

Arenediazonium Salts: New Probes of the Interfacial Compositions of Association Colloids. 3.^{1,2} Distributions of Butanol, Hexanol, and Water in Four-Component Cationic Microemulsions[†]

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Abstract: Product yields from dediazonation of 4-hexadecyl-2,6-dimethylbenzediazonium tetrafluoroborate, 16-ArN₂BF₄, bound to aggregates of four-component microemulsions composed of cetyltrimethylammonium bromide, (CTA)Br, H₂O, hexadecane, and an alcohol, R'OH, either 1-butanol, BuOH, or 1-hexanol, HexOH, were used to estimate changes in H₂O and R'OH compositions at the microemulsion interface over a range of microemulsion compositions. Analysis of % 16-ArOR'/% 16-ArOH product percent yield ratios obtained in the water-in-oil microemulsion region of the phase diagram at low water content show that mass action binding constants for the distributions of BuOH and HexOH between the interfacial and oil regions in these microemulsions are independent of [R'OH]. These results indicate that (CTA)Br mixes ideally with both alcohols and that alcohol binding is driven primarily by the hydrophobic effect with minimal contributions from specific interactions between R'OH and (CTA)-Br. We also show that our approach provides estimates of molar concentrations of BuOH and H₂O in the oil, interfacial, and water regions at any composition of these 4-component microemulsions. Changes in the molar concentrations of H₂O and BuOH mark the oil-in-water droplets to bicontinuous to water-in-oil droplets transitions. Potential applications of the dediazonation method are discussed.

Introduction

Microemulsions are thermodynamically stable dynamic aggregates of an anionic, cationic, or nonionic surfactant and a cosurfactant, typically a medium chain length alcohol or other other polar organic molecule such as an amine or formamide, which form in water (three-component microemulsions) or water–oil (four-component microemulsions) mixtures.^{3–8} Mi-

croemulsions have many applications, e.g., in foods,⁹ cleaning products,¹⁰ pharmaceuticals,¹¹ tertiary oil recovery,⁵ and as media for chemical reactions.^{12–15} Formation of four-component microemulsions depends upon the molecular structures of the surfactant, cosurfactant, and oil components and their compositions.^{3,7,8} Aggregate stability depends on the balance between the hydrophobic effect, i.e., the tendency of the hydrocarbon tails of the surfactants and additives to minimize their contact with water by aggregating, and a combination of electrostatic, hydration, H-bonding and polarization interactions of the surfactant and additives with the aqueous phase.⁸ Microemulsion aggregates and other types of surfactant aggregates such as monolayers, micelles, and vesicles, all have an interfacial region which separates the oil and water regions and is composed of surfactant head groups, associated counterions and coions, and any added polar additives, Figure 1. Determining the compositions of aggregate interfaces is an active area of research because interfacial compositions, not stoichiometric concentrations of components, reflect the balance of forces controlling aggregate structure and stability.^{3,6,8}

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[†] Abbreviations. 1. Constants: K_a , mole fraction partition constant for R'OH between interfacial and oil regions, eq 1; K_a^i , mass action binding constant for R'OH between interfacial and oil regions, eq 7; K_A^O , identical to K_a^i but expressed as molar ratios, eq 11; K_A^I , mass action binding constant for R'OH between interfacial and aqueous regions, eq 10; K_A^W , identical to $55.5K_A^I$, but expressed as molar ratios, eq 10; S_w^A , selectivity of aryl cation toward R'OH and H₂O, eq 5; S_w^{Br} , selectivity of aryl cation toward Br⁻ and H₂O, eq A-1. 2. Compositions in aqueous, interfacial, and oil regions: component concentrations are expressed as ratios of moles of a particular component, N_x , to moles (stoichiometric) of CTABr, N_s ; e.g., $\frac{N_x}{N_s}$. (a) for stoichiometric concentrations of oil (hexadecane), alcohol (R'OH), and water, subscript $x = o, a, \text{ and } w$; (b) for interfacial concentrations of water and oil, subscript $x = mw \text{ and } ma$; (c) for aqueous concentrations of water and alcohol, subscript $x = ww \text{ and } wa$; and (d) for concentrations of alcohol in oil, subscript $x = oa$.

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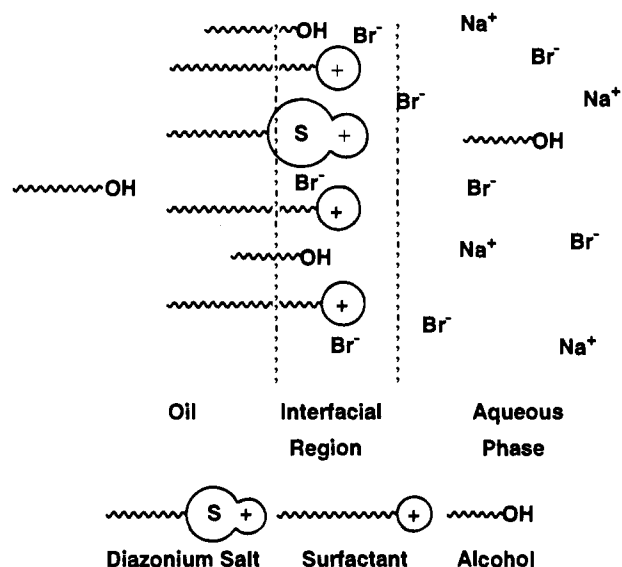


Figure 1. Interfacial region of a four-component microemulsion composed of a cationic surfactant, an alcohol, oil, water, Br^- counterions and Na^+ and H^+ coions. The amphiphilic arenediazonium salt substrate is shown with its reactive group located in the interfacial region.

Added alcohols have marked effects on microemulsion properties such as the critical micelle concentration of three-component microemulsions (also called alcohol swollen micelles), the degree of counterion binding of microemulsions composed of ionic surfactants, the aggregation number,¹⁶ and the capacity of microemulsions to dissolve oil.^{5,7} Alcohol partition or binding constants are estimated by a variety of methods.^{17–35} Much of this work has been carried out in aqueous three-component microemulsions, with some work in four-component water-in-oil microemulsions^{28,31,33} and in the bicontinuous region.³⁶

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(17) Methods include: solubility,^{16,18–20} changes in critical micelle concentrations,²¹ density changes,^{22,23} excess enthalpies of solution,²⁴ heat capacities,²⁵ ultrafiltration,²⁶ head space analysis at equilibrium vapor pressure,^{27,28} alcohol induced changes in fluorescence intensity,^{29–31} conductivity,³² small angle neutron scattering,³³ and product yields from dediazonation reactions.^{1,2,34,35}

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At low alcohol concentrations, mole fraction partition constants for medium chain length alcohols depend upon alcohol chain length and head group charge.^{23,37} Partitioning of hexanol in aqueous mixed micelles of an ionic and nonionic surfactants is not ideal,³⁸ suggesting that alcohol partitioning in these systems depends upon interactions between the $-\text{OH}$ group of hexanol and the surfactant head group in the interfacial region. A careful determination of alcohol binding constants over a wide range of surfactant types and microemulsion solution compositions is needed to understand the contributions of the various factors affecting alcohol binding. Using a chemical trapping method (see below), we have found that mass action binding constants of butanol, BuOH, and hexanol, HexOH, to cetyltrimethylammonium bromide, (CTA)Br, microemulsions are constant up to the solubility limits of the alcohols.² The numerical values of the binding constants agree with estimates obtained by solubility^{16,19,20} and, despite the difference in surfactant chain length, are similar to those obtained from density measurements in dilute solutions of dodecyltrimethylammonium bromide.²² Together, these results suggest that medium chain length alcohols, $\text{R}'\text{OH}$, mix ideally with cationic surfactants in aqueous microemulsions.

