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Effects of Monovalent and Divalent Anionic Dodecyl Sulfate Surfactants on the Dediazoniation of 2-, 3-, and 4-Methylbenzenediazonium Tetrafluoroborate[†]

Carlos Bravo-Diaz,[*,‡] Mercedes Soengas-Fernandez,[‡]
M. Jose Rodriguez-Sarabia,[‡] and Elisa Gonzalez-Romero[§]

Departamento Quimica Fisica y Quimica Organica and Departamento Quimica Analitica y Alimentaria, Facultad de Ciencias, Universidad de Vigo, 36200 Vigo-Pontevedra, Spain

We have examined the kinetics and mechanism of dediazoniation of 2-, 3- and 4-methylbenzenediazonium tetrafluoroborate (OMBD, MMBD, and PMBD) in aqueous micellar solutions of sodium dodecyl sulfate and copper dodecyl sulfate at two different NaCl concentrations by combining spectrophotometric and high-performance liquid chromatography (HPLC) measurements. The method allows simultaneous determination of product yields and rates of formation for all dediazoniation products and, indirectly, the rate of decomposition of the diazonium salt. The preferential location of OMBD, MMBD, and PMBD is in the Stern layer, a very anisotropic region. A substantial fraction of diazonium ions are bonded to the micellar aggregates, and formation of strong ion pairs between OMBD, MMBD, and PMBD diazonium salts with the sulfate headgroup of the surfactants is not significant. HPLC analysis of dediazoniation products indicates that, within experimental error, quantitative conversion to products is achieved, with cresol as the major product. Observed rate constants for the dediazoniation reaction in the presence of both monovalent and divalent surfactants are constant for OMBD but decrease slightly for MMBD and PMBD with increasing surfactant concentration. The data are interpreted in terms of the polarity of the environment of diazonium salts in the micellar aggregate. All evidence is consistent with an $D_n + A_n$ mechanism, i.e., rate-determining formation of an aryl cation that reacts immediately with any available nucleophile.

Introduction

Considerable attention has been paid for more than 1 century to diazonium salts.[1–3] Their reactions have been widely used in the dyestuff industry,[4] as synthetic precursors,[2] and as intermediates in many synthetic routes.[5] They have been studied in a wide variety of solvents,[1–3] water, methanol, tetrahydrofuran, dimethylformamide, trifluoroethanol, dimethyl sulfoxide, hexafluoro-2-propanol, etc., but the bulk of the available kinetic data refers to the arenediazonium ions, probably reflecting their stability and the way they can be handled in relation to their aliphatic analogues.[6] Arenediazoniation chemistry has been subject to great controversy[1] because their rich chemistry varies dramatically with experimental conditions,[1,2,7,8] changing not only the mechanism of the reactions but also the relative amount of dediazoniation products, and because the many reaction pathways are still not completely understood.[1,3] The field is still very active. They are currently being used as aryl radical sources for synthetic precursors,[1,7,9] and their role in DNA arylations[10,11] and DNA deaminations[12] is being explored.

Scant attention has been given to their reactions in micellar systems.[1] Micelles are dynamic aggregates of amphiphilic molecules[13,14] that are composed of nonpolar hydrocarbon tails attached to polar, nonionic, zwitterionic, or ionic headgroups.[14] Surfactant solutions may spontaneously form aggregates creating a highly anisotropic interfacial region that lines the boundary formed by the highly polar aqueous and nonpolar oil regions, imparting new chemical and physical properties to the system.[13,14] Micelles, as well as other association colloids, can act as microreactors concentrating, separating, or diluting reactants, and thereby they may have dramatic effects on chemical reactivity.[14]

The first kinetic studies involving diazonium salts and micellar systems are those by Poindexter and Mackay[15]

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Scheme 1. (a) Heterolytic Mechanism for Dediazoniations and (b) Heterolytic Dediazoniation Mechanism in the Presence of SDS and Cu(SD)₂ Micellar Aggregates

a

$$Ar\!\leftarrow\!N_2^+ \rightleftharpoons Ar^+ + N2 \xrightarrow{Nu^{n-}} Ar\text{-}Nu^{(n-1)-}$$

