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Analysis of the Bromide Ion Distribution in the Water Pool of Reverse Micelles of Hexadecyltrimethylammonium Bromide in Chloroform/*n*-Dodecane and Isooctane/ *n*-Hexanol by Chemical Trapping

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Chemical trapping of bromide ions in reverse micelles prepared with hexadecyltrimethylammonium bromide, CTAB, in *n*-dodecane/CHCl$_3$ and isooctane/*n*-hexanol has been obtained for 2,4,6-trimethylbenzenediazonium (1-ArN$_2^+$) and 2,4-dimethyl-4-hexadecylbenzenediazonium (16-ArN$_2^+$) tetrafluoroborates. Quantitative analysis of the reaction products of 1-ArN$_2^+$ and 16-ArN$_2^+$ with water and bromide ion, the corresponding phenol and bromo derivatives, and comparison with appropriate standard curves yielded the local concentrations of Br$^-$ in the water pool, [Br]$_f$, and micellar interface, [Br]$_b$, in reverse CTAB micelles prepared in *n*-dodecane/CHCl$_3$ and isooctane/*n*-hexanol. The determination of [Br]$_b$ in reverse micelles by chemical trapping with 16-ArN$_2^+$ can be obtained after correction for probe distribution between the reverse micelle and the organic solvent, especially in the case of *n*-dodecane/CHCl$_3$. This correction was possible after demonstrating that 16-ArN$_2^+$, upon dediazoniation in wet *n*-dodecane/CHCl$_3$, yields exclusively the corresponding bromo derivative. A Poisson−Boltzmann (PB) equation above a water/ detergent molar ratio, *W/S*, of 14 appropriately describes the values of [Br]$_f$. Comparison of the experimental values of [Br]$_b$ with those predicted by PB with changing *W/S* suggest that 16-ArN$_2^+$ extends from the interface 0.6−1.2 nm with increasing *W/S*. Both PB calculations and experimental data indicate that the degree of counterion dissociation from CTAB reverse micelles in *n*-dodecane/CHCl$_3$ reaches a value of ca. 0.2 above *W/S* 15.

Introduction

The local concentrations of ions and reactive species in interfaces control a variety of chemical transformations in interfaces. In particular, essential biological properties, such as energy biotransformation and excitability, are determined by the local ion concentration at relevant proteolipid sites.[1] Experimental determinations of local ion concentrations in biological membranes are troublesome and complicated by their compositional complexity.[1] Micelles and vesicles are convenient and simpler models used to understand selected properties of biological membranes.[2] Even in these models the determination of local interfacial ion concentrations is particularly difficult due, in part, to the lack of positional definition of the ions in the surface and the selection of the volume elements used in the calculations.

Interfacial ion concentrations in charged micelles ranging from 1.5 to 4.0 M can be calculated by assuming a spherical form and using independently determined parameters such as the total micellar volume, radius, aggregation number, and ion dissociation degrees.[3] A major problem in this approach is the definition of the volume elements used for concentration calculations.[4]

Poisson−Boltzmann equations, PBE, have also been used to calculate the local counterions and co-ions at several distances from the surface, taking into account the same physical parameters used in the geometrical calculations.[4,5]

Local ion concentrations have also been deduced from kinetic experiments.[4] When a bimolecular reaction is studied in micelles, it is possible to estimate the local concentration of reactive ions by using the rate constants in the micellar pseudophase as the only adjustable parameter. Again in this case the reactive volume has to be chosen.[5,6]

Estimation of reaction volume elements has been attempted by incorporation of probes at the micellar surface, using molecules bearing a charge opposite to that of the micelle and changing the distance between the fixed center at the surface of micelle and the reaction center in the probe, thus mapping local ion concentrations.[7] A similar approach was used in the study of ion adsorption in zwitterionic surfactants with a variable distance between the charged groups.[8]

Recently Romsted and co-workers[9−16] introduced a method that directly determines local composition of interfaces without recourse to a definition of the reactive

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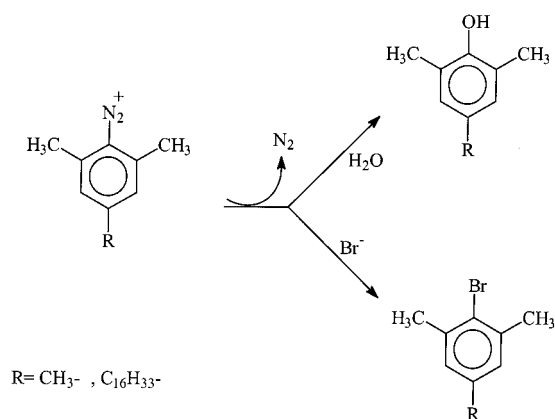(6) Blasko, A.; Bunton, C. A.; Armstrong, C.; Gotham, W.; He, Z.-M.; Nickes, J.; Romsted, L. S. *J. Phys. Chem.* **1991**, *95*, 6747.
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Scheme 1

R= CH$_3$- , C$_{16}$H$_{33}$-

volume. In this method, named chemical trapping, a diazonium salt is added to an interface and, due to its high reactivity, essentially all molecules with nucleophilic centers react with low selectivity. This technique allows the direct determination of local concentrations of ions and other molecules in several systems, without the necessity of defining a reaction volume, because the ratio of products is proportional to the nucleophile concentrations at the reaction site. The principles of the method have been extensively discussed, and only some experimental details are presented here.[9−16]

2,4,6-Trimethylbenzenediazonium tetrafluoroborate, 1-ArN$_2^+$, a water-soluble arenediazonium salt, is allowed to undergo thermal dediazoniation in acidified aqueous solutions containing variable salt concentrations. For example, with added bromide ion, the concentrations of reaction products, e.g., 2,4,6-trimethylphenol (1-ArOH) and 2,4,6-trimethylbromobenzene (1-ArBr) are quantified; see Scheme 1. A standard curve relating added Br$^-$ concentration, [Br]$_f$, to the relative percentage yield of 1-ArBr, % 1-ArBr, allows the determination of local Br$^-$ concentrations, [Br]$_b$, in other systems. The main assumption of the chemical trapping method is that identical relative product yields reflect identical *local* concentrations.