We have developed a novel chemical trapping method for estimating, simultaneously, the quantities of weakly basic nucleophiles such as alcohols, water, and halide ions in the interfacial regions of micelles and microemulsions from products formed by reaction of aggregate bound 4-hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate, 16-ArN₂BF₄,^{1,2,34,35,39} in aqueous acid in the absence of light, arenediazonium ions react via rate-determining loss of N_2 to generate an aryl cation which traps nucleophiles in the interfacial region to give stable products (see Scheme 1 and Figure 1). We have used product yields from reactions of aggregate bound 16-ArN₂⁺ in aqueous micelles of cetyltrimethylammonium halides (CTAX, X = Br, Cl) to estimate, simultaneously, the interfacial concentrations of Cl^- and Br^- and H_2O and the interfacial concentrations of Br^- , $\text{R}'\text{OH}$, and H_2O in (CTA)Br microemulsions,¹ the ion exchange constant for Br^- and Cl^- in CTAX micelles over a range ionic strengths and counterion ratios,³⁹ and as noted above, $\text{R}'\text{OH}$ binding constants.²

Our trapping method can also be used to estimate the distribution of alcohols between the interfacial and oil regions of four-component water-in-oil microemulsions composed of $\text{R}'\text{OH}/(\text{CTA})\text{Br}/\text{hexadecane}/\text{H}_2\text{O}$ ($\text{R}'\text{OH} = \text{BuOH}$ and HexOH). Experiments with BuOH were of particular interest because this system is known to form monophasic solutions across the phase diagram,^{14,15,28,40} Figure 2. HexOH was used to explore the effect of $\text{R}'\text{OH}$ chain length on alcohol binding. Mass action binding constants of BuOH and HexOH estimated from 16-ArOR' product yields (Scheme 1) are constant over a range of $\text{R}'\text{OH}/\text{hexadecane}$ ratios as in aqueous microemulsions.² We also show that the moles of both H_2O and BuOH can be estimated in the oil, interfacial, and aqueous regions of the solution at any point in the monophasic portion of the phase diagram from the mass action binding constants for the distribution of BuOH between the aqueous–interfacial and oil–interfacial regions and the selectivity of the dediazonation reaction toward BuOH compared to H_2O . Certain molar ratios of interfacial water and alcohol coincide with published

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Scheme 1

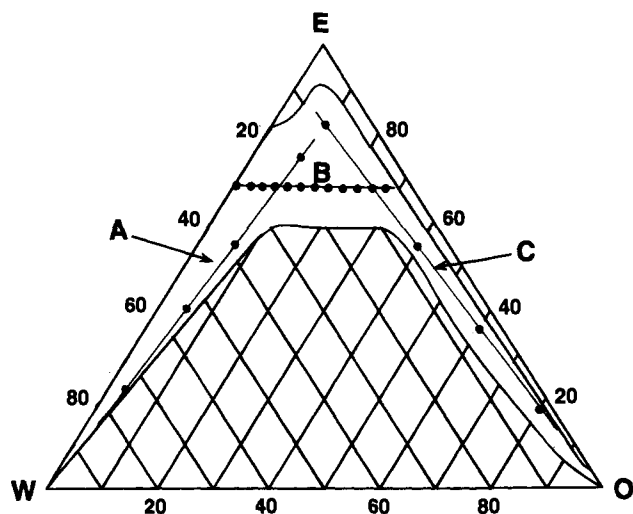
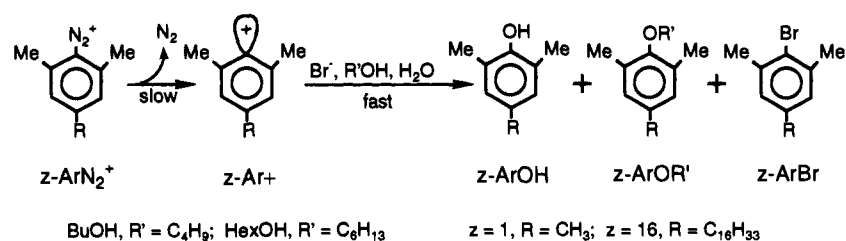


Figure 2. Pseudoternary phase diagram of the (CTA)Br/butanol/hexadecane/water system (E = 5:1 molar ratio of BuOH:(CTA)Br, O = hexadecane, W = water). Data points lines indicate compositions listed in Tables 1 and 2 (see text). Adapted from ref 14 by permission of the authors and the American Chemical Society.

estimates of the oil-in-water, o/w, droplets to bincontinuous to water-in-oil, w/o, droplets transitions.

Experimental Section

Materials. Hexadecane (Aldrich, 99+%) and BuOH (Aldrich, HPLC grade) were used as received. HexOH (Aldrich, 98%) was freshly distilled. Preparation and purification of cetyltrimethylammonium bromide, (CTA)Br, 2,6-dimethyl-4-hexadecylbenzenediazonium tetrafluoroborate, 16-ArN₂BF₄, and its dediazonation products, 4-*n*-hexadecyl-2,6-dimethylphenol, 16-ArOH, 4-*n*-hexadecyl-2,6-dimethylbromobenzene, 16-ArBr, *n*-butyl 4-*n*-hexadecyl-2,6-dimethylphenyl ether, 16-ArOBu, and 4-*n*-hexadecyl-2,6-dimethylphenyl ether, 16-ArOH_{Hex}, are described in the first paper in this series.¹

Dediazonation Reactions in Microemulsions. Microemulsion solutions were prepared by adding weighed amounts of crystalline (CTA)Br (0.3–0.6 g) and then using syringes to add aliquots of R'OH, hexadecane, and water (distilled, passed over beds of activated carbon and ion exchange resin, and redistilled) to Teflon stoppered flasks to give total weights of 1–5 g. Volumes of liquids required were calculated from the needed weights and their literature densities. Dediazonation was initiated by adding small amounts of crystalline 16-ArN₂BF₄ (0.5–6 mg) to each microemulsion solution (final 16-ArN₂BF₄:(CTA)Br molar ratios ≤ 1:100) thermostated at 40.0 ± 0.1 °C. After the reaction was complete (at least 6 h, > 10 half-lives),¹ the solutions were cooled to room temperature, and an aliquot of each solution was transferred to separate 5 mL volumetric flasks which were then diluted to the mark with absolute EtOH and analyzed by HPLC. Aliquot sizes were selected such that the integrator signal intensity for 16-ArBr was about 3 × 10⁵ μV. Dilution factors ranged from about 3 to 20. Dilution with EtOH prevented base line drift and distortion and overlap of 16-ArBr and 16-ArOR' peaks that were often observed in HPLC chromatograms of samples containing high concentrations of hexadecane or R'OH.