b
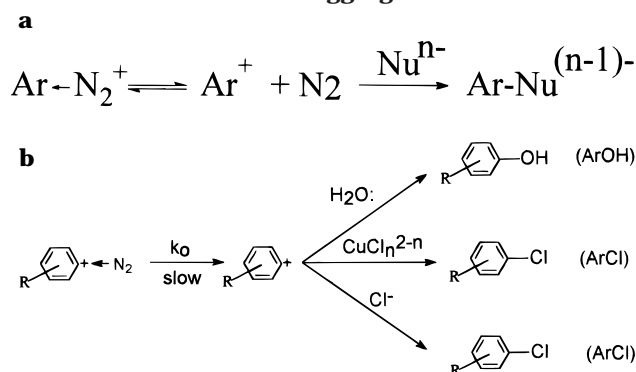
who showed that rate constants for the coupling of *p*-nitrobenzenediazonium with 2-naphthol-6-sulfonic acid (2N6S) are depressed by the presence of anionic, cationic, or nonionic surfactants. Later, Moss[16] explained this observation by simple electrostatic arguments: Cationic micelles solubilize the anionic coupling agent but exclude the cationic arenediazonium salt, while anionic micelles solubilize the arenediazonium salt but exclude the coupling agent. However, if the coupling component is not ionic, more dramatic effects occur.[17,18] Tentorio[18] used 1-naphthylamine as the coupling agent in the presence of SDS micelles, finding that the rate of its coupling reaction with cationic arenediazonium ions increased up to 1100 times when the surfactant concentration was higher than its critical micelle concentration (cmc).

Romsted et al.[19,20] are currently using arenediazonium salts to probe interfacial compositions, the degree of ionization, and counterion selectivity of cationic micelles and microemulsions. Their work is based on that, to date, all kinetic data available about decomposition of arenediazonium salts in aqueous acid, in the dark, suggest that the reaction goes through an heterolytic mechanism (Scheme 1): Arenediazonium salts decompose by rate-determining formation of a very reactive aryl cation that reacts competitively with any nucleophile available to form stable products that can be determined quantitatively (the arrow bonding Ar to N₂ in Scheme 1A indicates a dative bonding model that represents the actual electron density distribution[21] more closely).

Here we study the effect of two anionic micelles, the monovalent sodium dodecyl sulfate (SDS) and the divalent copper dodecyl sulfate (Cu(SD)₂), on the kinetics and product yields of the dediazoniation of three methyl-substituted diazonium salts, 2-, 3-, and 4-methylbenzenediazonium tetrafluorborate (OMBD, MMBD, and PMBD), by quenching the reaction at selected times with a suitable coupling agent like 1-naphthylamine (1NA). Recently we have reported a new method for monitoring dediazoniations in aqueous systems by combining coupling reactions with high-performance liquid chromatography (HPLC) analysis.[22] This coupling step must be faster than dediazoniation (see below), so that it provides reliable estimates of the quantity of unreacted arenediazonium ion and the formation of a stable azo dye prevents unwanted side reactions of unreacted arenediazonium ion.

Experimental Section

Instrumentation. UV−vis spectra and some kinetic experiments were followed on a Beckman DU-640 UV−vis spectrophotometer equipped with a thermostated cell carrier attached to a computer for data storage. Product analysis was carried out on a Waters HPLC system which included a model 560 pump, a model 717 automatic injector, a model 486 vis−UV detector, and a computer for data storage. Products were separated on a Microsorb-MV C-18 (Rainin) reverse phase column (25 cm length, 4.6 mm internal diameter, and 5 μm particle size) using a mobile phase of 65/35 v/v MeOH/H₂O containing 10^{-4} M HCl. The injection volume was 25 μL in all runs, and the UV detector was set at 210 nm (PMBD) and 220 nm (OMBD and MMBD). pH and conductivity were measured using a previously calibrated Metrohm model 713 pH-meter and a Metrohm model 712 conductometer both equipped with temperature sensors. ¹H NMR spectra were obtained on a Brucker ARX 400 spectrometer.

Materials. Reagents were of maximum purity available and were used without further purification. Cresols, ArOH, chlorotoluenes, ArCl, copper(II) chloride (99.999%), the surfactant SDS (99.9%), and the reagents used in the preparation of diazonium salts (as tetrafluoroborates) were purchased from Aldrich. 2-Naphthol-6-sulfonic acid, sodium salt (2N6S), was purchased from Pfaltz & Bauer. CuSO₄·5H₂O was supplied by Fluka and 1-naphthylamine (1NA) by Merck. Other materials employed were from Riedel de Haen. All solutions were prepared by using Milli-Q grade water.

