $K'_1$  and  $K_3$ , the  $\epsilon_{\text{app}}$ -dependence on AOT concentration is described by eq 9 derived from the pseudophase model.<sup>7</sup> [Dn], the concentration of the micellized surfactant, [AOT] – cmc, can be used when [AOT]<sub>total</sub> is not significantly different from [AOT]<sub>free</sub>, i.e., when [AOT] is markedly larger than [Br<sub>2</sub>]. This requirement is met for [AOT] larger than 0.05 M.

$$\epsilon_{\text{app}} = \frac{\epsilon_{\text{C1}^o}^o + \epsilon_{\text{C2}^i}^i K_3 [\text{Dn}]}{1 + K_3 [\text{Dn}]} \quad (9)$$

## SCHEME 1

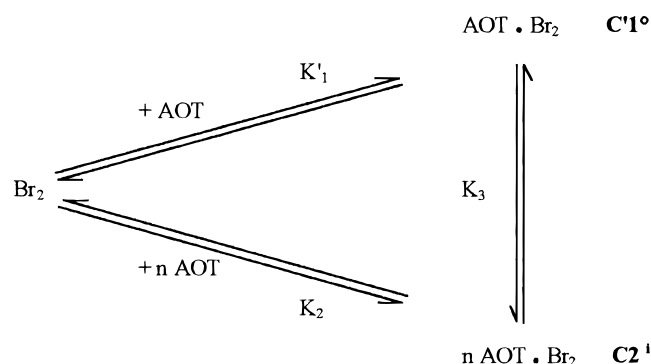


TABLE 2:  $\epsilon$ -Values at 315 nm and Formation Constants of Brominated Species<sup>a</sup> in AOT–Isooctane–H<sub>2</sub>O Solutions at 25 °C

	$\epsilon$ , cm <sup>-1</sup> M <sup>-1</sup>	$K$ , M <sup>-1</sup>
Br <sub>2</sub> <sup>o</sup>	6 ± 10	
Br <sub>2</sub> <sup>i</sup>	20 ± 10	
Br <sub>2</sub> <sup>w</sup>	30 ± 5	
Br <sub>3</sub> <sup>-w</sup>	(6.3 ± 0.1) × 10 <sup>3</sup>	16 <sup>b</sup>
(Br <sub>3</sub> <sup>-</sup> ) <sup>μE</sup>		60 ± 7 <sup>c</sup>
C'1 <sup>o</sup> <sup>d</sup>	(1.4 ± 0.2) × 10 <sup>3</sup>	(4 ± 2) × 10 <sup>3</sup>
C2 <sup>i</sup> <sup>e</sup>	(5 ± 1.5) × 10 <sup>3</sup>	1.3 ± 0.7
C3 <sup>m</sup> <sup>f</sup>	700 ± 150	1.1 ± 0.4

<sup>a</sup> The superscripts, o, i, m,  $\mu$ E, and w refer to species in isooctane, “dry” reverse micelles, aqueous reverse micelles ( $W < 12$ ), w/o microemulsions ( $W > 12$ ), and bulk water, respectively. <sup>b</sup> Equilibrium constant for the formation of tribromide ion from free bromine and bromide in bulk water; ref 8. <sup>c</sup> Equilibrium constant for the formation of Br<sub>3</sub><sup>-</sup> from Br<sub>2</sub> and Br<sup>-</sup> in highly aqueous AOT–w/o microemulsions,  $W \geq 20$ . <sup>d</sup> Bromine complex with monomeric AOT, eq 1. <sup>e</sup> Bromine complex with “dry” reverse micelles, eq 9 and Scheme 1. <sup>f</sup> Bromine complex with aqueous reverse micelles,  $W = 9$ , eq 13, and Scheme 2.

Moreover, the fact that the C2<sup>i</sup> stoichiometry is not available makes the definition of  $K_3$  in terms of reagent concentrations uncertain.