Determination of Product Yields. All product analyses were carried out in duplicate on a Kratos HPLC system as described.^{1,2}

Table 1. Effect of Added Hexadecane in Weight Percent, $W_{\text{oil}}\%$, on Normalized Product Yields of 16-ArOH, 16-ArBr, and 16-ArOBu from Dediazonation of 16-ArN₂⁺ in (CTA)Br/BuOH/Hexadecane/H₂O Water-in-Oil Microemulsions^a

sample ^b	$W_{\text{oil}}\%$	N_0/N_s	normalized product yields ^c (%)		
			16-ArOH	16-ArBr	16-ArOBu
1	10.0	0.248	32.1	52.2	15.7
			31.1	53.1	15.8
2	25.0	1.20	32.5	53.0	14.5
			31.1	54.2	14.7
3	40.0	1.50	31.7	54.9	13.4
			31.7	54.8	13.5
4	60.0	5.41	32.6	55.5	11.9
			32.1	55.9	12.0
5	80.0	14.4	33.3	56.8	9.9
			33.5	56.5	10.0

^a The weight ratio of (CTA)Br/BuOH (1:5 molar ratio) to H₂O is 90/10. The H₂O/(CTA)Br ratio = 4.54. ^b Sample compositions are indicated by the points in Figure 1, line C. ^c Average yields from duplicate runs.

Dediazonation products, Scheme 1, were separated on a Varian 15 cm C-18 reversed phase column (particle size = 5 mm) with 64% MeOH:36% i-PrOH (v:v), flow rate = 0.4 mL min, injector loop = 100 μL at 219 nm with AUFS = 0.300. Product peaks were calibrated by using independently synthesized products dissolved in absolute EtOH. Normalized mole percent product yields are used in all calculations because we used very small amounts of 16-ArN₂BF₄ to conserve materials and sample weights were only approximate. To confirm that 16-ArN₂BF₄ was converted quantitatively to products, three samples containing 20.2% hexadecane, 6.1% H₂O, 7.8% (CTA)Br, and 65.9% BuOH ((CTA)Br:BuOH = 1:8.45) were prepared containing larger amounts of 16-ArN₂BF₄ (10.00–15.00 mg). The average total product yield of 16-ArOH, 16-ArOBu, and 16-ArBr in the three samples was 102.6%. On the basis of these results, and previous results using the dediazonation method in micelles and microemulsions,^{1,2,39} we assume that conversion to products is quantitative and that small variations in total yield are caused by weighing errors. Details on sample composition, HPLC peak areas, product yields, and calibration curves are in the supplementary material.

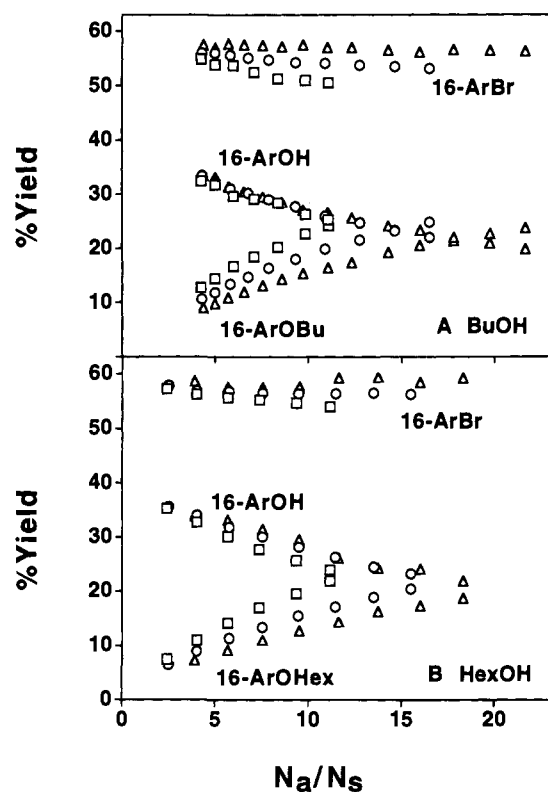
Results

Table 1 illustrates typical changes in averaged normalized product yields of 16-ArOH, 16-ArOBu, and 16-ArBr in mole percent from duplicate runs as a function of the weight percent, $W_{\text{oil}}\%$, of added hexadecane. The (CTA)Br/BuOH molar ratio is 1:5 in these microemulsions with a ((CTA)Br + BuOH) to H₂O weight ratio of 90:10 (points on line C in Figure 2). Increasing $W_{\text{oil}}\%$ (and the N_0/N_s ratio, where N_0 and N_s are the moles of added hexadecane and (CTA)Br, respectively) reduces % 16-ArOBu showing that the amount of aggregate bound BuOH decreases significantly with added hexadecane.

Figure 3 shows the changes in 16-ArOH, 16-ArBr, and 16-ArOR' yields in w/o microemulsions with added BuOH (Figure 3A) and added HexOH (Figure 3B), i.e., with increasing N_0/N_s ratios, where N_s is the moles of added R'OH. The H₂O/(CTA)Br molar ratio is the same in all solutions, $N_w/N_s = 4.54$, and the hexadecane/(CTA)Br ratio, N_0/N_s , increases about 10-fold

Table 2. Effect of Added Hexadecane and Water in Weight Percent, $W_{oil}\%$ and $W_{H_2O}\%$, on Normalized Product Yields of 16-ArOH, 16-ArBr, and 16-ArOBu from Dediazonation of 16-ArN₂⁺ in (CTA)Br/BuOH/Hexadecane/H₂O Microemulsions at BuOH/(CTA)Br = 5:1

	16-ArOH (%)	16-ArBr (%)	16-ArOBu (%)		16-ArOH (%)	16-ArBr (%)	16-ArOBu (%)
$W_{oil}\%$ ^a				$W_{oil}\%$ ^a			
0.00	60.6	30.6	8.8	15.0	48.9	40.4	10.7
2.50	59.3	31.7	9.0	17.5	45.6	43.1	11.3
5.00	57.5	33.2	9.1	20.0	41.7	46.1	12.2
7.50	55.9	34.6	9.5	22.5	37.0	59.8	13.2
10.0	53.7	36.4	9.9	25.0	31.3	54.1	14.6
12.5	51.5	38.3	10.2	27.5	23.7	59.9	16.4
$W_{H_2O}\%$ ^b				$W_{H_2O}\%$ ^b			
18.2	45.9	41.1	14.0	57.2	70.4	22.3	7.3
40.0	64.6	26.9	8.5	76.9	75.3	18.5	6.2

^a Line B in Figure 2. ^b Line A in Figure 2.**Figure 3.** Normalized product yields from dediazonation of 16-ArN₂⁺ in (CTA)Br/alcohol/hexadecane/water microemulsions: A, BuOH; B, HexOH; $N_w/N_s = 4.54$; $N_o/N_s = 1.20$ (□), 5.41 (○), 14.4 (△).

from 1.20 to 14.4. The BuOH solutions at $N_a/N_s = 5.00$ have the same compositions as samples 2, 4, and 5 in Table 1 and Figure 2. Added R'OH increases 16-ArOR' yields significantly and produces a decrease in 16-ArOH yields and 16-ArBr yields. Reducing the N_o/N_s ratio also affects product yields; 16-ArOR' increases, 16-ArBr decreases, but 16-ArOH remains essentially unchanged. Added BuOH and added HexOH have qualitatively similar effects in aqueous three-component (CTA)Br microemulsions² except that the mol % yields of 16-ArBr are much higher and the mol % yields of 16-ArOH are much lower in these w/o microemulsions. The lowest values of N_a/N_s in Figure 3 are close to the lower limit of the amounts BuOH and HexOH needed to make transparent homogeneous solutions. No phase separation was observed at the highest R'OH concentrations used.