Diazonium salts were prepared under nonaqueous conditions[23] and were stored in the dark at low temperature to minimize their decomposition. The copper dodecyl sulfate surfactant, Cu(SD)₂·4H₂O, was prepared by ion exchange using an acidic Dowex 50WX8 resin activated with concentrated CuSO₄ solutions. Once activated, a warm ($T = 30-35$ °C, ca. 0.5 M) solution of SDS was added slowly and the eluted solution collected in a flask (the eluted solution showed a blue color, indicative of the presence of Cu²⁺ ions). This blue solution was selectively precipitated by cooling it down to ca. $T = 21$ °C, and a blue crystalline precipitate was obtained (Krafft point for Cu(SD)₂ was reported as $T = 23$ °C[24] or $T = 24$ °C[25] and that for SDS below $T = 10$ °C[26] or $T = 16$ °C[27] or T). The precipitate was filtered under vacuum and washed several times with cool water. cmc for Cu(SD)₂·4H₂O was determined at room temperature by a conductometric method yielding cmc $= 1.03 \times 10^{-3}$ M, in agreement with literature values of cmc $= 1.17 \times 10^{-3}$ M[25] and cmc $= 1.0 \times 10^{-3}$ M.[28]

Methods. Kinetic data were obtained both spectrophotometrically and chromatographically. Observed rate constants were obtained by fitting the absorbance−time or percent yield−time data to the integrated first order eq 1 using a nonlinear least-squares method provided by a commercial computer program, where M is the measured magnitude of the UV−vis absorbance or percent yields (The word "yield" will be used to represent percent yield here and throughout the text, except in figures and equations where we will employ the symbol "Y").

$$\ln(M_t - M_\infty) = \ln(M_0 - M_\infty) - k_0 t \tag{1}$$

All runs were done at $T = 60 \pm 0.1$ °C (PMBD) and at 35 °C (MMBD and OMBD) with diazonium salts as the limiting reagents.

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Table 1. Values of Parameters a and b (eq 2) and Their Typical Retention Times for the Dediazoniation Products of OMBD, MMBD, and PMBD

analyte	t_r/min	$10^{-4}a$	$10^{-9}b$
OMB−OH	6.1	4.19	8.11
OMB−Cl	27.5	4.88	8.07
MMB−OH	5.9	−1.58	8.62
MMB−Cl	28.0	−6.09	8.90
PMB−OH	6.2	−0.83	11.10
PMB−Cl	27.7	2.70	20.00

Spectrophotometric kinetic data were obtained by following the disappearance of diazonium salt at an appropriate wavelength to minimize interference mainly by chlorocuprate(II) complexes. Beer's law plots for aqueous PMBD, MMBD, and OMBD solutions up to 2.00×10^{-4} M are linear (correlation coefficient = 0.999) yielding $\epsilon_{310} = (15.0 \pm 0.3) \times 10^2$ M^{-1} cm^{-1} (MMBD) and $\epsilon_{320} = (19.1 \pm 0.5) \times 10^2$ M^{-1} cm^{-1} (OMBD). Values for PMBD are published.[22] Stock solutions were prepared dissolving the diazonium salt in aqueous HCl, to minimize diazotate formation,[29] to give final concentrations of about 1×10^{-4} M and [HCl] = 3.6 $\times 10^{-3}$ M. Stock solutions were generally used immediately or within 90 min with storage in an ice bath to minimize decomposition.

Preliminary HPLC experiments showed that only two decomposition products are formed: ArOH and ArCl. Calibration curves for converting HPLC peak areas into concentrations were obtained simultaneously for these dediazoniation products, ArOH and ArCl, by employing commercial samples dissolved in solutions of similar composition to those used in the HPLC analysis of dediazoniation products (see below). Table 1 lists the slopes and intercepts obtained by linear least-squares fits to eq 2 for each product and their typical retention times under our chromatographic conditions

$$\text{Area} = a + b[\text{analyte}] \qquad (2)$$

Percent yields of the dediazoniation products were obtained from the ratio of the dediazoniation product concentration, [analyte], and the initial diazonium salt concentration (estimated by weight), eq 3. To calculate yields we did not consider intercept values.