To probe the interface of a particular system, it is essential that the arenediazonium probe reside exclusively at the interface. Hydrophobic analogues such as 2,6-dimethyl-4-hexadecyllbenzenediazonium ion, 16-ArN$_2^+$, have been shown to remain preferentially in micelles above the critical micelle concentration (cmc) of a variety of detergents.[9−16]

Chemical trapping has been used to estimate local ion concentrations and ion-exchange selectivity in several aqueous micellar systems, including counterion concentration at the surfaces of hexadecyltrimethylammonium halide micelles, CTAX (X = Br, Cl),[9,10] the ion-exchange constant between these two ions in micelles,[9] Cl$^-$ concentrations at the surface of zwitterionic phospholipid

micelles and lecithin vesicle;[12] co-ion concentrations at the surface of sodium dodecyl sulfate micelles,[13] micelle monomer concentration,[16] the degree of ionization (α) of cationic micelles,[14] and halide concentrations at the interface of zwitterionic micelles.[15] The chemical trapping method was also used to determine binding constants of neutral molecules such as long-chain alcohols in CTAB microemulsions.[11]

The increasing knowledge about the properties of reverse micelles, RM, has been accompanied by expanding practical applications. However, some fundamental questions concerning RM properties such as the properties of water, especially in low water/detergent molar ratios, *W⁄S*, and ion distribution between the interface and the water pool remain to be clarified.[2,17] Ion distribution between the interface and the interior of the water pool has been the focus of interest of many investigators, who have used a wide range of experimental techniques such as conductivity, fluorescence, NMR, UV/visible spectroscopy, and reaction kinetics.[18]

For RM, the volume of experimental information about ion concentrations at the micellar interface is small. Only recently, Das and co-workers[19,20] determined, by chemical trapping, the value of [Br]$_b$ in cationic RM prepared with CTAB/isooctane/*n*-hexanol/water and water and headgroup concentrations in the interfacial region of Aerosol OT RM. In these RM the values of [Br]$_b$ decrease from 3.6 to 2.7 M as *W⁄S* increases from 12 to 44.

Here we have used chemical trapping to obtain detailed experimental information on counterion distribution in a RM prepared with CTAB/*n*-dodecane/CHCl$_3$/water. The bromide ion concentration calculated from chemical trapping at the interface decreases from 7 to 3 M, while the concentration of bromide at the water pool decreases from 6 M to ca. 0.19 M as *W⁄S* increases from 10 to 40. Theoretical analysis of the data by a simple geometrical model as well as a Poisson−Boltzmann equation[21−24] indicates that 16-ArN$_2^+$, used here to probe the interfacial region, may be reporting the ion concentration of a rough spherical shell extending at least 0.6 nm from the headgroup/oil boundary. Both experiment and theory indicate that α of CTAB RM in *n*-dodecane/CHCl$_3$/water is ca. 0.2 in *W⁄S* > 12.

Experimental Section

Materials. CTAB (Merck) was recrystallized from acetone/methanol (×3) and dried in vacuum. Isooctane, *n*-dodecane, and *n*-hexanol (Merck) were used as received. Chloroform was washed with water, dried over CaCl$_2$, and distilled immediately before use.

The dediazoniation products 2,6-dimethyl-4-hexadecylphenol (16-ArOH), 2,6-dimethyl-4-hexadecylbromobenzene (16-ArBr), and 2,6-dimethyl-4-hexadecylaniline were kindly furnished by Dr. L. S. Romsted (Rutgers University). 2,4,6-Trimethylaniline, 2,4,6-trimethylbromobenzene (1-ArBr), and 2,4,6- trimethylphenol (1-ArOH) were obtained from Aldrich. 2,4,6-Trimethylbenzenediazonium tetrafluoroborate (1-ArN$_2$BF$_4$) and 2,6-dimethyl-4-hexadecylbenzenediazonium tetrafluoroborate (16-ArN$_2$BF$_4$) were prepared as described.[10] All other salts were of

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analytical grade. Bidistilled and deionized water was used in the preparation of all solutions.

Methods: Reverse Micelles. The reverse micelle solutions were prepared from a stock solution containing 0.125 M CTAB in CHCl$_3$/*n*-dodecane (6:4 v/v) or 0.1 M CTAB in isooctane/*n*-hexanol (9:1). To solubilize CTAB in this solvent mixture, it was necessary to add a small amount of water to the stock solution, usually 0.0013 mL (containing HBr or phosphate buffer, P$_i$) to each milliliter of 0.1 M CTAB. This amount of water was included in the calculation of *W/S* ratios. Solutions of CTAB at different *W/S* values were prepared by adding HBr or 0.02 M P$_I$, pH 6.0, to 1 mL solutions in a volumetric flask of 2.0 mL.

Standard Curve of NaBr vs Percent 1-ArBr. The dediazoniation reactions were initiated by adding 0.005 mL of an aqueous solution of the 1-ArN$_2^+$ (usually 0.02 M) to 1 mL of NaBr solutions, yielding a final concentration of 1×10^{-4} M. Cyclohexane, 0.05 mL, was added to the top of the solutions to avoid product evaporation.[14] After complete reaction (24 h at 30 °C), the solutions were diluted with 1 mL of *n*-propanol and the samples were injected onto the HPLC column. Concentrations were calculated from the (calibrated) HPLC areas of the product peaks by use of a standard curve (see below). Taking the reaction with Br$^-$ as an example, the percentage of each product was calculated from the concentrations:

$$\% \text{ 1-ArB} = 100 \times [\text{1-ArB}]/([\text{1-ArBr}] + [\text{1-ArOH}]) \quad (1)$$

Dediazoniation Reactions in Reverse Micelles. The reactions were initiated by adding 0.005 mL of a CH$_3$CN solution of the diazonium salt (usually 0.02 M) to 1 mL of RM solution, giving a final concentration of 1×10^{-4} M. After complete reaction (24 h at 30 °C), the solutions were diluted with *n*-propanol (0.1 mL of sample plus 0.4 mL of *n*-propanol) and injected onto the HPLC column.

Dediazoniation Reaction in Two Phases. The organic phase (1 mL) and 1 mL of water containing P$_i$ or HBr and NaBr at the desired concentration were added to a 2.0 mL tube equipped with a Teflon stopper. The diazonium salts, dissolved in water (1-ArN$_2$BF$_4$, 0.024 M) or acetonitrile (16-ArN$_2$BF$_4$, 0.012 M), were added (usually 0.01 mL) to samples that, after vortexing for 1 min, were maintained for 24 h at 30 °C. Before injection onto the HPLC column, the samples were homogenized by dilution with 4 mL of *n*-propanol.

HPLC. Product distribution analysis was carried out in a Shimadzu HPLC equipped with a SPD-10A UV–vis detector, C-R6A integrator, LC-6AD pump, and a 20 µL loop. The wavelength of the detector was set at 225 nm, and a Microsorb C18 (Rainin) reverse-phase column (4.6 mm i.d. × 25 cm; 5 µm particle size) was used to separate the reaction products of both 1-ArN$_2^+$ and 16-ArN$_2^+$. The products of the 16-ArN$_2^+$ reactions were eluted with methanol/2-propanol (90/10 v/v), with a flux of 1 mL/min and pressure of 62 atm. Typical retention times for 16-ArOH, 16-ArBr, and 2,6-dimethyl-4-hexadecylphenyl *n*-hexyl ether (16-ArOHex) are 6.3, 12.5, and 13.7 min, respectively.

