the gap created by the mutation at position 117 has also entered the coordination sphere of the Cu.

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(21) In subsequent experiments we have found that excess Cu is not needed to produce absorption bands at 420 or 630 nm but that excess imidazole is needed to obtain maximal absorption at 630 nm. Preliminary experiments with other N-donor or O-donor ligands show that the H117G protein in the presence of Cu has a preference for N-donors and that the spectral features qualitatively resemble either the spectra represented here for the "Cu only" form or the "Cu + MeIm" form. Further experiments are in progress.

Simultaneous Determination of Counterion, Alcohol, and Water Concentrations at a Three Component Microemulsion Interface Using Product Distributions from a Dediazoniation Reaction

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Solutions of association colloids such as micelles, vesicles, and microemulsions are composed of dynamic aggregates of surfactants and additives such as alcohols, salts, oils, and water.[1] All have highly anisotropic interfaces between their water and oil regions, and the interfacial concentrations of ions and molecules are usually several orders of magnitude greater than their overall concentrations in solution (Figure 1). Various methods are used to estimate the fraction of ions and molecules "bound" to association colloids, primarily from aggregate-induced shifts in a bulk solution property.[2] However, their local concentrations within the interfacial region can be calculated from their fraction bound only by making assumptions about their distributions within the aggregate and the volume of the interfacial region.[3]

We have developed a novel chemical method for estimating, simultaneously, the local interfacial concentrations of different nucleophiles, Y_m, in moles/liter of effective volume, at the surfaces of association colloids. Product distributions from dediazoniation of aggregate-bound, amphiphilic 16-ArN_2^+ (Scheme I), with its cationic head group oriented in the interfacial region like a surfactant molecule (Figure 1),[4] will be proportional to the local nucleophile concentrations in the interfacial region. To estimate Y_m, we assume that the selectivity of the dediazoniation reaction of 16-ArN_2^+ toward different nucleophiles, which cannot be measured independently, is the same as that of its short-chain analogue, 1-ArN_2^+, in aqueous solution.[4] Here we report the first simultaneous, experimental estimates of Br^-_m, H_2O_m, and $BuOH_m$ in cetyltrimethylammonium bromide, CTABr, microemulsions (Figure 2).

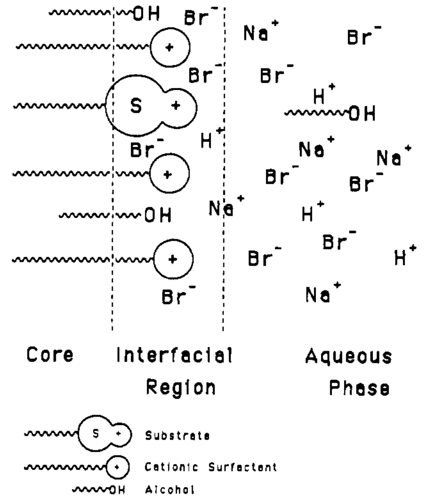


Figure 1. Cartoon of the interfacial region of a three-component microemulsion composed of a cationic surfactant, an alcohol, and an amphiphilic diazonium salt substrate, with its reactive group located in the interfacial region counterions, Br^-, and co-ions, Na^+ and H^+.

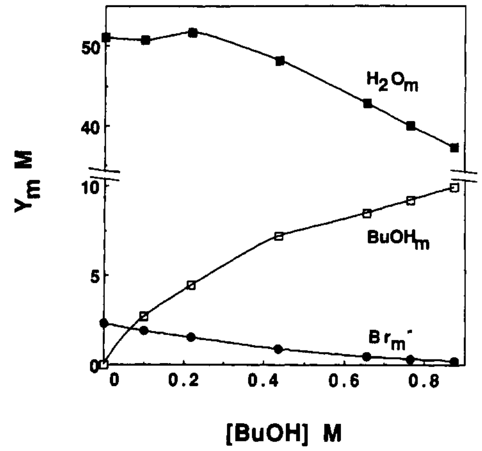
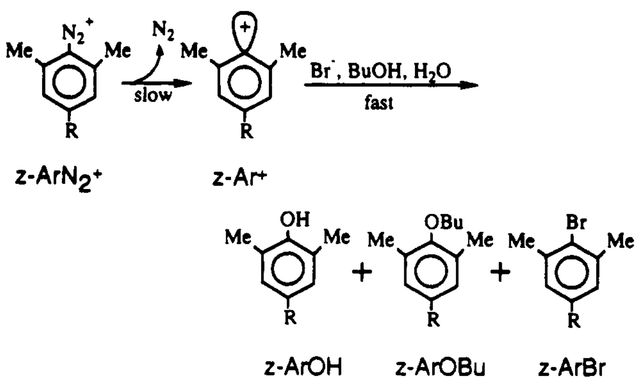


Figure 2. Effect of added BuOH on the local interfacial concentration, Y_m, of H_2O, Br^-, and BuOH; note ordinate scale change.

Scheme I[a]



[a] z = 16 when R = n-$C_{16}H_{33}$; z = 1 when R = CH_3.