$$Y = 100[\text{analyte}]/[\text{PMBD}] \qquad (3)$$

Chromatographic kinetic data for all dediazoniation products were obtained following a published procedure by[22] quenching the dediazoniation reaction at convenient times with an aliquot of a stock quenching solution prepared by dissolving 1-naphthylamine (1NA) in a 0.02 M aqueous SDS solution containing TRIS buffer ([TRIS] = 0.05 M) to give, after mixing, final 1NA concentrations about 20-fold excess over that of arenediazonium salts and final pH about pH = 7. This pH was chosen to maximize the rate of azo dye formation[1,29,30] because coupling rates change dramatically with pH because free amines are much more reactive than their protonated forms,[8,31] but as pH increases, the competing reaction of arenediazonium ions with OH$^-$ to form diazotates becomes significant.[29] The use of a coupling reaction to stop the dediazoniation reaction requires that its rate is faster than the dediazoniation rate. 1NA was chosen as coupling agent because an extra coupling rate enhancement (micellar catalytic effect) can be obtained since 1NA is sparingly soluble in water but SDS micelles can solubilize it.[18] Auxiliary experiments done by following azo dye formation spectrophotometrically show that under our experimental conditions the coupling reaction is essentially over in the time of mixing reagents; i.e., the rate of azo dye formation is, at least, 100 times faster than that of dediazoniation.

This procedure also allows us to estimate k_0 for the decomposition of arenediazonium salts. Sufficient concentrated HCl

Table 2. Changes (in ppm) in the ^{1}H Chemical Shifts of SDS ($\sim$0.1 M) upon Addition of OMBD, MMBD, and PMBD to a Concentration of ca. 0.001 M

	OMBD	MMBD	PMBD
C_α	0.1025	0.0974	0.1041
C_β	0.0799	0.0833	0.0933
C_γ	0.0007	0.0007	0.0008

was added dropwise to each volumetric flask to give final [H$^+$] $\approx$ 0.2 M, and the absorbance of each solution was measured at λ_{max} of the corresponding azo dyes: λ_{max} = 529 nm (OMBD), λ_{max} = 484 (MMBD), and λ_{max} = 500 nm (PMBD). The added HCl ensures that only the protonated form of the azo dye is present and that the measured absorbance is directly proportional to the concentration of the azo dye and therefore the concentration of unreacted diazonium salt.

Results

(1) Location of Diazonium Salts. Estimation of Their Association Constants and Investigation for Possible Ion-Pair Formation. Proper understanding of the behavior of substrates in micellar phases requires knowledge of their location in the micelle. A number of methods can be used to locate substrates in micellar aggregates.[13,14] We have used in this work ^{1}H NMR spectroscopy, which allows aromatic rings to be located via the upfield shift induced by the ring current (ring current effect) in the signals of neighboring surfactant hydrogen atoms, an effect that depends on the distance between the ring and the proton.[32,33] This method has already been used to locate other compounds containing benzene rings in micellar aggregates.[33] Table 2 shows that the greatest upfield shift is that for the protons on the α and β carbons of the hydrocarbon chain. It is, therefore, in the neighborhood of these carbons where the aromatic ring of the diazonium salt is predominantly located in SDS micelles and, consequently, very close to the micellar surface.

Association constants, K_s, of substrates to the micellar aggregates can be estimated by a number of methods.[13,14,34] K_s for OMBD was estimated spectrophotometrically by monitoring changes in the absorbance of its UV−vis spectrum due to its incorporation to the micellar aggregate. This method could not be used to determine K_s for PMBD because its spectral shift gives rise to very low absorbance differences (<0.2 AU when [SDS] = 0.1 M), so we used a kinetic method by measuring the effects of added SDS or Cu(SD)$_2$ on the coupling rate constant of the arenediazonium ions with naphthoxide ions: one can expect a decrease in the rate when increasing SDS[16] since arenediazonium ions are incorporated significantly in the micellar aggregate but 2N6S$^-$ will be excluded from it, decreasing significantly the local 2N6S$^-$ concentration in the Stern layer. So, we obtained spectrophotometrically the observed rate constants for the coupling reaction between the arenediazonium ion with of 2N6S by monitoring azo dye formation at T = 25 °C (λ = 500 nm, pH = ca. 7). According to the PIE model,[14] the observed rate constant, k_0, is given by eq 4