The equations used to calculate concentrations from peak areas are the following: [16-ArOH] = {area of 16-ArOH (µV)}{4.5 × 10^{-11} (µV^{-1}·M)} and [16-ArBr] = {area of 16-ArBr (µV)}{4.13 × 10^{-11} (µV^{-1}·M)}. These relationships were obtained by injection in the HPLC of known amounts of solutions of pure standards.

The products of dediazoniation of 1-ArN$_2^+$ were separated under the same conditions used to separate 16-ArN$_2^+$ products, with a mixture of methanol/water (70/30 v/v) as eluent, a flux of 1 mL/min, and pressure of 140 atm. The retention times for 1-ArOH and 1-ArBr are 4.3 and 11.7 min, respectively. The equations used to calculate concentrations from peak areas are the following: [1-ArOH] = {area of 1-ArOH (µV)}{5.55 × 10^{-11} µV^{-1}·M} and [1-ArBr] = {area of 1-ArBr (µV)}{4.39 × 10^{-11} µV^{-1}·M}. These relationships were obtained by injection in the HPLC of known amounts of solutions of pure standards

Results and Discussion

Local ion concentrations obtained by chemical trapping are calculated from interpolations of standard curves relating the percent product yield to aqueous salt concentrations.[9] The interfacial ion concentration in aqueous
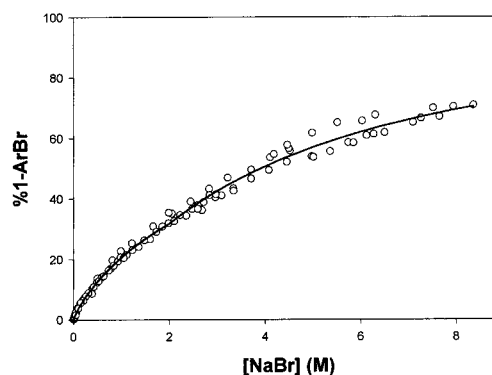

Figure 1. Effect of [NaBr] on the percent yield of 1-ArBr in 0.001 M HBr. The concentration of 1-ArN$_2^+$ was 2×10^{-4} M.

micelles decreases upon alcohol incorporation;[11] therefore, the interfacial ion concentration in CTAB RM prepared in CHCl$_3$/*n*-dodecane could be higher than those determined by Das and co-workers.[19,20]

Standard curves relating product yields with [Br]$_f$ have been published[9–15] and were extended here to higher salt concentrations (Figure 1). The product distributions resulting from the dediazoniation of 1-ArN$_2^+$ in aqueous solution containing HBr (0.0013 M) were determined as a function of [NaBr], chosen on account of its high solubility. The data shown in Figure 1, relating the percent yield of 1-ArBr with added [NaBr], is nonlinear, as has been described previously over a narrower concentration range.[9–15] The nonlinearity of the standard curve has been attributed to ionic strength effects.[25] We have shown recently that ion pair formation between anions and the arenediazonium ion can account for the reactivity of these salts with nucleophiles, including such weak reactive species as sulfates and sulfonates.[16] Assuming that ion pairs between Br$^-$ and 1-ArN$_2^+$ are formed in a fast equilibrium prior to dediazoniation, the data in Figure 1 can be fitted to

$$\% \text{ 1-ArBr} = \frac{100[\text{NaBr}]^n}{K_{eq} + [\text{NaBr}]^n} \quad (2)$$

where K_{eq} (liters per mole) is the equilibrium constant for the dissociation of the bromide/arenediazonium ion pair and *n* is the apparent reaction order. The best-fit values were $n = 0.84 \pm 0.01$ and $K_{eq} = 3.82 \pm 0.03$ for [NaBr] ≤ 1.98 M (% 1-ArBr ≤ 31.8%) and $n = 1.14 \pm 0.04$ and $K_{eq} = 4.72 \pm 0.26$ for [NaBr] > 1.98 M (% 1-ArBr > 31.8%). The changes in apparent reaction order and equilibrium constant probably reflect ionic strength effects on complex formation. A precise fit to the experimental data was essential to obtain consistent values for local ion concentrations. It is clear that the product yield variation with salt concentration can be described by assuming complex formation.

Probing the aqueous compartment of RM with 1-ArN$_2^+$, under conditions identical to those used by Das and co-workers[19,20] (isooctane/*n*-hexanol 9:1, P$_i$ 0.02 M, pH 6, CTAB 0.05 M), we confirmed their values of [Br]$_f$ (Table 1). By use of HBr (1.3×10^{-3} or 2×10^{-4} M) in the aqueous phase and maintenance of the isooctane/*n*-hexanol ratio, comparable concentrations of [Br]$_f$ were obtained (Table 1), indicating that phosphate does not significantly displace Br$^-$ from the surface of the RM.

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Table 1. Normalized Product Yields[a] of the Dediazoniation of 1-ArN$_2^+$ and 16-ArN$_2^{+\ b}$ in Reverse Micelles of CTAB in Isooctane/*n*-Hexanol and HCCl$_3$/*n*-Dodecane

W/S	conditions[c]	% 1-ArOH	% 1-ArBr	[Br]$_f$ (M)	% 16-ArOH	% 16-ArBr	[Br]$_b$ (M)
			Isooctane/Hexanol				
44	HBr, 1.3×10^{-3} M	90.9	9.1	0.32	53.0	42.0	2.9
30	HBr, 1.3×10^{-3} M	86.2	13.8	0.56	50.7	44.3	3.2
20	HBr, 1.3×10^{-3} M	77.2	22.8	1.15	46.6	48.4	3.7
44	HBr, 3×10^{-4} M	90.0	10.0	0.36	53.0	42.0	2.9
30	HBr, 3×10^{-4} M	85.4	14.6	0.60	50.5	44.5	3.2
20	HBr, 3×10^{-4} M	75.8	24.2	1.26	46.4	48.6	3.7
44	P$_i$, 0.02 M, pH 6.0	91.3	8.7	0.30	45.8	49.2	3.8
30	P$_i$, 0.02 M, pH 6.0	85.7	14.3	0.59	46.5	48.5	3.7
20	P$_i$, 0.02 M, pH 6.0	73.1	26.9	1.49	43.5	51.5	4.1
			HCCl$_3$/Dodecane				
40.7	HBr, 1.3×10^{-3} M	95.1	4.9	0.15	14.6	85.4	18.3
30.7	HBr, 1.3×10^{-3} M	91.1	8.6	0.30	15.6	84.4	17.1
20.7	HBr, 1.3×10^{-3} M	87.3	12.7	0.50	14.5	85.5	18.5

[a] Quantitative conversions to expected dediazoniation products were always observed. The actual observed yields, HPLC areas, and HPLC calibration curves used in determining the product yields are available upon request. [b] The yield of 16-ArOHex at all *W/S* in RM prepared in isooctane/*n*-hexanol is ca. 5%. This amount was taken in account in the calculations of percent yield of 16-ArOH and 16-ArBr. [c] [CTAB] is 0.05 M in all conditions.