Arenediazonium salts are believed to decompose in aqueous acid in the dark via rate-determining formation of a very reactive aryl cation,[5,6] which traps available, weakly basic nucleophiles,[5] Scheme I. We assume that the observed selectivity of the dediazoniation reaction toward available nucleophiles[4,5] reflects the

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Table I. Dediazoniation of 1 × 10^{-4} M 16-ArN_2^+ in 0.01 M CTABr and 0.01 M HBr with Added BuOH at 40 ± 0.1 °C[a] Normalized Product Yields of 16-ArOH, 16-ArBr, and 16-ArOBu[b]

[BuOH], M	% yield 16-ArOH	% yield 16-ArBr	% yield 16-ArOBu
0.000	72.9	27.1	
0.100	75.6	22.6	1.8
0.219	78.9	18.2	3.0
0.437	83.6	11.8	4.6
0.656	87.0	7.3	5.8
0.765	88.0	5.7	6.3
0.874	88.5	4.7	6.8

[a] Reaction is initiated by injection of 50 μL of 0.01 M 16-ArN_2^+ in MeCN into a 5-mL thermally equilibrated volumetric containing the needed reagents. After >10 half-lives (about 325 min), large aliquots are injected into the HPLC, overfilling the injector loop. [b] HPLC peak areas, measured % yields, and calibration curves are in Table S1.

microenvironment of the diazonium salt ground state in equilibrium with its surroundings. Thus, product distributions from reaction of 1-ArN_2^+ in aqueous solution are proportional to stoichiometric nucleophile concentrations, and product distributions from reaction of hydrophobic 16-ArN_2^+ bound to aggregates are a "snapshot" of interfacial nucleophile composition.[7]

Table I gives a typical reaction protocol for dediazoniation of 16-ArN_2^+ and the normalized mole percent yields of products.[9] Product yields are calculated from HPLC peak areas by using calibration curves obtained with independently synthesized products. Figure 2 shows Y_m values as a function of added BuOH calculated from product yields in Table I and the selectivity of 1-ArN_2^+ in aqueous solution toward Br^-, S_w^{Br}, and BuOH, S_w^{BuOH}, compared to water over wide ranges of [NaBr] and [BuOH], respectively.[10] The calculation of Y_m is based on our assumption that the selectivities of 16-ArN_2^+ in microemulsions and 1-ArN_2^+ in aqueous solution toward different nucleophiles are the same; e.g., when the yields of 16-ArBr (in microemulsions) and 1-ArBr (in aqueous solution) are the same, Br^-_m (in microemulsions) = [NaBr] (in aqueous solution).

Added BuOH displaces both Br^- and H_2O from the interfacial region (Figure 2). At the highest [BuOH], 0.87 M, just below its solubility limit in 0.01 M CTABr,[8a] $BuOH_m \cong 10$. We estimate the concentration of bound BuOH to be ca. 8 mol/L of total aggregate volume at [BuOH] = 0.87 M from its binding constant, $K = 1\ M^{-1}$,[8a] and by assuming that the volumes of aggregated CTABr and BuOH are additive. As $BuOH_m$ increases from 0 to 10 with added BuOH, there is a concomitant decrease in H_2O_m from 50 to 37, indicating an approximately 1:1 exchange of BuOH for H_2O in the interfacial region. However, % 16-ArOH increases modestly (Table I) because the dediazoniation reaction is less selective toward BuOH than Br^-, i.e., $S_w^{BuOH} < S_w^{Br}$.[10] At [BuOH] = 0, $Br^-_m = 2.30$, slightly below literature estimates of 3–5 mol/L of interfacial volume[3] and our previous estimate of 3.3 in 0.01 M CTABr, 0.1 M HBr (10 times greater than the [HBr] here), using a different diazonium salt.[4] The decrease in Br^-_m with added BuOH parallels the drop in the fraction of Br^- bound to myristyltrimethylammonium bromide micelles with added BuOH.[11]

Our dediazoniation reaction is an excellent probe of association colloid interfaces. It distinguishes between chemically similar nucleophiles (e.g., Cl^- and Br^-;[4] H_2O and BuOH), and it can be used with all weakly basic nucleophiles which react by the same mechanism[5] over a wide range of solution compositions. Future results should provide new information on the interfacial compositions of three- and four-component microemulsions.[1]

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Supplementary Material Available: Appendices S1 and S2, detailing diazonium salt preparation, dediazoniation kinetics, and the procedure for calculating interfacial concentrations of H_2O, BuOH, and Br^-, and Tables S1–S3, providing product yields and HPLC calibration data for dediazoniations of 16-ArN_2^+ and 1-ArN_2^+ (6 pages). Ordering information is given on any current masthead page.

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[7] 16-ArN_2^+ is assumed to be completely microemulsion bound.[4] It is water insoluble and more hydrophobic than CTABr, added BuOH reduces the cmc of CTABr,[11] and the CTABr monomer concentration is always <10% of total [CTABr] (at 40 °C, CTABr's cmc = 1.08 × 10^{-3} M in the absence of added salt[8b]).

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[9] Details on the preparation and dediazoniation rates of the tetrafluoroborate salts of 16-ArN_2^+ and 1-ArN_2^+ are in Appendix S1. Normalized mole percent product yields are reported because the measured product yields range from 87 to 100% and the HPLC chromatograms are free of stray peaks (>1%).

[10] Selectivities $S_w^{Br} = 8.3$ and $S_w^{BuOH} = 0.31$ were determined by standard methods (Appendix S2).[4] Tables S1–S3 give product yields and calibration data for z-ArN_2^+.

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Lithium Diisopropylamide Mixed Aggregates: Structures and Consequences on the Stereochemistry of Ketone Enolate Formation

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Stereochemical and regiochemical studies of ketone enolization by lithium dialkylamides have elicited extensive mechanistic discussions that typically invoke kinetic pathways in competition with enolate equilibrations.[1-4] Noticeably absent from most (but not all)[5] treatments are the possible roles of mixed aggregates and autocatalysis as determinants of selectivity and reactivity.[6] Where

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