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Arenediazonium Salts: New Probes of the Interfacial Compositions of Association Colloids. 2. Binding Constants of Butanol and Hexanol in Aqueous Three-Component Cetyltrimethylammonium Bromide Microemulsions

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Abstract: Yields of aryl ether products, 16-ArOR′, were determined by HPLC with excellent reproducibility from dediazoniation of 4-hexadecyl-2,6-dimethylbenzenediazonium tetrafluoroborate (16-ArN_2BF_4) bound to surfactant aggregates in three-component microemulsions of cetyltrimethylammonium bromide ((CTA)Br), H_2O, and an alcohol (R′OH), either 1-butanol (BuOH) or 1-hexanol (HexOH). The results were used to estimate the mole fractions (X_A) of R′OH bound to the microemulsions, their mole fraction partition constants (K_A), and mass action binding constants (K_A'). Values of K_A decrease with added R′OH consistent with literature results. Unexpectedly, values of K_A' are constant at all values of X_A, indicating that (CTA)Br mixes ideally with both BuOH and HexOH in aqueous microemulsions and that binding of R′OH to (CTA)Br microemulsions is driven by a hydrophobic effect with minimal contributions from specific interactions between R′OH and (CTA)Br.

Introduction

Association colloids such as micelles, reverse micelles, and three- and four-component microemulsions are dynamic aggregates of nonionic, ionic, or zwitterionic surfactants that form transparent, thermodynamically stable solutions in water and in water–oil mixtures.[1-5] All association colloids have an interfacial region between their aqueous and oil regions which is composed of surfactant head groups, associated counterions, and any added polar additives such as alcohols. Three–component microemulsions, also called alcohol–swollen micelles, form in aqueous solutions containing surfactant and a medium-chain-length alcohol, which typically has four to seven carbons. The stability of three-component microemulsions and other association colloids is determined primarily by the balance between the hydrophobic effect, e.g., the tendency of the hydrocarbon tails of surfactants and alcohols to minimize their contact with water by aggregating, and the strong interactions of surfactant and alcohol head groups with the aqueous phase.

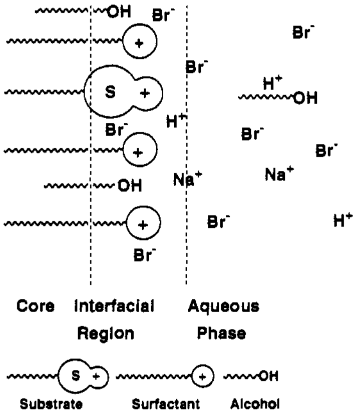

Figure 1. Interfacial region of a three-component microemulsion composed of a cationic surfactant, an alcohol, and an amphiphilic diazonium salt substrate with its reactive group located in the interfacial region and showing counterions, Br^-, and co-ions, Na^+ and H^+.

Medium-chain-length alcohols are soluble to varying extents in the aqueous, interfacial, and oil regions of microemulsions (Figure 1). Alcohol partitioning between these regions and the shape and size of the homogeneous region(s) in the phase diagram for these components depend on the chain length of the alcohols.[1,3] The critical micelle concentration, or cmc, the aggregation number, and the degree of counterion binding of microemulsions also depend upon alcohol type and concentration.[6] Thus thermodynamic models for microemulsion structure and stability require a clear understanding of the factors affecting the partitioning of alcohols among the water, interfacial, and oil regions.

Several research groups have explored alcohol partitioning, mainly in aqueous three-component microemulsions,[7] but some work has been carried out in four-component water-in-oil microemulsions[8] and in the bicontinuous region.[9] In aqueous solutions, alcohol partition constants are often determined from solubilities,[6,10-14] but this approach is limited to alcohol-saturated

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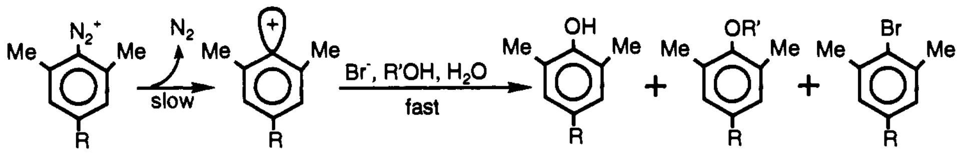
Scheme I



z-ArN_2^+ z-Ar+ z-ArOH z-ArOR' z-ArBr

BuOH, R' = C_4H_9; HexOH, R' = C_6H_{13} z = 1, R = CH_3; z = 16, R = $C_{16}H_{33}$