With the water-soluble diazonium probe 1-ArN$_2^+$, in agreement with previous results, the expected product for the reaction between the arenediazonium and *n*-hexanol was not detected.[19,20] Since *n*-hexanol in RM resides preferentially in the interface, this latter result strongly suggests that, in these RM, 1-ArN$_2^+$ exclusively probes the water compartment.

The interface of CTAB/isooctane/*n*-hexanol RM was probed with 16-ArN$_2^+$. The values of [Br]$_b$, calculated from the standard curve by use of eq 2, range from 4.4 to 3.1 M when the bulk water composition is changed from P$_i$ to HBr (Table 1). The yield of the reaction of 16-ArN$_2^+$ with *n*-hexanol, producing 16-ArOHex, was ca. 5%. Both [Br]$_b$ values and *n*-hexanol product ratios were in excellent agreement with published data.[19,20]

With CHCl$_3$/*n*-dodecane as the organic phase of CTAB RM, the percent yield of 1-ArBr, at some *W/S* ratio, in 0.05 M CTAB (0.001 M HBr) was obtained by chemical trapping with 1-ArN$_2^+$, to compare the results obtained with isooctane/*n*-hexanol (Table 1). The 1-ArBr yields and [Br]$_f$ values at some *W/S* are presented in Table 1 to permit comparison with the data obtained in isooctane/*n*-hexanol. The values of [Br]$_f$ in CHCl$_3$/*n*-dodecane are lower than those in isooctane/*n*-hexanol at all *W/S*, reaching half of the [Br]$_f$ obtained in isooctane/*n*-hexanol at *W/S* 40. This difference can be attributed to a lower dissociation of the Br$^-$ at the surface in the absence of *n*-hexanol in this system.

Dediazoniation of 16-ArN$_2^+$ in CTAB/CHCl$_3$/*n*-dodecane gave high values of % 16-ArBr (Table 1). The [Br]$_b$ calculated from % 16-ArBr by use of eq 2 is ca. 18 M, a value much higher than that calculated in CTAB/isooctane/*n*-hexanol RM (Table 1).

A detailed analysis of CTAB RM by chemical trapping was made in 0.1 M CTAB and CHCl$_3$/*n*-dodecane with both 1-ArN$_2^+$ and 16-ArN$_2^+$. The values of % 1-ArBr decreased with increasing *W/S*, reaching a plateau (Figure 2a). The values of [Br]$_f$, calculated from % 1-ArBr by use of eq 2, also decreased sharply, with *W/S* reaching an apparent plateau at *W/S* 40 (Figure 2b). The values of % 1-ArOH and % 1-ArBr and the calculated values of [Br]$_f$ are presented in Table 2 for clarity. Note that the values of [Br]$_f$ obtained in 0.10 M CTAB are very similar to those obtained in 0.05 M CTAB (compare Tables 1 and 2), as expected for RM that remain unchanged with varying detergent at a single *W/S*.
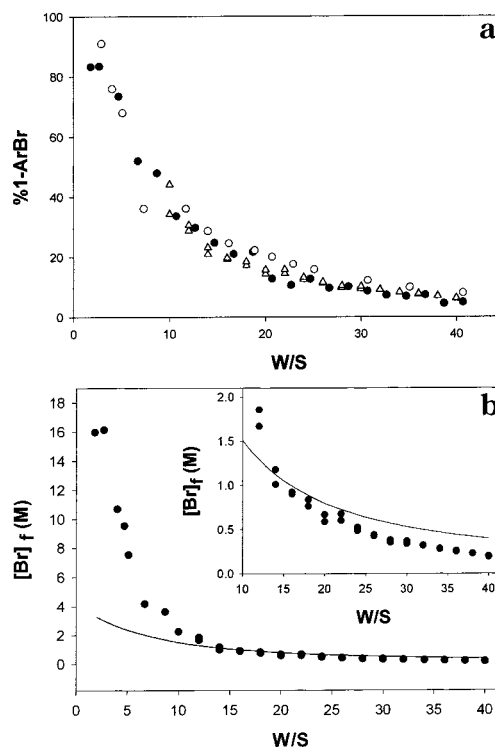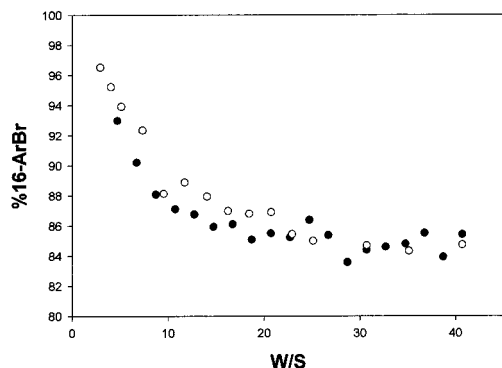

Figure 2. (a) Effect of *W/S* on the percent yield of 1-ArBr in CTAB RM prepared in CHCl$_3$/*n*-dodecane 6:4. The different symbols are different sets of experiments. [CTAB] = 0.1 M, [HBr] = 0.001 M, and [1-ArN$_2^+$] = 2×10^{-4} M. (b) Calculated [Br]$_f$ as a function of *W/S*. The line was obtained from PBE calculations (see text). The inset shows data in the high *W/S* region.

The product yields of 16-ArN$_2^+$ in CTAB/CHCl$_3$/*n*-dodecane RM were determined at several *W/S* ratios (Figure 3). The values of % 16-ArBr decreased sharply with increasing *W/S*, reaching 85% at *W/S* 40. The striking feature of those results is that the values of % 16-ArBr, even at *W/S* 40, are much higher than those determined in isooctane/*n*-hexanol and exceed the values obtained at the highest [NaBr] in the standard curve (Figure 1). From the data of % 16-ArBr, by use of eq 2, we obtained the values for [Br]$_b$ at the interface of CTAB reverse micelles in CHCl$_3$/*n*-dodecane. Between *W/S* 40 and 20, the calculated [Br]$_b$ was close to 18 M. We note

Table 2. Effect of *W/S* in the [Br]$_f$ in CTAB Micelles in HCCl$_3$/*n*-Dodecane

W/S	% 1-ArOH	% 1-ArBr	[Br]$_f$ (M)
40	93.86	6.14	0.193
36	92.44	7.57	0.252
30	90.26	9.75	0.318
26	88.59	11.41	0.431
20	85.00	15.01	0.627
16	80.48	19.53	0.913
10	60.81	39.20	2.975