Table 2 summarizes averaged (duplicate) normalized product yields of 16-ArOH, 16-ArBr, and 16-ArOBu as a function of added hexadecane, $W_{oil}\%$ (line B, Figure 2), and added H₂O, $W_{H_2O}\%$ (line A, Figure 2) at constant BuOH/(CTA)Br = 5:1. Note the marked changes in yields of all three products.

Estimation of R'OH Distribution Constants. Distributions of alcohols between aggregates and the surrounding bulk phase can be described by a mole fraction partition constant, K_a ^{2,29,37}

$$K_a = \frac{X_{ma}}{Y_{oa}} \quad (1)$$

where X_{ma} and Y_{oa} are the mole fractions of R'OH in the interfacial and oil regions, respectively:

$$X_{ma} = \frac{N_{ma}}{N_s + N_{ma}} \quad (2)$$

$$Y_{oa} = \frac{N_{oa}}{N_o + N_{oa}} \quad (3)$$

Following convention⁴¹ and our previous work with aqueous 3-component microemulsions,² the microemulsions in this study are assumed to be "dry"; i.e., the moles of water are not included in the total moles within the interfacial region. Activity coefficients of R'OH in the aggregates and hexadecane are assumed to be 1.⁴¹ Combining eqs 2 and 3 with the mass balance equation for the moles of R'OH in the aggregate interface and the oil region, $N_a = N_{ma} + N_{oa}$, gives

$$\frac{N_a}{N_s} = \left(\frac{Y_{oa}}{1 - Y_{oa}} \right) \frac{N_o}{N_s} + \frac{X_{ma}}{1 - X_{ma}} \quad (4)$$

Equation 4 predicts a linear relation between the stoichiometric molar ratios N_a/N_s and N_o/N_s for microemulsion solutions which have different R'OH and oil concentrations but the same fraction of bound R'OH, i.e., the same value of X_{ma} . Equations 1 and 4 can be used to estimate K_a over a range of R'OH and (CTA)-Br concentrations from sets of N_a/N_s , N_o/N_s values obtained at constant X_{ma} . Sets of N_a/N_s , N_o/N_s values can be obtained from plots of % 16-ArOR'/% 16-ArOH yield ratios against N_a/N_s ratios at different N_o/N_s ratios. The primary requirement is that each set of % 16-ArOR'/% 16-ArOH yield ratios be obtained at the same X_{ma} . The relationship between % 16-ArOR'/% 16-ArOH yield ratios and X_{ma} is derived from the definition for aryl cation selectivity toward R'OH and H₂O, S_w^A :

$$S_w^A = \frac{\% \text{ 16-ArOR}' N_{mw}}{\% \text{ 16-ArOH } N_{ma}} \quad (5)$$

Equation 5 can be rearranged to give

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$$\frac{\% \text{ 16-ArOR}'}{\% \text{ 16-ArOH}} = S_W^A \frac{N_{ma}}{N_{mw}} = S_W^A \frac{N_{ma}/N_s}{N_{mw}/N_s} = S_W^A \frac{X_{ma}/(1-X_{ma})}{f_m(N_w/N_s)} \quad (6)$$

where $f_m = (N_{mw}/N_w)$ is the fraction of water bound to the interface. Equation 6 shows that for any microemulsion composition in which the % 16-ArOR'/% 16-ArOH yield ratios are the same, X_{ma} will be the same provided that f_m , N_w/N_s , and S_W^A (see below) are constant. The N_w/N_s ratio is fixed experimentally at 4.54 in all the w/o microemulsions used to estimate binding constants (data in Table 1 and Figure 3), and this ratio is approximately half the hydration number, $n = 8-10$, of (CTA)Br in D_2O as estimated from NMR relaxation times and self-diffusion coefficients^{42,43} and from dielectric relaxation measurements in H_2O .⁴⁴ Thus, we assume that all water present in these w/o microemulsions is hydrating the $-CH_2N(CH_3)_3^+$ head groups and Br^- counterions and that separate pools of free water do not exist, i.e., $f_m = 1$. Therefore, R'OH can only partition between the interfacial and oil regions, Figure 1.

Estimating values of K_a from the data in Figure 3 is a two-step process. First, % 16-ArOR'/% 16-ArOH yield ratios obtained from the data in Figure 3 are plotted against N_a/N_s ratios, Figure 4. As predicted by eq 6, values of % 16-ArOR'/% 16-ArOH yield ratios are linear functions of $X_{ma}/(1-X_{ma})$, $cc = 1.000$, for both BuOH and HexOH (see least-squares fits in Table 3, footnote b). Second, sets of horizontal lines at constant % 16-ArOR'/% 16-ArOH ratios (eq 6), are drawn through the lines at each N_o/N_s ratio (see example lines in Figure 4) generating N_a/N_s , N_o/N_s data sets at constant X_{ma} which are replotted as in Figure 5. The values of % 16-ArOR'/% 16-ArOH yield ratios used (see caption of Figure 5) are restricted to the experimental range of measured % 16-ArOR'/% 16-ArOH yield ratios. Note that the slopes in Figure 5 are linear (see correlation coefficients in Table 3), consistent with the assumptions represented by eq 4, except at higher % 16-ArOR'/% 16-ArOH ratios for HexOH. Table 3 lists estimates of X_{ma} and Y_{oa} and K_a obtained from the slopes and intercepts of the lines in Figure 5 by using eqs 1 and 4.

We also estimated the selectivity of the reaction of the aryl cation toward R'OH compared to H_2O at the microemulsion interfaces from the slopes (not shown) of % 16-ArOR'/% 16-ArOH yield ratios against $X_{ma}/(1-X_{ma})$ (eq 6) using the data in Table 3. The selectivities for the alcohols are $S_W^A = 0.38$ for BuOH and $S_W^A = 0.34$ for HexOH, assuming $f_m = 1$ and $N_w/N_s = 4.54$. These selectivities are similar to those obtained for dediazotization of 1-ArN₂⁺, the water soluble short chain analog of 16-ArN₂⁺, in very different media: up to 1.0 M aqueous BuOH ($S_W^A = 0.31$) and at BuOH/ H_2O volume ratios of 9:1 ($S_W^A = 0.28$). The linearity of the plots in Figure 4 and the similarities of the four S_W^A values support our assumption that the selectivity of the dediazotization reaction toward R'OH compared to H_2O is independent of solution composition.