Table I. Normalized Product Yields (%) of 16-ArOBu from Dediazoniation of 0.1 mM 16-ArN_2^+ in 0.01 M HBr and Six [(CTA)Br_t]'s with Added BuOH at 40 ± 0.1 °C

	[(CTA)Br_t][a]					
[$BuOH_t$], M	0.01 M	0.02 M	0.03 M	0.04 M	0.05 M	0.10 M
0.101	$\langle 1.7\rangle^2$	1.7	1.6	1.6	1.5	1.5
0.219	$\langle 3.0\rangle^3$	3.0	2.9	2.7	$\langle 2.5\rangle^3$	2.4
0.328	$\langle 4.0\rangle^2$	3.7	3.7	3.6	3.5	3.1
0.437	$\langle 4.7\rangle^3$	4.5	4.3	4.2	4.1	3.8
0.546	$\langle 5.3\rangle^2$	4.9	4.9	4.7	4.6	4.3
0.656	$\langle 5.8\rangle^2$	5.6	5.6	5.4	5.3	4.7
0.765	$\langle 6.3\rangle^2$	6.1	6.0	5.7	5.6	5.2
0.874	$\langle 6.9\rangle^2$	6.6	6.4	6.2	6.1	5.5
0.984	$\langle 7.3\rangle^2$	7.0	6.8	6.7	$\langle 6.4\rangle^2$	5.8
1.093		7.6	7.3	7.0	6.6	6.1
1.202			7.9	7.5	$\langle 7.3\rangle^2$	6.4
1.311				8.1	7.8	6.7
1.421					8.3	7.2
1.53						7.5
1.639						7.8
1.749						8.1
1.858						8.3
1.967						8.8

[a] Angular brackets indicate average values of % 16-ArOBu from duplicate ($\langle\ \rangle^2$) or triplicate ($\langle\ \rangle^3$) experiments.

Table II. Normalized Product Yields (%) of 16-ArOHex from Dediazoniation of 0.1 mM 16-ArN_2^+ in 0.01 M HBr and Six [(CTA)Br_t]'s with Added HexOH at 40 ± 0.1 °C

	[(CTA)Br_t][a]					
[$HexOH_t$], M	0.01 M	0.02 M	0.03 M	0.04 M	0.05 M	0.10 M
0.016	2				1.6	
0.019			1.8			
0.02	2.3[b]	2.1	2.0	1.7	1.6	
0.021	2.4					
0.024					1.7	
0.029	2.9[b]					
0.03	3	2.5	$\langle 2.3\rangle^2$	2.2	2.1	
0.032						1.7
0.036					2.2	
0.04	3.4[b]	3.0	2.6	2.5	2.3	1.8
0.041	3.4					
0.048					2.5	
0.049	3.6[b]		$\langle 3.1\rangle^2$	2.8		
0.054	3.9					
0.056					2.8	
0.06	4.1[b]	3.7	$\langle 3.4\rangle^2$	3.2		
0.064						2.4
0.067	4.6					
0.068					3	
0.069					3.2	
0.08	5.3	4.3	$\langle 3.9\rangle^2$			2.6
0.088					3.4	
0.1			4.2			
0.103						3.2
0.112					4	
0.127						3.4
0.151						3.6

[a] Angular brackets indicate average values of % 16-ArOHex from duplicate ($\langle\ \rangle^2$) experiments. [b] [(CTA)Br_t] = 0.012 M.

solutions and provides no information on the effect of alcohol concentration on its partitioning. A few studies with variable alcohol concentration have been carried out by methods that give estimates of the mole fraction of the alcohol bound to the aggregate or solubilized in the aqueous phase, such as ultrafiltration,[7] vapor pressure determinations,[15,16] and monitoring alcohol-induced changes in the fluorescence intensity of an aggregate-bound probe.[8,7-19]