Figure 3. Percent yield of 16-ArBr as a function of *W/S* in CTAB RM, prepared in CHCl$_3$/*n*-dodecane 6:4. The different symbols are different set of experiments. [CTAB] = 0.1 M, [HBr] = 0.001 M, and [16-ArN$_2$$^+$] = 2 × 10^{-4} M.
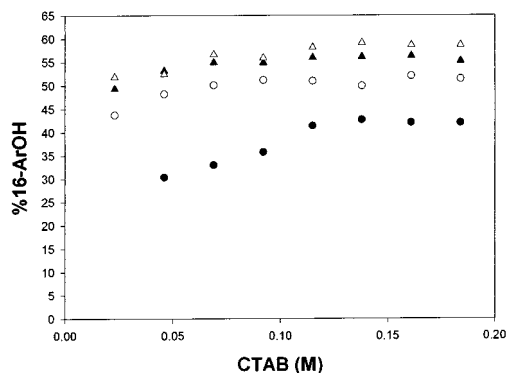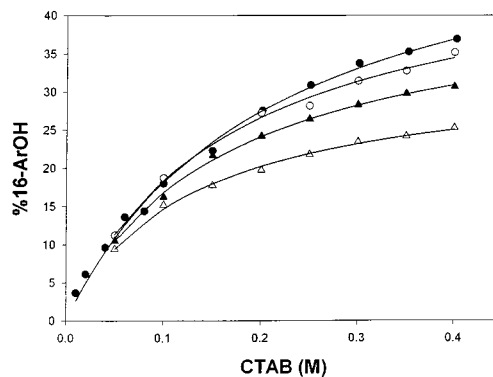
that in CTAB RM prepared in isooctane/*n*-hexanol, [Br]$_b$ is 3.1 M at *W/S* 40 and increases at lower *W/S* (Table 1).

Although it is expected that the incorporation of *n*-hexanol can produce a significant decrease in the local concentration of bound counterions,[10] the magnitude of the difference in the interfacial counterion concentrations was unexpected.

A source for this significant difference in [Br]$_b$ in the two RMs could be the distribution of the probe between the micelle and the bulk solvent and different product yields upon dediazoniation of 16-ArN$_2$$^+$ in the two environments. The formation of a tight ion pair between 16-ArN$_2$$^+$ and both counterions and neutral additives has been proposed repeatedly.[10,16] We have recently shown that even weak nucleophiles such as sulfates and sulfonates react with diazonium salts in aqueous solution by forming ion pairs.[16] Furthermore, it is known that CHCl$_3$ stabilizes ion pairs.[26] RM−bulk solvent distribution of 16-ArN$_2$$^+$ should yield differences in product composition upon variation of [CTAB] if the probe increasingly incorporates into the RM phase as detergent concentration increases and the product composition upon reaction in both pseudophases is different.

Properties of RM are unchanged upon increasing detergent at constant *W/S*.[27] Increasing CTAB concentration, at fixed *W/S*, for a probe that distributes between the RM and the organic phase, should favor the partition of the probe to the RM. The contribution of the probe in the aqueous compartment of the RM can be ignored, since even in normal CTAB micelles the concentration of free 16-ArN$_2$$^+$ is negligible.[10]

The effect of increasing [CTAB] on the yield of products obtained upon dediazoniation of 16-ArN$_2$$^+$ was determined for both isooctane/*n*-hexanol and CHCl$_3$/*n*-dodecane. The % 16-ArOH increased with [CTAB] at several (fixed) *W/S* in both solvents, suggesting that 16-ArN$_2$$^+$ distributes between the RM and the solvent (Figures 4 and 5).

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(27) Zulauf, M.; Eicke, H. F. *J. Phys. Chem.* **1979**, *83*, 480.

Figure 4. Effect of [CTAB] on the percent 16-ArOH in RM prepared in isooctane/hexanol 9:1. [HBr] = 0.001 M and [16-ArN$_2$$^+$] = 2 × 10^{-4} M. *W/S* = 10 (●), 20 (○), 30 (▲), or 40 (△).

Figure 5. Effect of [CTAB] on the percent 16-ArOH in RM prepared in CHCl$_3$/*n*-dodecane 6:4. [HBr] = 0.001 M and [16-ArN$_2$$^+$] = 2 × 10^{-4} M. *W/S* = 10 (△), 20 (▲), 30 (○), or 40 (●), Line was calculated from eq 11 (see text).

For RM of CTAB prepared in isooctane/*n*-hexanol 9:1, the % 16-ArOH increases slightly with [CTAB] and a plateau is reached at 0.2 M CTAB, at least with *W/S* > 20 (Figure 4). In CHCl$_3$/*n*-dodecane, at all *W/S*, % 16-ArOH increases with [CTAB] and a plateau is not reached, even at 0.4 M detergent (Figure 5). Taken together, these data clearly showed that 16-ArN$_2$$^+$ distributes between the RM and the bulk solvent at all *W/S* and that the incorporation of the probe is essentially quantitative for the RM prepared with *n*-hexanol above 0.2 M detergent. Furthermore, it can be concluded that as 16-ArN$_2$$^+$ increasingly incorporates into the RM interface, the yield of 16-ArOH increases.

The remaining question is how much of the total 16-ArOH is formed in the bulk solvent and at the interface of RM. Experiments in a two-phase system, an aqueous phase containing 0.001 M HBr and NaBr and an organic phase of the solvent mixtures used in RM preparation, permitted a rational answer to this question.

The diazonium salts (16-ArN$_2$$^+$ or 1-ArN$_2$$^+$) was added to a two-phase mixture, and after complete reaction, addition of propanol yielded a single phase and the products were determined (see Experimental Section).

With 1-ArN$_2$$^+$ as probe, both in CHCl$_3$/*n*-dodecane/water and in isooctane/*n*-hexanol/water, the calculated [Br]$_f$, obtained from % 1-ArBr by use of eq 2, corresponds, within 10% error, to the [NaBr] added to the aqueous phase (Table 3). It can be assumed, therefore, that in these two-phase systems 1-ArN$_2$$^+$ reacts with water and bromide exclusively in the aqueous phase.