A nonlinear fitting to eq 9 of the experimental data for which  $[AOT]_{\text{total}} \geq 5 \times 10^{-2}$  M gives the absorption coefficient and the formation constant of C2<sup>i</sup> from C'1<sup>o</sup> shown in Table 2 with reasonably small errors. Furthermore, the agreement between experimental and calculated  $\epsilon_{\text{app}}$ -values is satisfactory (Figure 2). It is noticeable that the  $\epsilon_{\text{C'1}^o}^o$ -value obtained from this fitting is only 500, i.e., about 3 times smaller than the value found previously for the complex between bromine and monomeric AOT. This small value could be attributed to the bromine complexation with linear, premicellar AOT-aggregates.<sup>21</sup>

According to Scheme 1,  $K_2$ , the constant for the formation of the micellized CTC, C2<sup>i</sup>, by direct interaction of free bromine with the micelle, calculated by eq 10, is about 2 M<sup>-1</sup>, in fair agreement with the value previously measured from kinetic data of 1-octene bromination in

$$K_2 = K_1 K_3 [\text{cmc}] \quad (10)$$

AOT–reverse micelles.<sup>7</sup>

This is a surprisingly large value, in particular when it is compared to the coefficient of bromine partition between isooctane and water  $K_o^w = 8.5 \times 10^{-3}$ . The straightforward conclusion of this comparison is that bromine in AOT–isooctane reverse micelles is located mainly at the interfacial region containing the surfactant headgroups, which agrees fairly well with the formation of strong bromine–AOT complex. This result is consistent not only with kinetic data in these microhetero-

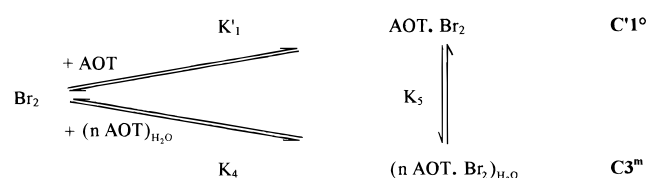
TABLE 3:  $W$ -Dependence ( $W = \text{H}_2\text{O}/[\text{AOT}]$ ) of Experimental  $\epsilon_{\text{app}}$ -Values<sup>a</sup> of Bromine<sup>b</sup> at 315 nm in AOT–Aqueous Reverse Micelles, at 25 °C

[AOT] <sup>c</sup>	$W$					
	<1 <sup>d</sup>	3	5	7	9	12
0.08	950	140	90	50	70	45
0.13	1160	240	120	65	90	40
0.23	1580	300	200	110	135	55
0.40	2050	435	490	190	235	90
0.53	2300	650	650	230		
0.67		770	780	270	270	190

<sup>a</sup> In cm<sup>-1</sup> M<sup>-1</sup>, at  $\pm 10\%$  when  $\epsilon < 200$ ; at  $\pm 2\%$  when  $\epsilon > 600$ .

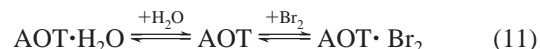
<sup>b</sup>  $[\text{Br}_2]_{\text{total}} = 1.5 \times 10^{-3}$  M. <sup>c</sup> In M in isooctane. <sup>d</sup> “dry” reverse micelles (see Experimental Section).

## SCHEME 2



geneous media but also with a previous investigation in SDS micelles showing that the preferential localization of iodine is at the micellar interface.<sup>26</sup>

**AOT–Bromine Charge-Transfer Complex in Aqueous Reverse Micelles.** When water is added to AOT solutions in isooctane, a marked decrease in the bromine  $\epsilon_{\text{app}}$ -values at 315 nm is observed. Nevertheless, at constant  $W$ , a significant  $\epsilon_{\text{app}}$ -increase is still associated to an increase in the AOT-concentration. Some typical results are given in Table 3. The absorbance is noticeably weak at  $W = 12$  and disappears at  $W > 15$ . The same behavior was observed previously with iodine solutions<sup>5</sup> and was interpreted in terms of AOT deactivation by hydration.<sup>27</sup> In these aqueous reverse micelles, in which water interacts strongly with the surfactant headgroups,<sup>4,28</sup> the  $\epsilon_{\text{app}}$ -decrease can be attributed to a decrease in the concentration of the micellized charge-transfer complex, the only bromine species which exhibits a significant absorption coefficient, (Table 2). A competition between AOT–bromine and AOT–water interactions (eq 11) is, therefore, suggested by the water-induced decrease in