Alcohol partition constants, expressed as the ratio of alcohol mole fractions in the aggregate and the aqueous phase, generally decrease with added alcohol and are apparently insensitive to surfactant chain length and head-group charge,[20] suggesting ideal mixing. However, solubilization of hexanol in mixed surfactant aggregates of ionic and nonionic surfactants is not ideal; i.e., its solubility is not directly proportional to the mole fraction of either surfactant. This nonideality suggests that alcohol partitioning between mixed micelles and the aqueous phase depends upon specific interactions between surfactant head groups and the alcohol as well as the hydrophobic effect.[21] Zana and co-workers have suggested that aggregate-bound alcohols having more than three carbons may be located in the microemulsion core as well as in the interfacial region.[6]

We have developed a new method for estimating the relative quantities of weakly basic nucleophiles in interfacial regions of association colloids from competitive product yields of micellar-bound arenediazonium salts (see refs 22–24 and preceding paper in this issue). In aqueous three-component cetyltrimethylammonium bromide (CTA)Br) microemulsions containing 1-butanol (BuOH) or 1-hexanol (HexOH), the conversion to expected products from dediazoniation of aggregate-bound 16-ArN_2^+ (Scheme I and Figure 1) is quantitative (≥95% based on the initial 16-ArN_2^+ concentration) as determined by HPLC. We used normalized product yields obtained over a range of BuOH and HexOH concentrations to estimate interfacial concentrations of H_2O, Br^-, and alcohol (R'OH) by assuming that the selectivities of the dediazoniation reaction toward these nucleophiles by 16-ArN_2^+ in aggregates and by 1-ArN_2^+ in aqueous solutions are the same (see preceding paper). Here we show that mole percent yields of 16-ArOR' from dediazoniation of 16-ArN_2^+ in these three-component microemulsions can be used to estimate the bound fraction (X_A) of R'OH, its mole fraction partition constant (K_A), and its mass action binding constant for the overall reaction between R'OH and the aggregates (K_A') by assuming that the yield of 16-ArOR' is directly proportional to X_A.

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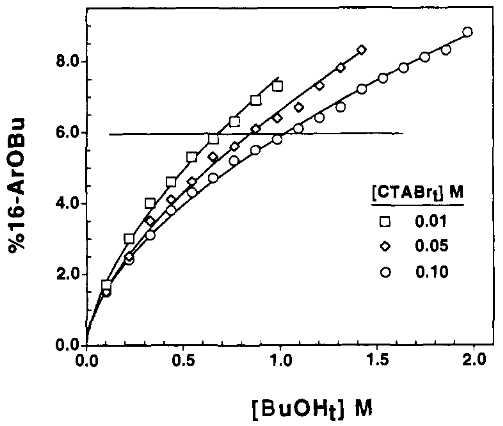

Figure 2. Percent yields of the ether product, 16-ArOBu, from the reaction of 16-ArN_2^+ with BuOH in (CTA)Br microemulsions at three [(CTA)-Br_t]'s (see Table I). Fitted curves were obtained with "best fit" parameters *A* and *B* (see Table III). Intersection points of fitted curves and the horizonal lines define [$R'OH_t$], [(CTA)Br_t] data sets at constant %16-ArOBu and X_A.

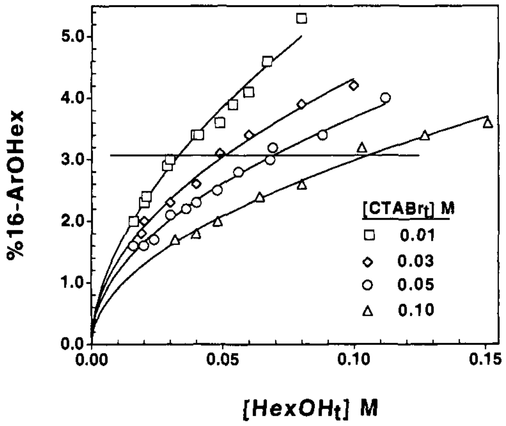

Figure 3. Percent yields of the ether product, 16-ArOHex, from the reaction of 16-ArN_2^+ with HexOH in (CTA)Br microemulsions at four [(CTA)Br_t]'s (see Table II). Fitted curves were obtained with "best fit" parameters *A* and *B* (see Table III). Intersection points of fitted curves and the horizontal lines define [$R'OH_t$], [(CTA)Br_t] data sets at constant %16-ArOHex and X_A.