Values of K_a for both BuOH and HexOH decrease linearly with increasing X_{ma} . Table 3 (least-squares fits are in footnote c). Literature estimates of K_a generally decrease with added R'OH in aqueous microemulsions of both anionic and cationic surfactants,³⁷ and we also observed a linear decrease for mole fraction partition constants of BuOH and HexOH to aggregates in aqueous, three-component cationic microemulsions.² The

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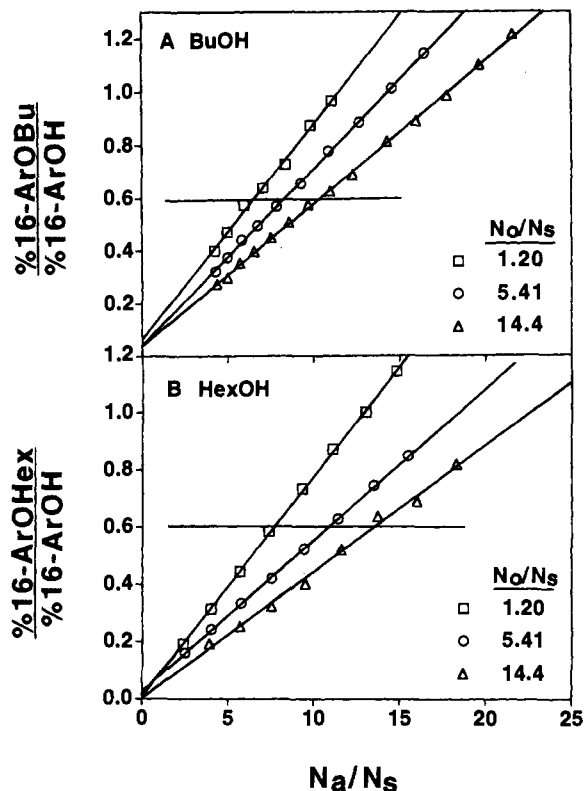


Figure 4. Product yield ratios from reaction of 16-ArN₂⁺ with R'OH and H_2O as function of added R'OH at $N_a/N_s = 4.54$. Example horizontal lines are drawn at constant X_{ma} ; see eq 6 and text.

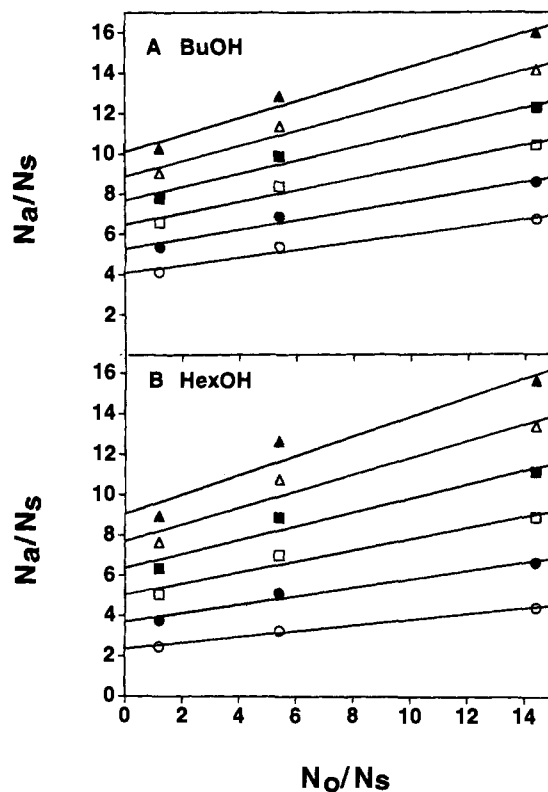


Figure 5. Plots of molar ratios of R'OH:(CTA)Br, N_a/N_s , against hexadecane:(CTA)Br, N_o/N_s , eq 4. The % 16-ArOR'/% 16-ArOH ratios used to estimate N_a/N_s , N_o/N_s data sets in Figure 4 are as follows: 0.4 (○), 0.5 (●), 0.6 (□), 0.7 (■), 0.8 (△), and 0.9 (▲) for BuOH and 0.2 (○), 0.3 (□), 0.4 (■), 0.5 (●), 0.6 (△), and 0.7 (▲) for HexOH.

distribution of R'OH between the interfacial and oil regions can also be defined by a mass action equilibrium constant, K_a ,

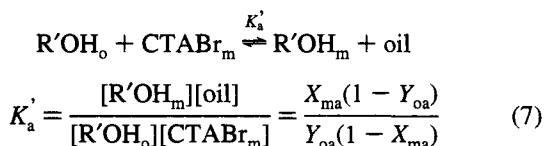
Table 3. Slopes, Intercepts, and Correlation Coefficients (cc) from Linear Least-Squares Fits of N_w/N_s versus N_o/N_s Plots (Figure 5) and the Calculated Values of X_{ma} , Y_{oa} , K_a , and K_a' for BuOH and HexOH

% 16-ArOR'	% 16-ArOH	slope	intercept ^a	cc	$X_{ma}^{a,b}$	Y_{oa}^a	K_a^c	$K_a'^d$
R' = Bu								
0.90	0.420	10.09	0.977	0.910	0.296	3.07	24.0	
0.80	0.374	8.890	0.976	0.899	0.272	3.31	23.8	
0.70	0.327	7.690	0.975	0.885	0.246	3.60	23.5	
0.60	0.281	6.489	0.973	0.866	0.219	3.95	23.1	
0.50	0.234	5.288	0.971	0.841	0.190	4.43	22.6	
0.40	0.188	4.087	0.967	0.803	0.158	5.08	21.7	(23.1) ^e
R' = Hex								
0.70	0.485	9.050	0.932	0.900	0.327	2.75	18.7	
0.60	0.417	7.711	0.938	0.885	0.294	3.01	18.5	
0.50	0.350	6.373	0.946	0.864	0.259	3.34	18.2	
0.40	0.282	5.036	0.956	0.834	0.220	3.79	17.9	
0.30	0.215	3.697	0.971	0.787	0.177	4.45	17.2	
0.20	0.147	2.359	0.991	0.702	0.128	5.48	16.0	(17.8) ^e

^a Equation 4, note intercept = $X_{ma}/(1 - X_{ma})$. ^b Equations for linear least squares fits of data in columns 1 and 5 according to eq 6; for BuOH: % 16-ArOBu:% 16-ArOH = $0.083(X_{ma}/(1 - X_{ma})) + 0.063$, cc = 1.000; for HexOH: % 16-ArOHex:% 16-ArOH = $0.075(X_{ma}/(1 - X_{ma})) + 0.022$, cc = 1.000. ^c Equation 1. For BuOH: $K_a = -18.7(X_{ma}) + 20.2$, cc = 0.999; for HexOH: $K_a = -13.7(X_{ma}) + 15.2$, cc = 0.998. ^d Equation 7. ^e Average of above values in the column. The average deviations are BuOH, $\pm 3\%$, and HexOH, $\pm 4\%$.