the CTC-absorbance. Since AOT–water interactions depend on  $W$  only, the constant for the CTC-formation is expected to depend also on  $W$  only. In Scheme 2, a mechanism consistent with this assumption is proposed. The  $\epsilon_{\text{app}}$ -dependence on

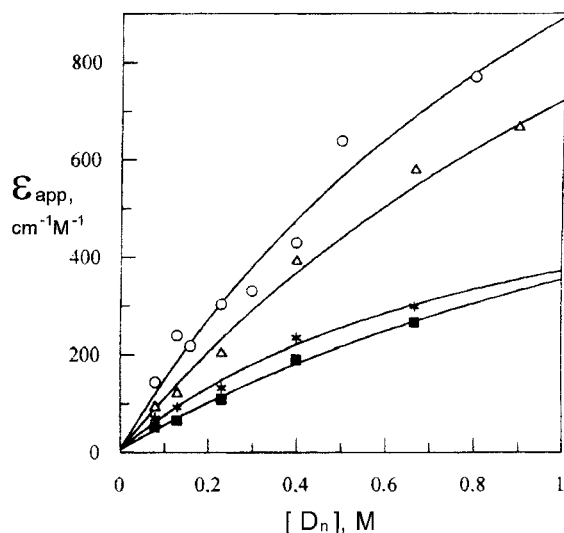
$$\epsilon_{\text{app}} = \frac{\epsilon_{\text{C'1}^o}^o + \epsilon_{\text{C3m}} K_5 [\text{Dn}]}{1 + K_5 [\text{Dn}]} \quad (12)$$

$[\text{AOT}]$  is given by eq 12, valid for a given  $W$ . However, the fittings of the experimental data to this equation provide, at every  $W$ , negative and highly imprecise values for  $\epsilon_{\text{C'1}^o}^o$  which was established above with a reasonable precision. In contrast, excellent fittings with eq 13 (Figure 3) are obtained when the absorbance of complex C'1<sup>o</sup> is neglected. This result implies that, in aqueous reverse micelles, bromine does not

$$\epsilon_{\text{app}} = \frac{\epsilon_{\text{C3m}} K_4 [\text{Dn}]}{1 + K_4 [\text{Dn}]} \quad (13)$$

associate with the monomeric or linearly aggregated AOT





**Figure 3.** Effect of  $W = [\text{H}_2\text{O}]/[\text{AOT}]$  on  $\epsilon_{\text{app}}$ -values of bromine, in  $\text{cm}^{-1} \text{M}^{-1}$ , in aqueous AOT-reverse micelles, ( $[\text{Dn}] = [\text{AOT}]$ , in M). Marked decrease of  $\epsilon_{\text{app}}$  with increasing water content. (O):  $W = 3$ , ( $\Delta$ ):  $W = 5$ ; (\*):  $W = 7$ ; ( $\blacksquare$ ):  $W = 9$ . Full lines: calculated values (eq 13).

**TABLE 4: W-Dependence ( $W = [\text{H}_2\text{O}]/[\text{AOT}]$ ) of the Molar Absorption Coefficient at 315 nm and of Equilibrium Constant of AOT- $\text{Br}_2$  Charge-Transfer Complex in Aqueous Reverse Micelles<sup>a</sup>, Scheme 2**

$W$	$\epsilon$ , $\text{cm}^{-1} \text{M}^{-1}$	$K$ , $\text{M}^{-1}$
$\ll 1$	$5000 \pm 1500$	$1.3 \pm 0.7$
3	$2100 \pm 640$	$0.7 \pm 0.3$
5	$2000 \pm 530$	$0.5 \pm 0.2$
7	$1000 \pm 250$	$0.5 \pm 0.2$
9	$700 \pm 150$	$1.1 \pm 0.4$