Results

Tables I and II list normalized mole percent yields of 16-ArOBu and 16-ArOHex as a function of added BuOH and HexOH, respectively, at six (CTA)Br concentrations. Figures 2 and 3 show respectively the results for BuOH and HexOH at selected (CTA)Br concentrations. The concentration of 16-ArN_2^+, ca. 0.1 mM, is sufficiently low to prevent significant perturbation of aggregate structure; ((CTA)Br + R'OH)/16-ArN_2^+ ratios were ≥100/1. The highest concentrations of R'OH used are just below their solubility limits in (CTA)Br solutions at 25 °C. Consistent with literature results,[13,14] the highest yields of 16-ArOBu increase steadily with increasing [(CTA)Br_t] (Table I, Figure 2), but the highest yields of 16-ArOHex decrease with increasing [(CTA)Br_t] from a maximum value in 0.01 M (CTA)-Br (Table II, Figure 3). In addition, the decrease in yield of 16-ArOR' with added (CTA)Br parallels the alcohol-induced decrease in fluorescence intensity of pyrene in three-component sodium dodecyl sulfate (SDS) microemulsions.[18]

Definitions of Partition and Binding Constants. The totality of the aggregates in microemulsions and other association colloids are generally treated as a separate phase of pseudophase,[25] and the distribution of an R'OH between the phases is usually reported as a mole fraction partition constant (K_A):[10,18,20]

$$K_A = X_A/Y_A \qquad (1)$$

where X_A and Y_A are the mole fractions of R'OH in the microemulsion and aqueous phases, respectively. We assume that activity coefficients of alcohols in both the aggregates and water are approximately 1.[26] X_A is defined as

$$X_A = \frac{[R'OH_m]}{[R'OH_m] + [(CTA)Br_m]} \qquad (2)$$

where subscript m indicates the microemulsion phase and square brackets, [], here and throughout the text indicate molarity in moles per liter of total solution volume. Following convention,[26] we define the mole fraction of bound alcohol in terms of the "dry" microemulsion as shown by the ratio on the right-hand side of eq 2. The mole fraction of R'OH in the aqueous phase is given by

$$Y_A = \frac{[R'OH_w]}{[R'OH_w] + \mathrm{cmc} + [H_2O_w]} \approx \frac{[R'OH_w]}{[H_2O_w]} \approx \frac{[R'OH_w]}{55.5} \qquad (3)$$

where subscript w indicates the aqueous phase. The approximation in eq 3 is reasonable. Medium-chain-length alcohols lower the cmc of ionic surfactants,[6,27] and in the absence of R'OH, the cmc of (CTA)Br is ca. 0.9 mM, which is less than 10% of the lowest [(CTA)Br] used. The volume occupied by the microemulsion aggregates is never more than 7% of the total solution volume, and we can neglect the excluded volume of the aggregates so that [H_2O_w] ≈ 55.5. Microemulsions and monomeric (CTA)-Br are assumed to have minimal effects on R'OH solubility in water, and [ROH_w] cannot exceed the solubility limits of BuOH and HexOH in water at 25 °C, 1.0 and 0.06 M, respectively.[28]

The distribution of R'OH or any neutral additive can also be described by a mass action model (Scheme II and eq 4). Concentrations are generally expressed in molarity but can be converted into mole fraction units by using eqs 2 and 3, as shown on the far right-hand side of eq 4.[29]

Scheme II

$$R'OH_w + (CTA)Br_m \overset{K_A'}{\rightleftharpoons} R'OH_m$$

$$K_A' = \frac{[R'OH_m]}{[R'OH_w][(CTA)Br_m]} = \frac{X_A}{(1 - X_A)(55.5Y_A)} \qquad (4)$$

Treatment of Data. Equation 6 relates the stoichiometric concentrations of alcohol ([$R'OH_t$]) and surfactant ([(CTA)Br_t]), and it was obtained by substitution of eqs 2 and 3 into the mass balance equation

$$[R'OH_t] = [R'OH_m] + [R'OH_w] \qquad (5)$$

$$[R'OH_t] = \frac{X_A[(CTA)Br_t]}{1 - X_A} + 55.5Y_A \qquad (6)$$

where cmc ≈ 0 and [(CTA)Br_t] = [CTA)Br_m]. Equation 6 expresses the fundamental assumption of our approach: any set of [$R'OH_t$], [(CTA)Br_t] values which have the same local

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(29) The relationship between K_A and K_A' is given by $K_A' = K_A/(55.5-(1 - X_A))$.