$$k_0 = \frac{k_W + k_M K_S D_n}{1 + K_S D_n} \qquad (4)$$

where K_s is the association constant and the subscripts

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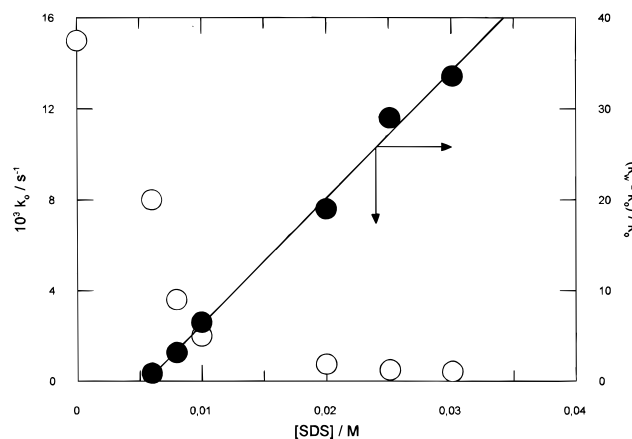(30) Zollinger, H. *Helv. Chim. Acta* **1953**, *34*, 1730−1736.
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Figure 1. Determination of the association constant K_s of PMBD with SDS by monitoring the effect of SDS micelles on the observed rate constant for the coupling reaction of PMBD with 2N6S (○) and plot according to eq 5 (●). Experimental conditions: $T = 25$ °C; [PMBD] = 9.88×10^{-5} M; [2N6S] = 3.15×10^{-3} M. Coupling reaction was done at pH ca. 7 with the aid of Tris buffer. Absorbance data were measured at $\lambda = 500$ nm.

W and M refer to the aqueous and micellar pseudophases. Assuming that the reaction in the Stern layer is negligible compared to that in water, i.e., $k_M \approx 0$, eq 4 can be rearranged to eq 5

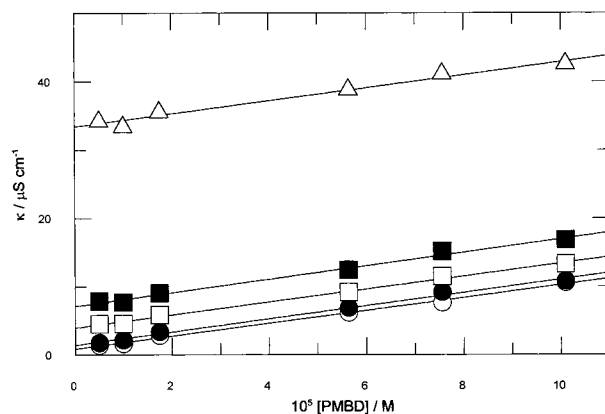$$\frac{k_W - k_o}{k_o} = K_S[\text{SURF}] - K_S \text{ cmc} \qquad (5)$$

which predicts that a plot of $(k_W - k_o)/k_o$ vs [SURF] should be linear. Figure 1 shows that our assumption is correct (i.e., $k_M \approx 0$), yielding values of $K_s(\text{PMBD}) = 1390 \pm 6$ M^{-1} (SDS) and $K_s(\text{PMBD}) = 4700 \pm 100$ M^{-1} (Cu(SD)$_2$).

As indicated, K_s for OMBD was estimated by monitoring absorbance changes at $\lambda = 262$ nm due to the incorporation of the substrate into the micellar aggregate and fitting the data (nonlinear regression) to eq 6 using a commercial computer program

$$\frac{1}{A - A_0} = \frac{1}{(A_\infty - A_0)K_S D_n} + \frac{1}{A_\infty - A_0} \qquad (6)$$

where A is the measured absorbance at any surfactant concentration, A_0 is the initial absorbance (no added surfactant), and A_∞ is the absorbance when all the substrate has been incorporated into the micelle. We have found that the UV−vis spectrum of OMBD is essentially the same at [SDS] = 0.5 M in the absence of NaCl and in the presence of 1.0 M NaCl, and both are different from that in the absence of SDS (The UV−vis spectrum of OMBD with Cu(SD)$_2$ in the presence of 1.0 M NaCl could not be obtained because of the absorbance of the chloro complexes[35−37]), so we obtained K_s values with no added NaCl, yielding $K_s(\text{OMBD}) = 250 \pm 8$ M^{-1} (SDS) and $K_s = 1020 \pm 20$ M^{-1} (Cu(SD)$_2$).