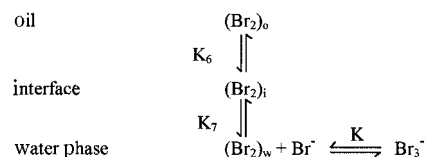
<sup>a</sup> Calculated from eq 13.

species but interacts with the hydrated micellized AOT only. In other terms, in Scheme 2 the pathway going through  $\text{C}^1\text{O}$  is negligible as compared to the direct transfer of bromine to the aqueous reverse micelles. The  $\epsilon_{\text{C}3\text{m}}$  and  $K_4$ -values obtained from the fitting to eq 13 with reasonably small errors are given in Table 4. The marked decrease of  $\epsilon_{\text{C}3\text{m}}$  with an increase in  $W$  illustrates the well-known effect of the medium polarity on the magnitude of EDA interactions.<sup>12,29,30</sup> This  $\epsilon$ -decrease would be expected to be associated to a parallel decrease in the formation constant. The small  $K_4$ -values calculated from eq 13 (Table 4) and their insignificant dependence on  $W$  are, therefore, surprising. Nevertheless, these results agree with the disappearance of any bromine-AOT interactions in AOT-w/o microemulsions.<sup>1</sup> They are also consistent with recent results<sup>31</sup> showing the marked decrease in the electron donor capacity of AOT when  $W$  increases.

**Bromine-Tribromide Ion Equilibrium, Solvation of Bromide Ion, and HBD Ability of Water in AOT-W/O Microemulsions.** In AOT-w/o microemulsions, i.e., in the ternary AOT-isooctane- $\text{H}_2\text{O}$  systems with  $W > 15$ , the 270 nm band, observed in the spectra of "dry" or aqueous reverse micelles and related to AOT-bromine complexes, disappears but is restored when bromide ions are added. This new band is readily attributed<sup>8</sup> to the formation of tribromide ion via equilibrium 2. The  $\epsilon_{\text{app}}$ -values measured at several bromide ion concentrations in microemulsions of various composition described by  $W$  and  $Z$  ( $Z = [\text{IO}]/[\text{AOT}]$ ; IO, isooctane) are given as Supporting Information.

In these microemulsions with high water content, a water core appears when the requirements for completing the first solvation

### SCHEME 3



shells of AOT are met. Nevertheless, this core water cannot be viewed as bulk water, because of long-distance AOT-water interactions. Therefore, the properties of water in microemulsions and, in particular, its polarity and its capacity of solvating ions are different from those of bulk, network-organized water.<sup>2,4,28</sup> A number of physicochemical data<sup>3,4,28,29</sup> has suggested that three different pseudophases coexist in a microemulsion, the oily (isooctane), interfacial, and water pseudophases. In accordance with this representation, Scheme 3 is proposed<sup>7,32,33</sup> to describe the tribromide ion-forming reaction between lipophilic bromine and hydrophilic bromide ion. From this Scheme, the overall absorbance is given by eq 14 in which the concentrations of the several brominated species are expressed by eqs 15–19, as a function of the bromine

$$\epsilon_{\text{app}}[\text{Br}_2]_{\text{tot}} = \epsilon^{\text{w}}[\text{Br}_2]_{\text{w}} + \epsilon^{\text{i}}[\text{Br}_2]_{\text{i}} + \epsilon^{\text{o}}[\text{Br}_2]_{\text{o}} + \epsilon_{\text{Br}_3^-}^{\text{w}}[\text{Br}_3^-]_{\text{w}} \quad (14)$$

concentration in isooctane and of the relative concentrations of the three pseudophases  $W$  and  $Z$ .