Table III. Values of "Best Fit" (A, B) and "Iterative Fit" (A') and Average B Parameters for Eq 7

	BuOH				HexOH			
[(CTA)Br$_t$], M	A	B	corr coeff	A'[a]	A	B	corr coeff	A'[a]
0.01	7.60	0.630	0.997	7.51	20.6	0.560	0.994	18.6
0.02	7.21	0.611	0.998	7.20	15.7	0.511	0.994	16.4
0.03	7.08	0.620	0.997	7.03	13.8	0.505	0.994	14.6
0.04	6.81	0.614	0.999	6.79	15.4	0.561	0.998	13.8
0.05	6.62	0.628	0.998	6.59	11.6	0.498	0.992	12.6
0.10	5.89	0.580	0.999	5.82	9.89	0.520	0.995	10.0
		0.614 ± 0.012 (±1.95%)[b]				0.526 ± 0.023 (±4.4%)[b]		

[a] All correlation coefficients are 1.000 for A' in data sets using average values of B. [b] Average of above values in the column; includes the average and percent average deviations.

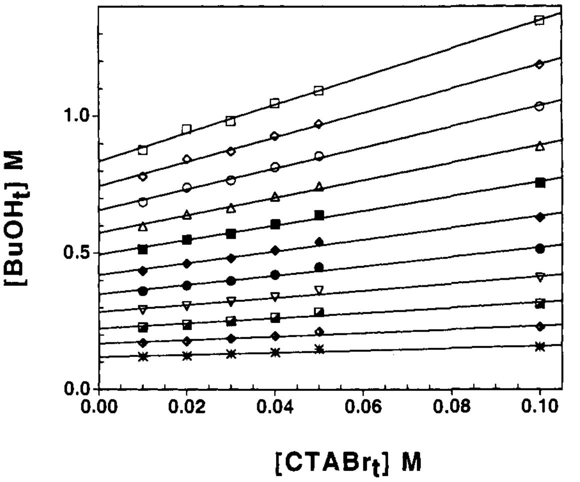

Figure 4. Plots of [BuOH$_t$], [(CTA)Br$_t$] data sets at six [(CTA)Br$_t$]'s (0.01, 0.02, 0.03, 0.04, 0.05 and 0.10 M) and at eleven %16-ArOBu values ((□) 7.0%, (◇) 6.5%, (○) 6.0%, (△) 5.5%, (■) 5.0%, (◆) 4.5%, (●) 4.0%, (▽) 3.5%, (▣) 3.0%, (◇) 2.5%, (*) 2.0%). Solid lines are least-squares fits.

concentration or mole fraction of micellar-bound R'OH, i.e., the same X_A, will give the same %16-ArOR. Thus, a horizontal line drawn through the data at constant %16-ArOR', as shown in Figures 2 and 3, intersects each [(CTA)Br$_t$] curve at constant X_A.

Conceptually, values of X_A and K_A or K_A' for a particular alcohol are estimated in a two-step process.[30] Sets of horizontal lines are drawn through the %16-ArOR', [R'OH] data obtained for a series of [(CTA)Br$_t$]. Each set of [R'OH$_t$], [(CTA)Br$_t$] values obtained at constant %16-ArOR' is plotted according to eq 6, and values for X_A and K_A and K_A' are estimated from the slopes and intercepts of the resulting sets of straight lines by using eqs 1 and 4.