Scheme 2, which can be expressed in molar or mole fraction

Scheme 2



units, eq 7. Values of K_a' are independent of X_{ma} for both BuOH ($\pm 3\%$) and HexOH ($\pm 4\%$), Table 3.

Estimation of BuOH and H₂O Distributions between the Oil, Interfacial, and Aqueous Regions. The mass action equilibrium constants determined under limiting conditions, i.e., between the aqueous and interfacial regions in the absence of added oil² and between the oil and interfacial regions in the absence of a "free" water pool, Table 3, can be used to estimate the molar ratios of both BuOH/(CTA)Br and H₂O/(CTA)Br in the aqueous, oil, and interfacial regions in any single phase region of the phase diagram, Figure 2, by assuming that these constants are independent of the weight percents of water and hexadecane in the system. To estimate the molar ratios, the equations for the mass action equilibrium constants for BuOH are combined with the selectivity of the phenyl cation toward alcohol versus water and the mass balance equations for BuOH and H₂O. The mass balances of BuOH and H₂O expressed in terms of the moles of (CTA)Br present are given by

$$\frac{N_w}{N_s} = \frac{N_{ww}}{N_s} + \frac{N_{mw}}{N_s} \quad (8)$$

$$\frac{N_a}{N_s} = \frac{N_{ma}}{N_s} + \frac{N_{wa}}{N_s} + \frac{N_{oa}}{N_s} \quad (9)$$

where N stands for the moles of a component and the subscripts s, w, and a indicate the stoichiometric quantities of (CTA)Br, H₂O, and BuOH, respectively. Subscripts ww and mw indicate the moles of H₂O in the aqueous and interfacial regions and

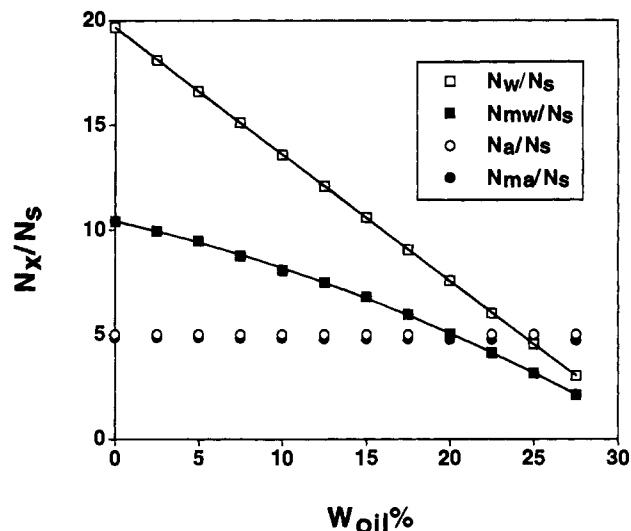


Figure 6. Effect of added hexadecane on the molar ratios of stoichiometric BuOH, N_w/N_s , and H₂O, N_w/N_s , and interfacial BuOH, N_{mw}/N_s , and H₂O, N_{mw}/N_s , to (CTA)Br, BuOH/(CTA)Br = $N_w/N_s = E \approx 5:1$, $W_E\% = 67.5$, $W_{oil}\% + W_{H_2O}\% = 32.5$, data on line B in Figure 2 and in Table 2. Solid lines added to aid the eye.

subscripts ma, wa, and oa indicate the moles of alcohol in the interfacial, water, and oil regions, respectively. The mass action binding constant for the distribution of BuOH between the aqueous and interfacial regions, K_A^w , expressed as molar ratios is given by

$$K_A^w = \frac{N_{ma}/N_s}{N_{wa}/N_{ww}} = 55.5 K_A' = 55.5 \frac{[\text{BuOH}_m]}{[\text{BuOH}_w][(\text{CTA})\text{Br}_m]} \quad (10)$$

assuming that BuOH occupies only a small fraction of the aqueous phase, i.e., $N_{wa}/N_{ww} \ll 1$. Equation 10 also shows the relationship between K_A^w and the mass action binding constant K_A' (third and fourth expressions in the equality) expressed in molarity where $[(\text{CTA})\text{Br}_m]$ is the concentration of micellized surfactant. K_A' for BuOH is 5.99.² The distribution of BuOH between the oil and interfacial regions is given by

$$K_A^o = \frac{N_{ma}/N_s}{N_{oa}/N_o} \quad (11)$$

Equation 11 is identical to eq 7, except that it is expressed as molar ratios, i.e., $K_A^o = K_a' = 23.1$ (Table 3). Equations 8–11 are combined and solved for N_{ma}/N_s to give

$$\frac{N_{ma}}{N_s} = \frac{\frac{N_a}{N_s}}{1 + \frac{1}{K_A^w} \left(\frac{N_w}{N_s} - \frac{N_{mw}}{N_s} \right) + \frac{1}{K_A^o} \frac{N_o}{N_s}} \quad (12)$$

Equation 12 is solved simultaneously with eq 6 to obtain estimates of the ratio of BuOH and H₂O to (CTA)Br in the interfacial region, i.e., N_{ma}/N_s and N_{mw}/N_s , respectively. Ratios of BuOH and H₂O in other regions are obtained by using the appropriate mass balance equations.

Figures 6 and 7 show, respectively, the effect of increasing weight percent of hexadecane, $W_{oil}\%$ (line B, Figure 2), and water, $W_{H_2O}\%$ (line A, Figure 2), on calculated interfacial molar ratios of BuOH and H₂O to (CTA)Br, N_{ma}/N_s and N_{mw}/N_s , and

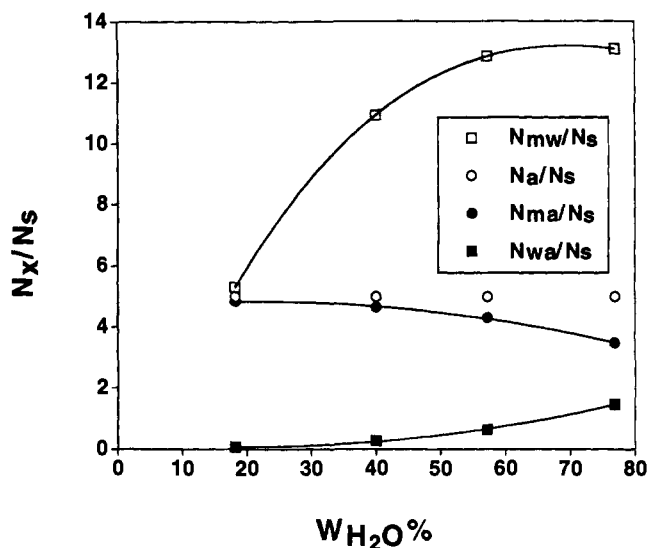


Figure 7. Effect of added water on the molar ratios of stoichiometric BuOH, N_a/N_s , aqueous BuOH, N_{wa}/N_s , and interfacial BuOH, N_{ma}/N_s , and H₂O, N_{mw}/N_s to (CTA)Br, $\text{BuOH}/(\text{CTA})\text{Br} = N_a/N_s = E = 5:1$, data on line A in Figure 2 and in Table 2. Solid lines added to aid the eye.

on calculated molar ratio of aqueous alcohol to (CTA)Br, N_{wa}/N_s , at fixed stoichiometric ratios of H₂O and BuOH to (CTA)Br, N_w/N_s and N_a/N_s , respectively, from the yield data in Table 2.