$$[\text{Br}_2]_{\text{i}} = K_6[\text{Br}_2]_{\text{o}} \frac{1}{Z} \quad (15)$$

$$[\text{Br}_2]_{\text{w}} = K_6 K_7 [\text{Br}_2]_{\text{o}} \frac{W}{Z} \quad (16)$$

$$[\text{Br}_3^-] = K K_6 K_7 [\text{Br}_2]_{\text{o}} [\text{Br}^-]_{\text{w}} \frac{W}{Z} \quad (17)$$

$$K_o^{\text{w}} = \frac{[\text{Br}_2]_{\text{w}}}{[\text{Br}_2]_{\text{o}}} = \frac{K_6}{K_7} \quad (18)$$

$$K = \frac{[\text{Br}_3^-]_{\text{w}}}{[\text{Br}_2]_{\text{w}} [\text{Br}^-]_{\text{w}}} \quad (19)$$

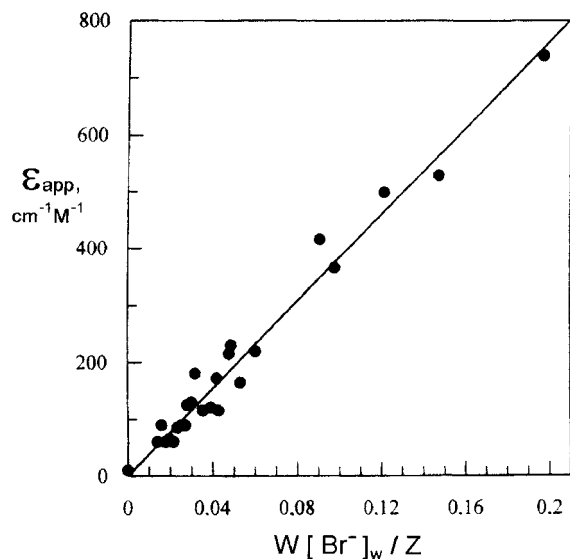
Moreover, when the experimental coefficient of bromine partition between isooctane and water  $K_o^{\text{w}}$  is taken into account, eq 20 is obtained.

$$\epsilon_{\text{app}} = \frac{\epsilon^{\text{o}} + \epsilon^{\text{i}} K_6 / Z + K_o^{\text{w}} (\epsilon^{\text{w}} + \epsilon_{\text{Br}_3^-}^{\text{w}} K [\text{Br}^-]_{\text{w}}) W / Z}{1 + K_6 / Z + K_o^{\text{w}} (1 + K [\text{Br}^-]_{\text{w}}) W / Z} = \frac{N}{D} \quad (20)$$

On one hand, the two first terms in  $N$  are negligible as compared to the last one since  $\epsilon^{\text{o}}$ ,  $\epsilon^{\text{i}}$ , and  $K_6/Z$  (see Table 2) are small. Moreover,  $\epsilon^{\text{w}}$  can be neglected. On the other hand, in  $D$ , the two last terms can also be neglected as compared to unity since  $K_6/Z$  and  $K_o^{\text{w}}$  are markedly smaller than unity. With these assumptions, eq 20 is transformed in the more simple eq 21.

$$\epsilon_{\text{app}} = \epsilon_{\text{Br}_3^-}^{\text{w}} K_o^{\text{w}} K [\text{Br}^-]_{\text{w}} \frac{W}{Z} \quad (21)$$

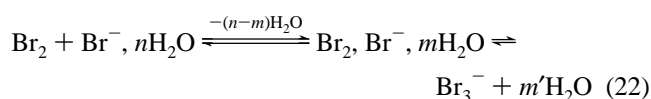
Despite the several simplifications, eq 21 describes the experimental data fairly well (Figure 4). In particular, the expected linear dependence of  $\epsilon_{\text{app}}$  on the product  $[\text{Br}^-]_{\text{w}} W/Z$  is observed when  $W$  is large.



**Figure 4.** Effect of the composition of AOT-isooctane-H<sub>2</sub>O microemulsions ( $W > 16$ ) with added bromide ions, in  $M^{-1}$ , on  $\epsilon_{app}$ -value of bromine, in  $cm^{-1} M^{-1}$ . Graphical representation of eq 21.