With 16-ArN$_2$$^+$ as a probe in the CHCl$_3$/*n*-dodecane/water two-phase system, % 16-ArOH was <0.4 and 16-ArBr was the only significant product, even when the

Table 3. Normalized Product Yields of Reactions of Diazonium Salts in Water/Organic Solvent

conditions[a]	[NaBr] (M)	% 1-ArBr	% 1-ArOH	[Br]$_f$ (M)	% 16-ArBr	% 16-ArOH	% 16-ArOHex
			1-ArN$_2^+$				
HCCl$_3$/n-dodecane	1.0	21.1	78.9	1.0			
HCCl$_3$/n-dodecane	2.0	32.9	67.1	2.1			
HCCl$_3$/n-dodecane	3.0	42.9	57.1	3.2			
isooctane/n-hexanol	1.0	21.7	78.3	1.0			
isooctane/n-hexanol	2.0	34.4	65.6	2.2			
isooctane/n-hexanol	3.0	43.4	56.6	3.3			
			16-ArN$_2^+$				
HCCl$_3$/n-dodecane	0.0				99.60	0.40	
HCCl$_3$/n-dodecane	1.0				99.92	0.08	
HCCl$_3$/n-dodecane	2.0				99.90	0.10	
HCCl$_3$/n-dodecane	3.0				99.75	0.25	
isooctane/n-hexanol	0.0				60.60	20.0	19.8
isooctane/n-hexanol	1.0				69.70	13.3	17.0
isooctane/n-hexanol	2.0				67.96	16.0	16.0
isooctane/n-hexanol	3.0				66.00	16.9	17.1

[a] In all aqueous solution [HBr] = 1.23 × 10^{-3} M. The diazonium concentrations were [1-ArN$_2^+$] = 2.4 × 10^{-4} M and 16-ArN$_2^+$ = 1.0 × 10^{-4} M, taking into account only the volume of aqueous solution.

aqueous phase contained only 1 mM HBr (Table 3). Therefore, it is clear that Br$^-$ forms a complex with 16-ArN$_2^+$ and the organic-phase solubilized complex yields exclusively 16-ArBr. It should be noted that the organic phase is water-saturated and, therefore, in the presumably hydrated ion complex (16-ArN$_2^+$·Br$^-$) the diazonium salt reacts preferentially with bromide.

In isooctane/n-hexanol/water, as opposed to CHCl$_3$/n-dodecane/water, a significant amount (13–20%) of 16-ArOH and 16-ArOHex (16–20%) was formed (Table 2). n-Hexanol, therefore, decreases the binding of Br$^-$ to 16-ArN$_2^+$ and increases water reaction with the diazonium ion in the organic phase or, alternatively, increases the solubility of the free diazonium ion in the aqueous phase.

From these data it can be concluded that, in CTAB reverse micelles in CHCl$_3$/n-dodecane, the major product of the dediazoniation of 16-ArN$_2^+$ reacting in the bulk solvent is 16-ArBr and that 16-ArOH is formed, from reaction of 16-ArN$_2^+$ with water, exclusively at the micellar interface.

Having demonstrated that 16-ArN$_2^+$ in CTAB RM distributes between the micelles and the bulk solvent and that 16-ArBr is the only product upon dediazoniation in CHCl$_3$/n-dodecane, we can calculate the product yields in the RM.

The distribution of the probe can be described by

$$(16\text{-ArN}_2^+)_f + \text{CTAB} \overset{K}{\longleftrightarrow} (16\text{-ArN}_2^+)_b \qquad (3a)$$

and

$$K = \frac{[16\text{-ArN}_2^+]_b}{[16\text{-ArN}_2^+]_f[\text{CTAB}]} \qquad (3b)$$

where [16-ArN$_2^+$]$_b$ is the concentration of 16-ArN$_2^+$ at the RM interface, [16-ArN$_2^+$]$_f$ is the concentration of 16-ArN$_2^+$ in the organic phase, and [CTAB] is the concentration of micellized detergent. Considering that the probe solubilized at the micellar interface reacts with both water and bromide ion while the probe in the organic phase only reacts with bromide, and assuming rapid equilibrium for the probe distribution, we can write

$$[16\text{-ArN}_2^+]_t = [16\text{-ArN}_2^+]_f + [16\text{-ArN}_2^+]_b \qquad (4)$$

and

$$100 = (\% \ 16\text{-ArN}_2^+)_f + (\% \ 16\text{-ArN}_2^+)_b \qquad (5)$$

and therefore

$$K = \frac{(\% \ 16\text{-ArN}_2^+)_b}{(\% \ 16\text{-ArN}_2^+)_f[\text{CTAB}]} \qquad (6)$$

The term (% 16-ArN$_2^+$)$_b$ can be substituted by the percentage of products formed at the reversed micelle interface, given by

$$(\% \ 16\text{-ArN}_2^+)_b = (\% \ 16\text{-ArOH})_b + (\% \ 16\text{-ArBr})_b \qquad (7)$$

and (% 16-ArN$_2^+$)$_f$ can be substituted by the percentage of 16-ArBr formed in the organic phase (% 16-ArBr)$_f$:

$$(\% \ 16\text{-ArN}_2^+)_f = (\% \ 16\text{-ArBr})_f \qquad (8)$$

The total product yield can be represented as

$$(\% \ 16\text{-ArBr})_f + (\% \ 16\text{-ArBr})_b + (\% \ 16\text{-ArOH})_b = 100 \qquad (9)$$

Since the properties of RM micelle are constant at fixed W/S,[17,27] it can be assumed that at any fixed W/S the ratio between (16-ArBr)$_b$ and (16-ArOH)$_b$ is constant and

$$(16\text{-ArBr})_b = \gamma(16\text{-ArOH})_b \qquad (10)$$

The product ratio at the micellar interface, γ, is independent of detergent concentration and constant at each W/S.

Upon observing that the dediazoniation of 16-ArN$_2^+$ in the bulk solvent does not produce the corresponding phenol and by use of eqs 3–10, the variation of (% 16-ArOH)$_b$ as a function of [CTAB] can be expressed as

$$(\% \ 16\text{-ArOH})_b = \frac{100K[\text{CTAB}]}{(1 + \gamma)(1 + K[\text{CTAB}])} \qquad (11)$$

The data representing the variation of % 16-ArOH as a function of [CTAB] were fitted by use of eq 11 (Figure 5). The fit of eq 11 to the experimental data was excellent (Figure 5), and the best-fit values of K and γ are shown

Table 4. Parameters Obtained with Eq 11 in Simulation of Data in Figure 5

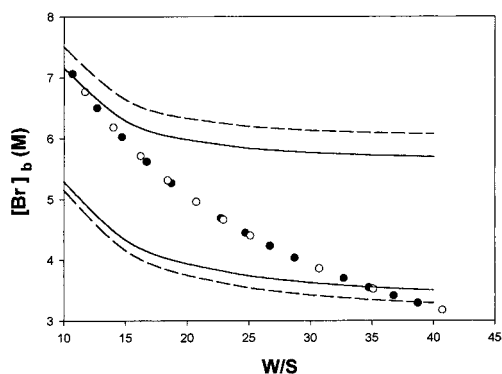| W/S	K (M^{-1})	γ
10	8.06	2.04
20	6.46	1.33
30	6.09	1.06
40	4.69	0.76

Figure 6. Calculated [Br]$_b$ at the surface of CTAB RM, prepared in CHCl$_3$/n-dodecane 6:4, from data of Figure 5 by use of eq 13 (see text). The different symbols are from different set of experiments. The lines were obtained from PBE calculations (see text). The upper lines were calculated with $r = 0.6$ (dashed line) and $r = 0.65$ nm (solid line), and the bottom lines were calculated with $r = 1.2$ (dashed line) and $r = 1.3$ nm (solid line).

in Table 4. The decrease in K with W/S can be rationalized since, in related systems, probe incorporation at the interface decreases upon growth because of decreasing surface defects caused by the high curvature radius of smaller assemblies.[28]

The variation of γ with W/S (Table 4) can be described by an empirical equation:

$$\gamma = a/[1 + b(W/S)] \qquad (12)$$

By use of the data in Table 4 and eq 12, we calculated the best-fit values for $a \cong 4.2$ and $b \cong 0.1$.