Discussion

Estimation of Binding Constants, K_a^0 . The basic assumption used in estimating alcohol partition constants, K_a , and mass action binding constants, K_a' , is that at any microemulsion composition in the single phase region of the phase diagram at low water content such that no free water pool is present, i.e., $N_{mw}/N_s \approx N_w/N_s$, the mole fraction of bound alcohol, X_{ma} , will be the same when the % 16-ArOR/% 16-ArOH product ratios from the dediazonation reaction are the same.⁴⁵ This assumption should be independent of medium effects on the selectivity of the aryl cation toward available nucleophiles because the medium properties of the interfacial region are determined primarily by X_{ma} . As in aqueous three-component microemulsions,² K_a for these four-component w/o microemulsions is a linear function of X_{ma} (see footnote c, Table 3). However, the mass action equilibrium constant, K_a' (eq 7), which in essence is K_a corrected for the molar fraction of the interfacial and oil regions occupied by R'OH, is independent of X_{ma} (and Y_{oa}). Note that the average differences in K_a' values is small for both alcohols (Table 3, footnote 3) indicating that the small curvatures in the plots for HexOH at high [HexOH] in Figure 4 do not affect our results significantly.

The values of K_a' for BuOH and HexOH are similar (Table 3), but that for BuOH is slightly larger, probably because BuOH is less hydrophobic than HexOH and it associates more strongly with the microemulsion interface. This trend has been observed by others.^{28,31,33} Our binding constant values for w/o microemulsions cannot be compared with published values because different surfactants or oils were used, although values of dissociation constants, K_m , reported by Damaszewski and

Mackay for BuOH in (CTA)Br/benzene/H₂O (see their Table 3)²⁸ are similar to our values of K_a' (where $K_m = 1/K_a$).

Constant values of K_a' (Table 3) suggest that R'OH distributions between the interfacial and oil regions of cationic w/o microemulsions depend primarily on the hydrophobic effect and that both BuOH and HexOH mix ideally with (CTA)Br in the microemulsion aggregates. Thus, R'OH binding in these microemulsions does not depend upon specific interactions, e.g., changes in hydration or charge-dipole interactions, between R'OH and (CTA)Br head groups that would depend upon R'OH/(CTA)Br head group ratios in the interfacial region, i.e., X_{ma} .

Distributions of R'OH and H₂O between the Oil, Water, and Interfacial Regions. At 0 (zero) $W_{oil}\%$ of hexadecane, Figure 6, about half of the water is in the interfacial region, i.e., $N_{mw}/N_s \approx 10$ and $N_w/N_s \approx 20$. As $W_{oil}\%$ of hexadecane increases, the difference between these ratios decreases until the molar ratios of stoichiometric and interfacial water are almost the same at 27.5 $W_{oil}\%$; consistent with our assumption that no free water is present in w/o microemulsions, compositions on line C in Figure 2. Note that $N_a/N_s \approx N_{ma}/N_s$; i.e., virtually all the BuOH is in the interfacial region; about 97% and 94% at 0 $W_{oil}\%$ and 27.5 $W_{oil}\%$, respectively.

At 18.5 $W_{H_2O}\%$, i.e., the lowest water content in Figure 7, the molar ratios of interfacial BuOH and H₂O are virtually equivalent. The stoichiometric H₂O/(CTA)Br ratio, N_w/N_s , is 10.2 (data not shown), indicating that about half of the total water is in the interfacial region. As $W_{H_2O}\%$ increases, the number of moles of interfacial water rises to a value of $N_{mw}/N_s \approx 13$, much less than the stoichiometric H₂O/(CTA)Br ratio, $N_w/N_s = 153$ at $W_{H_2O}\% = 77$ (data not shown). At 77 $W_{H_2O}\%$, about 30 mol % of the BuOH is in the aqueous region. The moles of BuOH in the oil region never exceed 1.5% of the stoichiometric [BuOH] (data not shown). The H₂O/(CTA)Br, N_{mw}/N_s , molar ratios provide estimates of all water within the interfacial region, including water of hydration of the -OH group of BuOH, the head group, and counterion of (CTA)Br and any "free" water. The maximum value of N_{mw}/N_s is slightly greater than the hydration number of (CTA)Br micelles in D₂O ($N_{mw}/N_s = 8-10$) estimated by NMR^{42,43} and the hydration number of (CTA)Br/BuOH/hexadecane/H₂O microemulsions ($N_{mw}/N_s \approx 10$) obtained from measurements of dielectric properties at microwave frequencies.⁴⁴

The results in Figures 6 and 7 suggest a simple explanation for transitions between bicontinuous and w/o and o/w droplet structures. Surface curvature, and therefore aggregate shape, is controlled primarily by the relative amounts of H₂O and BuOH molecules in the interfacial region. The bicontinuous-w/o droplets transition occurs as the molar concentration of H₂O in the interfacial region drops below that of BuOH, i.e., when $N_{mw}/N_s \leq N_{ma}/N_s$, at about 20 $W_{oil}\%$ (Figure 6). Insufficient H₂O is available to fully hydrate BuOH and CTABr, and droplets form because not enough H₂O is available to stabilize a lamellar water layer between the surfactant and oil layers. Hermansky⁴⁰ reported marked changes in conductivity of these microemulsion solutions at 20 $W_{oil}\%$ which was attributed to the bicontinuous w/o droplets transition. At low $W_{oil}\%$ along line A, Figure 2, the bicontinuous-o/w droplets transition occurs as the molar concentration of H₂O exceeds that of interfacial BuOH and when BuOH begins to dissociate from the interfacial region into the aqueous phase. Curved droplets are formed because of increased head group size due to hydration and a change in aggregate packing because of loss of BuOH from the interface. Mackay and co-workers observed a significant decrease in the diffusion coefficients of microemulsion bound ferrocene at 25 °C across the same concentration range in this

(45) A similar assumption was used to estimate binding constants of BuOH and HexOH in aqueous three component (CTA)Br microemulsions which are in good agreement with binding constants estimated by solubility.²

(46) Mackay, R. A.; Myers, S. A.; Bodalbhai, L.; Brajter-Toth, A. *Anal. Chem.* 1990, 62, 1084-1090.

microemulsion system which they interpreted as inhibition of ferrocene diffusivity by binding ferrocene to large, isolated droplets which diffuse more slowly than ferrocene in the bicontinuous regions.⁴⁶ These results show that product yields from dediazonation reactions can be used to determine water alcohol ratios that mark the o/w droplet–bicontinuous–w/o droplet transitions in virtually any microemulsion system.