The  $K$ -values, at constant  $W$ , for the bromine-tribromide equilibrium are calculated (Table 5) assuming that  $\epsilon_{Br_3}^w$  and  $K_o^w$  in the water phase are constant and very close to those in bulk water.<sup>34</sup> The values thus obtained depend significantly on  $W$ , as shown in Figure 5. After a marked decrease in  $K$  from aqueous reverse micelles to w/o microemulsions,<sup>1</sup> a leveling occurs at  $W$ -values larger than 18. It is noticeable that a similar leveling in the activity coefficients of water in w/o microemulsions, has been previously observed<sup>4a</sup> in the same  $W$ -range. Of particular interest is the fact that the minimum value of  $K$  is about  $60 M^{-1}$ , i.e., significantly greater than that of 16 measured in bulk water.<sup>8</sup>

The hydrogen bond donor (HBD) ability<sup>35</sup> of water in AOT-w/o microemulsions and its dependence on  $W$  can be estimated from the change in  $K$  with  $W$  (Table 5). It has been established<sup>8b</sup> that these  $K$ -values in protic solvents are directly related to the solvation of bromide ions and, therefore, to the HBD ability of these solvents since the bromine-bromide reaction consists of two steps: exchange between

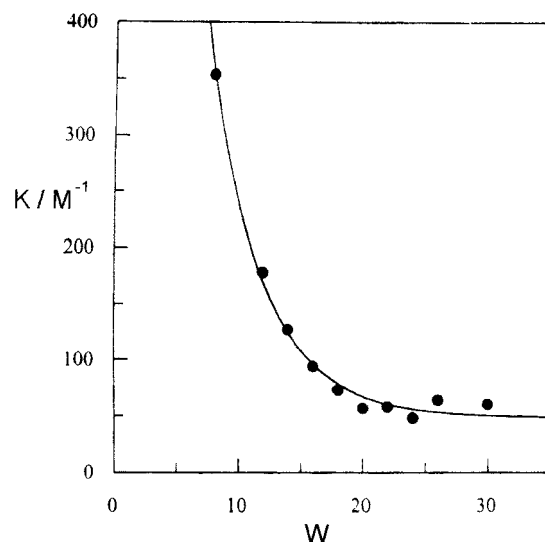


bromine and solvent molecules in the solvation shell of bromide, followed by a very close to diffusion-controlled reaction leading to tribromide (eq 22). According to this statement, the  $K$ -values in AOT-w/o microemulsions are inversely related to the strength of the  $Br^- \cdots H-OH$  hydrogen bonds. The data of Table 5 can, therefore, be interpreted in terms of bromide ion solvation and HBD ability of w/o microemulsion water. The  $K$ -limiting value of  $60 M^{-1}$  at  $W$  larger than 20, as compared to  $16 M^{-1}$  in bulk water is, therefore, a reasonable evidence for a core water in microemulsions markedly less efficient than network-organized water, in solvating bromide ions by hydrogen bonding. This result supports quite large long-distance interactions<sup>28-30</sup> between core water and sulfonate headgroup, which decreases markedly the HBD ability of microemulsion water. Moreover, the leveling of  $K$  seems to show that these long-distance interactions are not significantly altered when  $W$ , i.e., the size of the water nanodroplets, increases beyond 20. In contrast, when  $W$  decreases, these interactions strengthen rapidly and at

**TABLE 5:  $W$ -Dependence of Bromine-Tribromide Ion Equilibrium Constant and of HBD Ability,<sup>a</sup> Evaluated<sup>b</sup> from  $\delta\Delta G_{tr}(Br^-)$ , of Water in AOT-w/o microemulsions at 25 °C**

$W$	$K, M^{-1}$	$-\delta\Delta G_{tr}(Br^-)^b$
8	354	3.2
12	178	2.6
14	127	1.9
16	94	1.8
18	73	1.3
20	57	1.3
22	58	1.3
24	48	1.3
26	64	1.3
30	60	1.3
MeOH	178	2.6
H <sub>2</sub> O	16	0

<sup>a</sup> Hydrogen-bond donor ability. <sup>b</sup> Transfer Gibbs free energy of bromide ion from bulk water to microemulsion water, in  $kcal mol^{-1}$ .