In practice, the curves in Figures 2 and 3 were first stimulated by using the exponential equation

$$\%16\text{-ArOR}' = A[\text{R}'\text{OH}_t]^B \tag{7}$$

Polynomials of several different orders were also tried, but eq 7 gave the best fit. The first set or "best fit" values of A and B and the correlation coefficients for BuOH and HexOH obtained by using eq 7 are listed in Table III. The values of A and B were used to generate the solid curves drawn through the data in Figures 2 and 3. A number of %16-ArOR' values were selected within the data point range and used in eq 7 to compute sets of [R'OH$_t$], [(CTA)Br$_t$] values at the intersection points with each (CTA)Br curve. Figures 4 and 5 are plots of [R'OH$_t$], [(CTA)Br$_t$] data sets obtained by using the "best fit" parameters for BuOH and HexOH, respectively. Values of X_A and Y_A at each %16-ArOR' were calculated from the slope and intercept of each line and used to compute values of K_A (eq 1). Values of K_A' were estimated directly from the slope:intercept ratios for each line (eq 6).

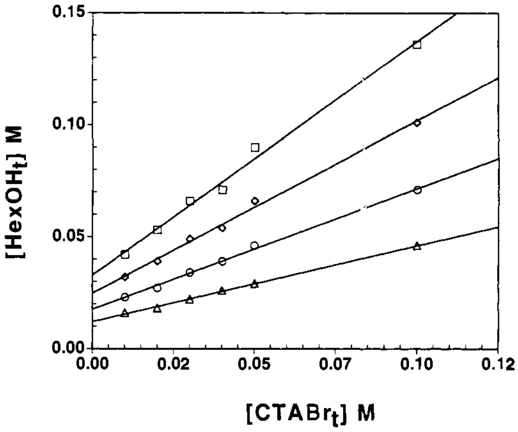

Figure 5. Plots of [HexOH$_t$], [(CTA)Br$_t$] data sets at six [(CTA)Br$_t$]'s (0.01, 0.02, 0.03, 0.04, 0.05, and 0.10 M) and at four %16-ArOHex values (□) 3.5%, (◇) 3.0%, (○) 2.5%, (△) 2.0%). Solid lines are least-squares fits.

Although the variation in the values of exponent B is small for both BuOH and HexOH (Table III), the correlation coefficients improved significantly when average values of B for BuOH and HexOH were used to generate a new set of coefficients A' from eq 7 (Table III). Correlation coefficients for the "iterative fit" of the data in Figures 2 and 3 using A', average B data sets are all 1.000. New [R'OH$_t$], [(CTA)Br$_t$] data sets were generated and plotted according to eq 6, and the slopes and intercepts were used to calculate a new set of X_A, K_A and K_A' values.

Table IV lists the slopes, intercepts, and correlation coefficients for the least-squares fits for both the "best fit" and "iterative fit" data sets. Note that the slope:intercept ratios for the "iterative fit" data sets in Table IV are essentially constant for both BuOH and HexOH. However, these ratios are not constant for the "best fit" data (not shown), and they change significantly at low %16-ArOR'. Figure 6 (data in Table V) shows the values of X_A, K_A and K_A' obtained by both methods.

Discussion

The primary assumption used in estimating alcohol partition constants (K_A) or binding constants (K_A') from dediazoniation product yields is that, at any [R'OH] and [(CTA)Br], when the 16-ArOR' yields from reaction of aggregate-bound 16-ArN$_2^+$ are equal, the mole fractions of bound R'OH (X_A's) are equal. This assumption is independent of medium effects on the selectivity of the reaction toward any nucleophiles present, in this system H_2O, R'OH, and Br$^-$, because the medium properties of the microemulsion interface are determined by X_A.

Values of K_A decrease with added BuOH and HexOH (Table V and Figure 6), consistent with the trend predicted by Rao and Ruckenstein for both cationic and anionic surfactants[20] and that

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[30] Our approach is based on one developed by Abuin and Lissi for estimating K_A for alcohols binding to SDS microemulsions by fluorescence quenching.[18]