The percent yield of 16-ArBr at the reverse micellar interface, (% 16-ArBr)$_b$, was redefined by taking as 100% the total interfacially bound 16ArN$_2^+$. The corrected value, (% 16-ArBr)$_{bcorr}$, calculated from eqs 7 and 10 is given by

$$(\% \ 16\text{-ArBr})_{bcorr} = \frac{100(16\text{-ArBr})_b}{(16\text{-ArN}_2^+)_b} = \\ \frac{100\gamma(16\text{-ArOH})_b}{(1 + \gamma)(16\text{-ArOH})_b} = \frac{100\gamma}{(1 + \gamma)} \quad (13)$$

From the (% 16-ArBr)$_{bcorr}$ calculated at the RM interface by use of eq 13 at $10 \leq W/S \leq 40$ and the standard curve shown in Figure 1, [Br]$_b$ at the RM interface can be calculated by taking into account probe distribution corrections. The experimental values presented in Figure 6 correspond to [Br]$_b$ at the interface, corrected for probe distribution between the RM and the bulk phase by use of eq 13. The corrected values of [Br]$_b$, significantly lower than those shown in Table 1, steadily decrease with W/S, approximating asymptotically ca. 3 M.

For CTAB RM prepared with CHCl$_3$/n-dodecane, we have shown, by determining the variation of % 16-ArOH with [CTAB], that total probe incorporation was not obtained under our experimental conditions (Figure 5).

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Table 5. Products Yields and [Br]$_b$ at CTAB Saturation in HCCl$_3$/n-Dodecane and Isooctane/n-Hexanol

W/S	%16-ArOH	%16-ArBr	[Br]$_b$ (M)
	HCCl$_3$/Dodecane		
40	54.05	45.95	3.38
30	50.00	50.00	3.90
20	43.48	56.52	4.90
10	34.48	65.52	6.84
	Isooctane/Hexanol[b]		
44			2.7[a]
40	58.0	37.0	2.44
30	55.5	39.5	2.68
20	51.0	44.0	3.15
12			3.6[a]
10	42.5	52.5	4.25

[a] Data from ref 20. [b] The percentage of 16-ArOHex is 5% in all reactions at all W/S.

Therefore, the limiting [Br]$_b$ was calculated from eq 13 at several W/S values. These calculations are shown for clarity in Table 5. It is evident that the values of [Br]$_b$ decrease with W/S from ca. 7 M to ca. 3.4 M at $W/S = 40$.

With n-hexanol/isooctane as organic solvent, the values of [Br]$_b$ were obtained experimentally, since, as we have shown (Figure 4), a constant value of % 16-ArOH is obtained at any W/S above 0.15 M [CTAB]. As discussed above, this indicated that 16-ArN$_2^+$ is totally micellar-bound. Thus, the values of [Br]$_b$ were obtained from eq 7, the values of (% 16-ArBr)$_b$, and the standard curve. Under these conditions, the values of [Br]$_b$ of CTAB RM in n-hexanol/isooctane decrease moderately with increasing W/S (Table 5). Previously obtained values of [Br]$_b$ are in good agreement with our data, indicating that probe distribution corrections were not needed for this system, even at 0.05 M CTAB.[19,20]

Table 5 permits a simple comparison of local counterion concentrations, which directly illustrates that the addition of an alcohol produces a marked decrease in bound ion concentration. This result is entirely consistent with the increased [Br]$_f$ in CTAB RM prepared with isooctane/n-hexanol when compared with those prepared with CHCl$_3$/n-dodecane, Table 1. The decrease of interfacial counterion concentration upon incorporation of long-chain alcohols in aqueous micelles is well documented.[3,4] It was therefore predictable that interfacial alcohol incorporation in CTAB RM would produce both a decrease in [Br]$_b$ and a corresponding increase in [Br]$_f$.

In a dimensionally restricted water environment such as that in RM, the values of local counterion concentration estimated at the interface by chemical trapping depend critically on probe location and the roughness of the internal RM interface.[4]

We estimated the local ion concentration using the Poisson–Boltzmann equation (see Appendix), assuming that 16-ArN$_2^+$ can probe a spherical layer that extends to the water pool at varying W/S. The upper lines in Figure 6 represent the calculated values of [Br]$_b$ for distances of 0.6 and 0.65 nm from the interface, and the lower lines were calculated for distances of 1.2 and 1.3 nm, respectively. The calculations obtained at varying distances show the sensitivity of the calculated results to distance. Experimental data are distributed between the distances used to calculate ion distribution from the PBE (Figure 6). From these results it is clear that the [Br]$_b$ values obtained by chemical trapping in RM do not reflect exclusively the Stern layer ions, since the probe appears to extend from the boundary as W/S increases.

PBE were also used to estimate [Br]$_f$ (Figure 2b). The continuous line in Figure 2b is a calculation with PBE
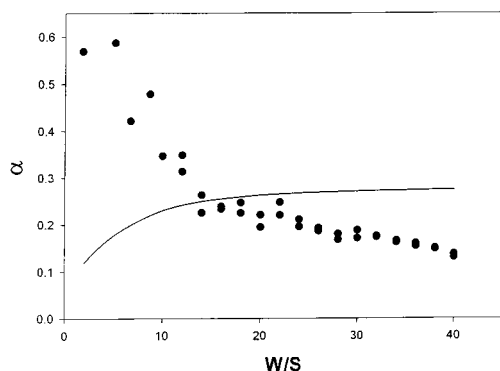
Figure 7. Ion dissociation, α, of CTAB RM prepared in CHCl$_3$/
n-dodecane as a function of W/S. The line was obtained from
PBE calculations with eq 14, and the symbols represent values
of α calculated from experimental [Br]$_f$ values (see text).

(see Appendix) where "free ions" were defined as those
occupying the water pool volume minus the Stern layer.
Formally, the Stern layer extends from the headgroup
0.23 nm into the water pool, a typical hydrated ionic radius.
Comparison between experimental data and PBE calcu-
lations shows that good agreement is obtained with W/S
$\geq$ 10 (Figure 2b).