**Figure 5.** Relationship between  $K$ , the bromine-tribromide equilibrium constant, and  $W$ , the water content of AOT-isooctane-H<sub>2</sub>O microemulsions. The  $K$ -value levels at about  $60 M^{-1}$  for  $W > 18$ , whereas in bulk water  $K$  is  $16 M^{-1}$  only.

$W = 12$ , the HBD ability of micelle water is in the same range as that of bulk methanol. An alternative interpretation would consider the role of sodium ions expelled from the interface to the water core by dissociation of the surfactant ion pairs and which could minimize the water ability to bromide ion solvation.<sup>36</sup> However, this is unlikely because the amount of  $Na^+$  ions liberated by AOT dissociation is certainly insignificant as compared to that of sodium bromide added in any  $K$ -measurement.<sup>8,34</sup>

A more quantitative approach to HBD of w/o microemulsion water uses eq 23 which

$$\delta\Delta G_{Br_3^-} = -0.6\delta\Delta G_{tr}(Br^-) \quad (23)$$

relates the change in Gibbs free energy of eq 2, calculated from  $K$ , to the transfer free energy of bromide ion from bulk water to protic solvents.<sup>37,38</sup> The data shown in the last column of Table 5 are thus obtained and provide a quantitative estimate of HBD ability and also of micropolarity of water in reverse micelles and microemulsions since  $\delta\Delta G_{tr}(Br^-)$  is considered as a reliable reference for solvent polarity.<sup>39</sup>

Qualitatively, the results of Table 5 are in agreement with the many investigations<sup>4,36</sup> on the state of water in microemulsions and, in particular, on its micropolarity<sup>40</sup> using various

techniques and probes. Almost all these studies are consistent with a leveling in the water properties beyond a limiting  $W$ -value. Nevertheless, there is no clear agreement on the value of the limiting  $W$ -value which spans from 12 to 16 or more. In this respect, the value close to 20 found in this work is at the upper limit of the usual range. The uncertainty of this limiting value can be readily understood since the measured water property depends on the probe localization within the water pseudophase. In this respect, it is important to note that bromide ions, the actual probe in this work, are located very probably in the water core or as far as possible from the interfacial region, because of their hydrophilicity and of electrostatic repulsions with sulfonate headgroups. Therefore, the data shown in Table 5 are mainly related to core water whereas most of the previous work involving organic, soft<sup>41</sup> ions or molecules afford data on a region closer to the interface.

The current model emerging from the many experiments on water micropolarity in reverse micelles consists of three different kinds of water, interstitial, bound, and free water, on going from very small to large  $W$ -values, with quite blurred frontiers.<sup>42</sup> However, other results are more reasonably interpreted in terms of a gradient in water properties from the surfactant containing interface to the water core.<sup>4d,40d</sup> This latter interpretation agrees better with our results showing a sharp decrease in HBD ability of water from  $W = 8$  to  $W = 20$  without any marked discontinuity around  $W$  12–16. More work is in progress in the view of investigating the complementarity of this HBD scale with the data obtained in the numerous spectroscopic studies on the state of water in aqueous reverse micelles and microemulsions.<sup>4,36,40</sup>

## Experimental Section

AOT (Sigma) was of the highest purity available and used without further purification after drying in a vacuum desiccator over  $P_2O_5$  for 2 days. 2,2,4-trimethylpentane (isooctane, Aldrich) was of spectrophotometric grade. Water was distilled over potassium permanganate and then bidistilled. Bromine and sodium bromide were Suprapur Merck reagents. A stock solution of bromine (1 mL in 25 mL of  $CCl_4$ ) was prepared shortly before use under protection of external light. The purity of 2,3-dimethyl-2-butene (99%+, Aldrich) was checked by GC – MS.