Table IV. Slopes, Intercepts, and Correlation Coefficients from Linear Least-Squares Fits of [R'OH$_t$] Versus [(CTA)Br$_t$] Plots for BuOH and HexOH Using "Best Fit" and "Iterative" Simulations

	best fit			iterative			
% 16-ArOR'	slope	intercept	corr coeff	slope	intercept	slope/intercept	corr coeff
			R' = Bu				
7.0	5.132	0.863	0.999	5.061	0.847	5.98	1.000
6.5	4.441	0.745	0.999	4.483	0.750	5.98	0.999
6.0	3.797	0.657	0.998	3.935	0.659	5.97	1.000
5.5	3.201	0.574	0.998	3.417	0.572	5.97	0.999
5.0	2.652	0.495	0.996	2.924	0.490	5.97	1.000
4.5	2.152	0.349	0.994	2.467	0.412	5.99	1.000
4.0	1.702	0.284	0.991	2.036	0.340	5.99	0.999
3.5	1.302	0.284	0.985	1.641	0.274	5.99	0.999
3.0	0.953	0.223	0.976	1.279	0.213	6.01	0.999
2.5	0.656	0.168	0.960	0.947	0.158	5.99	1.000
2.0	0.413	0.292	0.931	0.662	0.110	6.02	1.000
			R' = Hex				
3.5	1.046	0.033	0.996	1.042	0.033	31.6	0.999
3.0	0.771	0.025	0.998	0.771	0.025	30.8	0.999
2.5	0.541	0.017	0.999	0.552	0.017	32.5	0.999
2.0	0.340	0.012	0.999	0.364	0.011	33.1	0.998

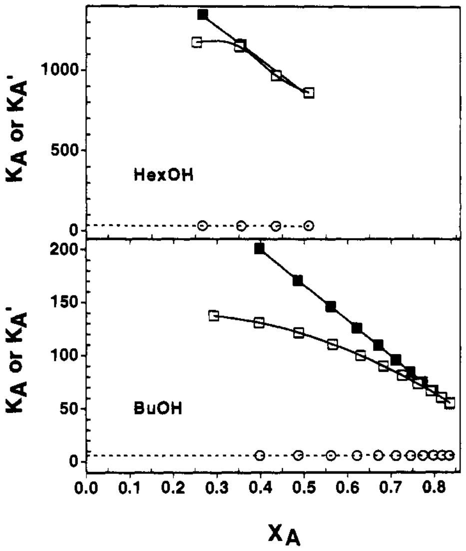

Figure 6. Plots of K_A versus X_A from "best fit" (□) and "iterative" (■) simulations calculated by using eqs 1 and 6 with data from Table IV and plots of K_A' (○) versus X_A calculated by using eq 4 with slope/intercept ratios in Table IV. Individual values are listed in Table V.

Table V. Values of X_A and K_A Obtained from "Best Fit" and "Iterative" Simulations and Values of $K_{A'}$ Obtained from Slope/Intercept Ratios of Plots of [BuOH$_t$] and [HexOH$_t$] versus [(CTA)Br$_t$]

	best fit		iterative		
% 16-ArOR'	X_A	K_A	X_A	K_A	slope/intercept $K_{A'}$, M^{-1}
			R' = Bu		
7.0	0.837	55.6	0.835	54.8	5.98
6.5	0.816	60.9	0.818	60.6	5.98
6.0	0.792	66.9	0.797	67.2	5.97
5.5	0.762	73.7	0.774	75.1	5.97
5.0	0.726	81.5	0.745	84.5	5.97
4.5	0.683	90.3	0.712	96.0	5.99
4.0	0.630	100.3	0.671	109.6	5.99
3.5	0.566	110.6	0.621	126.0	5.99
3.0	0.488	121.6	0.561	146.4	6.01
2.5	0.396	131.0	0.486	171.0	5.99
2.0	0.292	137.6	0.398	201.2	6.02
					5.99 ± 0.01 (±0.2%)[a]
			R' = Hex		
3.5	0.511	861	0.510	859	31.6
3.0	0.435	967	0.435	967	30.8
2.5	0.351	1147	0.356	1162	32.5
2.0	0.254	1175	0.267	1348	33.1
					32.0 ± 0.8 (±2.5%)[a]

[a] Average of above values in the column; includes the average and percent average deviations.