Divalent salts of alkyl sulfates quite often exhibit a greater solubility capacity than the corresponding monovalent salt for materials included in the micellar core,[38] presumably reflecting the increased packing density attainable due to decreased headgroup repulsion, and ion

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Figure 2. Conductivity values of solutions containing different amounts of PMBD and SDS surfactant: ○, [SDS] = 0 M; ●, [SDS] = 1×10^{-5} M; □, [SDS] = 5×10^{-5} M; ■, [SDS] = 1×10^{-4} M; △ = 5×10^{-4} M. Experimental conditions: $T = 23 \pm 0.5$ °C.
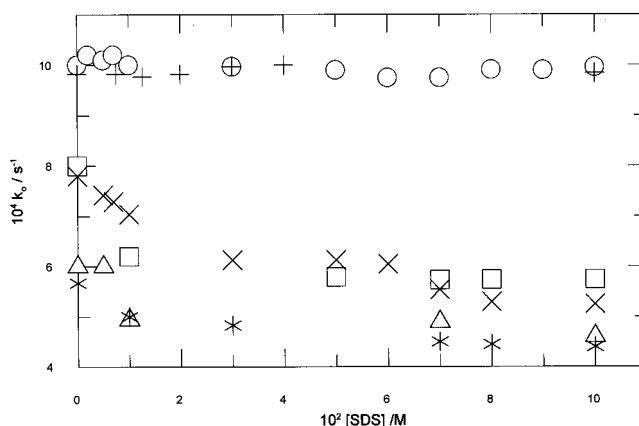
Figure 3. Effect of SDS on k_o for dediazoniation of OMBD, MMBD, and PMBD. Experimental conditions: OMBD and MMBD $T = 35$ °C, PMBD = 60 °C. [OMBD] = 2.09×10^{-4} M, [HCl] = 10^{-2} M: ○, [NaCl] = 0 M; +, [NaCl] = 1.0 M. [MMBD] = 1.00×10^{-4} M, [HCl] = 2×10^{-2} M: □, [NaCl] = 0 M, ×, [NaCl] = 1.0 M. [PMBD] = 1.13×10^{-4} M, [HCl] = 10^{-2} M: △, [NaCl] = 0 M; *, [NaCl] = 1.0 M.

exchange might be significant since diazonium ions are incorporated as "free" counterions; i.e., one Cu^{2+} ion can be exchanged by two arendiazonium ions. These effects are reflected in the values of $K_s = 1020$ M^{-1} for OMBD and $K_s = 4700$ M^{-1} for PMBD, about four times higher than those for SDS.

One possibility that needs to be considered before attempting any quantitative calculation of concentrations of dediazoniation products and loss of starting material is the possible formation of ion pairs between the diazonium ion and the surfactant headgroups since its formation will lead to a decrease in the "free" arenediazonium ion concentration. This point was investigated for the three arenediazonium salts (OMBD, MMBD, and PMBD) by measuring the conductivity of different solutions containing a fixed amount of surfactant and increasing amounts of arenediazonium salt. Plots of conductivity vs [diazonium salt] are straight lines, and no curvature or changes in the slope were detected at different surfactant concentrations below cmc (representative data are shown in Figure 2) suggesting that formation of ion pairs between the diazonium salts and the anionic surfactants is not important.

(2) Dediazoniation in the Presence of SDS and Cu(SD)2 Micellar Aggregates. (2a) Spectrophotometric Determination of the Observed Rate Con-

Table 3. Effect of SDS on k_o Obtained by Monitoring the Disappearance of Diazonium Ion Spectrophotometrically[a]

run	10^4[OMBD]/ M	[HCl]/ M	[NaCl]/ M	10^2[SDS]/ M	$10^4 k_{obs}$/ s^{-1}
1	0.97	0.01			10.20
2	0.97	0.01		1.00	10.00
3	0.97	0.01		3.00	9.97
4	0.97	0.01		5.00	9.90
5	0.97	0.01		6.00	9.75
6	0.97	0.01		7.00	9.75
7	0.97	0.01		8.00	9.91
8	0.97	0.01		9.00	9.90
9	0.97	0.01		10.00	9.96
10	2.09	0.02	1.0	0.00	9.82
11	2.09	0.02	1.0	0.76	9.77
12	2.09	0.02	1.0	1.27	9.82
13	2.09	0.02	1.0	2.02	9.92
14	2.09	0.02	1.0	3.04	9.97
15	2.09	0.02	1.0	4.05	10.05
16	2.09	0.02	1.0	5.06	9.80
17	2.09	0.02	1.0	10.00	9.84