The solutions of AOT in isooctane were prepared by weighing and dilution. The water content of these solutions (“dry” micelles) was estimated, from Karl Fisher titrations, to correspond to  $W$ -value ( $W = [H_2O]/[AOT]$ ) of 0.1 at most. The aqueous micellar solutions and w/o microemulsions at given  $W$  were obtained by addition of calculated amounts of water or aqueous NaBr solutions. These solutions were pretreated<sup>7</sup> by addition of small amounts of bromine solution in  $CCl_4$  in order to prevent bromine consumption by impurities and/or the solvent in the spectroscopic measurements. All these solutions were prepared and stored in the dark to avoid the formation of bromine atoms.<sup>18</sup>

The absorption spectra were recorded on a Perkin-Elmer  $\lambda 2$  spectrophotometer. The cell was thermostated at  $(25 \pm 0.1)^\circ C$ . The  $\epsilon_{app}$ -values of bromine solutions were measured at  $\lambda = 315$  nm, a wavelength far from  $\lambda_{max}$  (270 nm) of the strongly absorbing bromine complexes. The values shown in tables and figures were obtained with a reproducibility of 2% and 10%, when  $\epsilon_{app}$  is larger than  $600\text{ cm}^{-1}\text{ M}^{-1}$  and smaller than  $200\text{ cm}^{-1}\text{ M}^{-1}$ , respectively. The overall bromine concentrations, which cannot be determined precisely by usual weighing because of the high vapor pressure of bromine and because of the necessary “presaturation” treatment, were measured indi-

rectly by means of 2,3-dimethyl-2-butene, an alkene which consumes bromine at a rate close to the diffusion-controlled limit.<sup>43</sup> Weighed amounts of a methanolic solution of this alkene of rigorously known concentration were added to the bromine solution after recording its spectrum. The molar absorption coefficient was given by the slope of the linear plot of  $\Delta A$ , the absorbance jump resulting from the addition of the alkene solution, versus  $\Delta c$ , with  $\Delta c = [\text{alkene}]_{added}$ .

The  $^1H$  and  $^{13}C$  NMR spectra of AOT ( $5 \times 10^{-2}\text{ M}$  in  $CCl_4$ , TMS) were recorded on a Bruker AC200 spectrometer at 200 MHz. They were identical to those previously reported.<sup>17</sup> No change in the chemical shifts was observed when bromine (up to  $5 \times 10^{-1}\text{ M}$ ) was added.

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**Supporting Information Available:** Dependence of the apparent molar absorption coefficient at 315 nm of the bromine–tribromide ion system on the composition ( $W = [H_2O]/[AOT]$  and  $Z = [IO]/[AOT]$ ) of the AOT-w/o microemulsion at  $25^\circ C$  (Table S1). Absorption spectra of bromine in AOT–isooctane solutions at AOT concentration smaller and larger than the “operational” cmc,  $4 \times 10^{-4}\text{ M}$  (Figures S1 and S2).

## References and Notes

- (1) In this paper, the term, “dry” reverse micelles, refers to AOT-microaggregates in isooctane solutions without added water ( $[H_2O]/[AOT] = W \leq 0.1$ ). Aqueous reverse micelles and w/o microemulsions are used for AOT- $H_2O$ -Isooctane solutions with  $1 < W < 15$  and  $W > 15$ , respectively.
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- (11) In the bromine spectra in the presence of AOT (Figures S1 and S2), there is no obvious isosbestic point between the free bromine band at 405 nm and the new band, which would be expected from equilibrium 1 (eq 1). This absence arises from the fact that the change in free bromine absorbance is not significant for two reasons: (i) very small value of the molar absorption coefficient ( $\epsilon_{Br_2} = 6\text{ cm}^{-1}\text{ M}^{-1}$ ) and (ii) experimental conditions (total bromine concentration much larger than those of AOT) imposed by the difficulty of obtaining highly diluted bromine solutions of well-defined concentrations (see Experimental Section).
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