observed by Abuin and Lissi for three-component SDS microemulsions.[18] Our values of K_A at 40 °C at the highest [R'OH] used and near the solubility limit at 25 °C (Table V; 7% 16-ArOBu, 3.5% 16-ArOHex) agree with values obtained by the solubility method in (CTA)Br for HexOH [K_A = 825 (35 °C),[13] 566 (25 °C)[28]] and BuOH [K_A = 55.5 (25 °C)[28]] when expressed in the same units. Our values for K_A are also of the same order of magnitude as those obtained by ultrafiltration in 0.09 M (CTA)Br, 0.16 M NaBr at 25 °C.[7]

What is most striking about our results is that the percent yield–[BuOH$_t$] data (Figures 2 and 3) fit a simple exponential equation (eq 7) and that the mass action binding constants, K_A' (eq 4), obtained for BuOH and HexOH appear to be true constants (Table V and Figure 6). These observations suggest that R'OH and (CTA)Br mix ideally, that binding of R'OH to (CTA)Br aggregates is primarily hydrophobically driven, that specific interactions between R'OH and (CTA)Br, e.g., hydrogen-bonding or charge–dipole interactions, are not significant, and that R'OH activity coefficients are essentially constant or the same in both microemulsions and water. Constant values of K_A' also suggest that R'OH is bound only in the interfacial region (Figure 1) or that partitioning of R'OH between the microemulsion interface and core does not depend on [R'OH]. From values of K_A', we estimated the free energy of transfer per methylene group, ΔG_{tr} = −525 cal mol^{-1}, using standard definitions.[31] This value is similar to those for *p*-*n*-alkylphenols and *p*-*n*-alkylphenoxide ions binding to (CTA)Br micelles in the absence of salt (ΔG_{tr} = −310 cal mol^{-1})[31] and for homologous alcohols binding to SDS microemulsions in the absence of salt (ΔG_{tr} = −600 cal mol^{-1}) but lower than the typical ΔG_{tr} = −700–800 cal mol^{-1} for micellization of zwitterionic, nonionic, and ionic surfactants in solutions containing added salts.[5]

Our dediazoniation method has several practical advantages. The substrate is prepared via standard synthetic methods (see preceding paper), the dediazoniation reactions are complete in less than 1 day, and the 16-ArOR' yields can be determined overnight with excellent reproducibility by using an HPLC with an autosampler. The method can be extended to lower [R'OH] than those shown in Figures 2 and 3 by increasing [16-ArN$_2^+$] by factors of 2 or more.

Conclusions

We have developed a new, precise method for estimating the mole fraction, X_A, of an alcohol bound to three-component cationic microemulsions, and we have shown that the mass action constants, K_A', for BuOH and HexOH in (CTA)Br microemulsions are independent of X_A. Values of X_A can be determined for alcohols of virtually any chain length over wide ranges of [surfactant] and [R'OH], including four-component water-in-oil microemulsions.[32] In principle, our diazonium salt probe can be used to estimate interfacial concentrations and binding constants of any weakly basic nucleophile, such as association colloids composed of nonionic surfactants with terminal –OH head groups, anionic surfactants with weakly basic head groups such as alkyl sulfates and sulfonates, and their mixtures with alcohols and inorganic salts of strong acids.

Experimental Section

Product yields were determined by HPLC by direct injection of the microemulsion solutions without workup after the dediazoniation reaction was complete (≥10 half-lives or 6 h). Reproducibility was generally

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(31) Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* **1979**, *83*, 680.
(32) Yao, J. Unpublished results.

within 0.1–0.2%, including separate preparations by A.C. and J.Y. Peak areas in microvolts (μV), measured and total yields obtained from calibration curves, and normalized yields are available as supplementary material, Tables S1–S12. Details on the preparation of substrates and products and determination of product yields by HPLC are in the preceding paper. Parameters listed in Table III were obtained by linear least-squares fits of the logarithmic form of eq 7 by using the 1987 graphics program PlotIT by Scott P. Eisensmith on an ULTRA-PC 386-33 computer. Data simulations were obtained by using CA-Cricket Graph III on a Macintosh IIci computer.

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Supplementary Material Available: Tables S1–S12, containing the peak areas from the HPLC chromatograms and measured, total, and normalized percent yields for the results listed in Tables I and II (12 pages). Ordering information is given on any current masthead page.