Reaction with Br⁻. Approximately half of the total product yield from reaction with 16-ArN₂⁺ is 16-ArBr, Figure 3. From the mol % yields of 16-ArBr we estimated S_w^{Br} , the selectivity of the phenyl cation toward Br⁻ versus H₂O at each N_a/N_s . The results, summarized in Appendix 1 and Figure 8, show that all our estimated values of S_w^{Br} in the interiors of these four-component water-in-oil microemulsions fall within the range of S_w^{Br} values obtained by reaction with 1-ArN₂⁺ in aqueous tetramethylammonium bromide, TMABr, solutions whose concentrations range from 0 to 3.5 M.¹ Thus, the high yields of 16-ArBr can be attributed to the high Br⁻ concentrations in the interior of the four-component microemulsions and not to increases in the selectivity of the phenyl cation toward Br⁻ compared to H₂O. We have not attempted to interpret the 16-ArBr yield data further because the values of S_w^{Br} in these microemulsions should depend on the ionic strength in the microemulsion interior, just as they do in H₂O.¹ A complete interpretation of these results requires a detailed study of S_w^{Br} in alcohol–water mixtures.

Conclusions

Product yields from reaction of aggregate bound arenediazonium salts in four-component, (CTA)Br, water-in-oil microemulsions can be used to obtain precise estimates of the mole fraction of alcohol, X_{ma} , at the aggregate interface. This dediazonation method has several practical advantages: the substrate is prepared by standard synthetic methods; the dediazonation reactions are complete in less than 8 h and give expected products quantitatively; and multiple samples can be analyzed rapidly and with high reproducibility by using an HPLC with an autosampler. Estimates of X_{ma} over a range of R'OH and hexadecane concentrations show that unlike the partition constants, K_a , the mass action binding constants, K_a' , for the distribution of BuOH and HexOH between the interfacial and oil regions are independent of [R'OH]. Changes in molar concentrations of interfacial H₂O and BuOH can be used to mark the o/w droplet–bicontinuous–w/o droplet transitions. Binding constants for BuOH and HexOH distributions between the water and interfacial regions of 3-component aqueous (CTA)Br microemulsions are also independent of [R'OH] suggesting that BuOH and HexOH mix ideally with (CTA)Br in the interfacial region throughout the single phase portion of the phase diagram. In principle, the dediazonation trapping method can be used over a range of temperatures: to estimate the degree of hydration of micelles, microemulsions, and vesicles composed of virtually any surfactant, including nonionic and anionic surfactants, which generally have weakly basic head groups; to estimate binding constants and interfacial concentrations of alcohols of virtually any chain length and structure; to correlate changes in structure of microemulsion aggregates with their interfacial compositions, e.g., alcohols, water and anions; and to estimate degrees of counterion binding and ionization of cationic micelles and the selectivity of cationic surfactant toward different counteranions at virtually any ionic strength.

Acknowledgment. We are grateful to Ray Mackay and C. A. Bunton for helpful discussions and to the Center for Advanced Food Technology (CAFT Publication No. D10535-

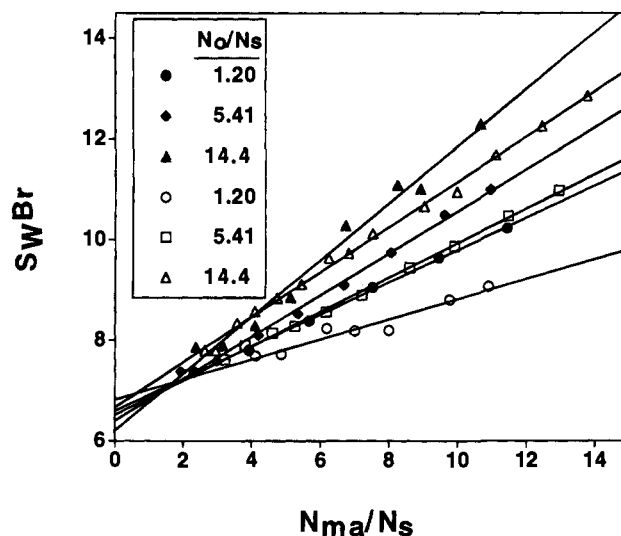


Figure 8. Values of S_w^{Br} as a function of N_a/N_s . Open points, BuOH; filled points, HexOH. Solid lines added to aid the eye.

3-94), a New Jersey Commission on Science and Technology Center at Rutgers University, which provided the primary financial support for this project. Additional support from the NSF U.S.–Latin American Cooperative Program–Brazil, the National Science Foundation (Grant CHE-9113331), and the Busch Fund of Rutgers University is appreciated.

Appendix 1

Estimates of the Selectivity of the Dediazonation Reaction toward Br⁻ versus H₂O in Four Component Water-in-Oil Microemulsions. Figure 8 shows estimates of S_w^{Br} (eq A-1) for each % 16-ArBr yield (Figure 3) plotted against N_a/N_s , the molar ratio of R'OH to (CTA)Br, for both BuOH and HexOH at the three oil/surfactant ratios used in these experiments, $N_o/N_s = 1.20, 5.14, \text{ and } 14.4$, where $N_{Br} = N_s$ and $f_m = 1$ and N_{mw}

$$S_w^{Br} = \frac{\% \text{ 16-ArBr } N_{mw}}{\% \text{ 16-ArOH } N_{Br}} = \frac{\% \text{ 16-ArBr } f_m N_w}{\% \text{ 16-ArOH } N_s} \quad (\text{A-1})$$

$= N_w$ because no free water pool exists (see Results) so that all the H₂O and Br⁻ are within the interfacial region of the aggregate. The results in Figure 8 show that S_w^{Br} increases gradually with added R'OH and depends on the N_o/N_s ratio. The range of S_w^{Br} values are within those shown by 1-ArN₂⁺ in aqueous tetramethylammonium bromide, TMABr, solutions.¹ Values of S_w^{Br} decrease with added TMABr: e.g., in 0.5 M TMABr, $S_w^{Br} = 14.5$, and $[\text{H}_2\text{O}]/[\text{Br}^-] = 102$; in 3.5 M TMABr, $S_w^{Br} = 8.5$ and $[\text{H}_2\text{O}]/[\text{Br}^-] = 9.3$. By comparison, values for the selectivity in Figure 8 range from a maximum of $S_w^{Br} = 12.8$ at $([\text{R}'\text{OH}] + [\text{H}_2\text{O}])/[\text{Br}^-] = 18.2$ to a minimum of $S_w^{Br} = 7.3$ at $([\text{R}'\text{OH}] + [\text{H}_2\text{O}])/[\text{Br}^-] = 6.8$. We attribute this change in S_w^{Br} to salt-induced changes in activity coefficient ratios of free ions and ion molecule pairs formed between the arenediazonium salt cations and Br⁻ and H₂O molecules.¹

Supplementary Material Available: Tables S1–S6 contain the experimental details on the results in Table 1 and Figure 3, respectively, including the weights of each component, HPLC peak areas, and normalized product yields for each solution in Table 1 and Figures 3A and 3B, respectively (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.