The dissociation degree of ions from the micellar
interface, α,[4] is a convenient parameter that has been
used to analyze a series of micellar properties and effects
including catalysis in both aqueous and reverse
micelles.[29-31] The definition of a bound ion implies the
separation of the volume containing the micelle and the
definition of a boundary that separates ions considered
bound from those that are defined as free. For CTAB
reverse micelles, α can be calculated from an estimate of
[Br]$_f$:

$$\alpha = \frac{[Br]_f V_f N_{av}}{n_{agg}} = \frac{4\pi [Br]_f (R_M - d)^3 N_{av}}{3 n_{agg}} \qquad (14)$$

where V_f is the volume of the aqueous pool where the free
counterions are found (in cubic decimeters), R_M is the
aqueous pool radius (see Appendix), N_{av} is Avogadro's
number, d is the distance that defines the Stern layer (2.3
Å), and n_{agg} is the aggregation number (see Appendix).

By use of the calculated [Br]$_f$ obtained from the PB model
and eq 14 and by defining bound ions up to 2.3 Å away
from the micellar surface, the α values at each [Br]$_f$ were
calculated (Figure 7). The α values, calculated from [Br]$_f$
estimated by chemical trapping, decrease with W/S,
reaching an almost constant value at W/S higher than 20
(Figure 7).

The α values obtained from the experimental [Br]$_f$
behave qualitatively differently from those obtained from
PBE calculations. The continuous line, obtained upon
calculating [Br]$_f$ from the PB model and eq 14, shows that
α increases with W/S, reaching a constant value above
$W/S = 20$.

The experimental errors and the limitation of the
pointlike ion model in a continuous solvent prevents
conclusions for $W/S < 10$. For $W/S > 10$, the PBE suggests
that α is almost constant, while the experimental data
suggest a small tendency for α to decrease with W/S. The
error in the experimental data for [Br]$_f$ can be estimated

as 10%. We can affirm that the detailed manner in which
[Br]$_f$ decreases with W/S produces a major difference both
in the asymptotic limit of these two estimates of α and in
the relatively small difference in the α vs W/S dependence.
This difference can be due to experimental errors (in the
experiments between $10 < W/S < 20$, which influence
the asymptotic behavior) or the possibility that the probe
is not sufficiently hydrophilic to remain in the water pool
at low W/S. For W/S lower than 15 (or even at W/S 20),
the probe may be partitioning between the aqueous pool
and the interface.

It is clear, however, that both calculations and experi-
mental data show that the value of α for $W/S > 15$ is very
close to 0.2. This value is very similar to that in aqueous
micelles and may reflect an intrinsic property related to
specific, noncoulombic interactions between the bromide
ion and the tetralkylammonium headgroup.

In conclusion, we have demonstrated that chemical
trapping is an adequate method for determining local ion
concentrations in RM obtained with CTAB in two different
solvents. We have also demonstrated that probe distribu-
tion between the RM and the bulk solvent can be analyzed
by measuring differences in product composition. These
data have been compared with Poisson−Boltzmann
calculations, and local counterion concentrations were
obtained both at a region close to the RM interface and
at the water pool. The degree of counterion dissociation
in CTAB RM above W/S 15 is comparable to that in
aqueous CTAB micelles.

Appendix

This PBE analysis, as used previously,[21-24] considers
the microemulsion as an ensemble of equal reverse
micelles. Each micelle is modeled as a spherical water
droplet with a smooth and uniformly charged inner surface
and the water pool is treated as a dielectric continuum.
The 1-ArN$_2^+$ ($q_p = +|e|$) is considered as a uniformly
charged sphere of radius R_p equal to 4×10^{-8} cm (the
spherical volume is equivalent to the volume obtained by
isodensity surface polarized continuum model, IPCM)[16]
positioned at the center of the aqueous pool, and 16-ArN$_2^+$
is considered to be at the micellar interface. The mean
field potential is calculated at a distance r(ort) from PBE
in the integral form:[22,24]

$$\epsilon \bar{\phi}(r) = \frac{4\pi}{r} \int_{R_p}^{r} t^2 q(t) \, dt + 4\pi \int_{r}^{R_M} t q(t) \, dt + \frac{q_P}{r} + \frac{q_M}{R_M} \qquad (15)$$

where $q(t) = \sum_i \rho_{M,i} q_i e^{-\beta q_i \bar{\phi}(t)} =$ total charge density, $q_M =$
reverse micelle charge $= n_{agg}|e|$, $n_{agg} =$ aggregation number
of the reverse micelle, $\epsilon =$ apparent dielectric constant in
the water pool, and $\rho_{M,i}$ and $q_i =$ number density at the
water pool/micelle interface (particles per cubic centime-
ter) and charge of the ith species, respectively.

(29) Wong, M.; Thomas, J. K.; Novak, J. J. *J. Am. Chem. Soc.* **1977**,
99, 4730.
(30) Eicke, H. F.; Christen, H. *J. Colloid Interface Sci.* **1974**, *46*, 417.
(31) El Seoud, O. A.; Chinelatto, A. M.; Shimizu, M. R. *J. Colloid
Interface Sci.* **1982**, *88*, 420.

The total pore volume is electrically neutral and the average positive and negative ion densities are related by charge conservation:[22]

$$V_M \sum_i \bar{\rho}_i q_i + q_P + q_M = 0 \tag{16a}$$

with

$$V_M \bar{\rho}_i = 4\pi \rho_{M,i} \int_{R_P}^{R_M} t^2 e^{-\beta q_i \bar{\phi}(t)} \, dt \tag{16b}$$

For an electrically neutral pore having the interfacial ion density defined by the expressions above, the mean field potential and the electrical field are zero at the water pool spherical boundary. The numerical solutions of the PBE were obtained by a simple Picard iteration procedure with an empirical parameter to obtain the convergence control. Integrals were computed with trapezoidal quadrature.

The (free or bound) local ionic concentration, $[Br]_{local}$, was calculated from a distribution function and a local spherical layer volume:

$$[Br]_{local} = \frac{3000 \rho_{M,Br}}{N_{av}(R_2^3 - R_1^3)} \int_{R_1}^{R_2} t^2 \, e^{-\beta q i \bar{\phi}(t)} \, dt \tag{17}$$

where R_1 and R_2 define the spherical layer ($R_2 > R_1$).

For the calculation of radius, R_M, and the volume, V_M, of the aqueous pool of the RM, we have used eq 18:[21]

$$V_M = \frac{4\pi R_M^3}{3} = n_{agg} v_w W/S \tag{18}$$

where v_W = volume of the water molecule = 30×10^{-24} cm^3.

The variation of n_{agg} with W/S was obtained from an empirical second-order equation obtained previously from experimental data:[32]

$$n_{agg} = 120.4 - 13.25 \, W/S + 1.61(W/S)^2 \tag{19}$$

LA001291S

(32) Lang, J.; Mascolo, G.; Zana, R.; Luisi, P. L. *J. Phys. Chem.* **1990**, *94*, 3069.