run	10^4[MMBD]/ M	[HCl]/ M	[NaCl]/ M	10^2[SDS]/ M	$10^4 k_{obs}$/ s^{-1}
1	0.94	0.01			8.00
2	0.94	0.01		0.50	7.94
3	0.94	0.01		1.00	6.20
4	0.94	0.01		5.00	5.79
5	0.94	0.01		7.00	5.73
6	0.94	0.01		8.00	5.74
7	0.94	0.01		10.00	5.74
8	1.00	0.01			8.04
9	1.00	0.02	1.0	0.50	7.42
10	1.00	0.02	1.0	0.70	7.29
11	1.00	0.02	1.0	1.00	7.04
12	1.00	0.02	1.0	3.00	6.13
13	1.00	0.02	1.0	5.00	6.13
14	1.00	0.02	1.0	6.00	6.05
15	1.00	0.02	1.0	7.00	5.54
16	1.00	0.02	1.0	8.00	5.30
17	1.00	0.02	1.0	10.00	5.25

run	10^4[PMBD]/ M	[HCl]/ M	[NaCl]/ M	10^2[SDS]/ M	$10^4 k_{obs}$/ s^{-1}
1	1.10	0.01			6.50
2	1.10	0.01		0.50	6.50
3	1.10	0.01		1.00	6.32
4	1.10	0.01		5.00	5.35
5	1.10	0.01		7.00	5.52
6	1.10	0.01		10.00	5.24
7	1.13	0.01	1.0		6.00
8	1.13	0.01	1.0	5.00	4.83
9	1.13	0.01	1.0	8.00	4.50
10	1.13	0.01	1.0	10.00	4.45
11	1.13	0.01	1.0	12.00	4.40
12	1.13	0.01	1.0	15.00	4.30

[a] Experimental conditions: OMBD and MMBD, $T = 35$ °C; PMBD, $T = 60$ °C.

Table 4. Effect of Cu(SD)$_2$ on k_o Obtained by Monitoring the Disappearance of Diazonium Ion Spectrophotometrically[a]

run	10^4[OMBD]/ M	[HCl]/ M	[NaCl]/ M	10^3Cu(SD)$_2$/ M	$10^4 k_{obs}$/ s^{-1}
9	2.09	0.02	1.0	0.53	10.10
10	2.09	0.02	1.0	0.80	9.93
11	2.09	0.02	1.0	1.07	9.66
12	2.09	0.02	1.0	2.66	9.89
13	2.09	0.02	1.0	4.00	9.88
14	2.09	0.02	1.0	8.00	9.84

run	10^4[MMBD]/ M	[HCl]/ M	[NaCl]/ M	10^3Cu(SD)$_2$/ M	$10^4 k_{obs}$/ s^{-1}
1	0.65	0.01			7.90
2	0.65	0.01		1.00	7.90
3	0.65	0.01		2.00	7.13
4	0.65	0.01		5.00	5.92
5	0.65	0.01		8.00	5.57
6	0.65	0.01		10.00	5.39
7	1.00	0.02	1.0	1.00	7.65
8	1.00	0.02	1.0	4.00	7.34
9	1.00	0.02	1.0	6.00	7.21
10	1.00	0.02	1.0	8.00	6.91
11	1.00	0.02	1.0	10.00	6.89

run	10^4[PMBD]/ M	[HCl]/ M	[NaCl]/ M	10^3Cu(SD)$_2$/ M	$10^4 k_{obs}$/ s^{-1}
1	0.97	0.01			6.82
2	0.97	0.01		1.00	6.80
3	0.97	0.01		2.00	6.85
4	0.97	0.01		5.00	6.00
5	0.97	0.01		8.00	5.83
6	0.97	0.01		10.00	5.63
7	1.13	0.01	1.0	1.0	5.67
8	1.13	0.01	1.0	2.5	5.67
9	1.13	0.01	1.0	5.0	5.33
10	1.13	0.01	1.0	7.5	5.50
11	1.78	0.01	1.0	10.00	5.00

[a] Experimental conditions: OMBD and MMBD, $T = 35$ °C; PMBD, $T = 60$ °C.

(Table 3) are in agreement with those reported by Crossley,[39] measured by N_2 evolution, and Brower[40] bearing in mind the activation energy for these reactions:[39] k_o(OMBD) $= 9.6 \times 10^{-4}$ s^{-1} ($E_A = 26\,200$ cal mol^{-1}), k_o(MMBD) $= 7.4 \times 10^{-4}$ s^{-1} ($E_A = 25\,700$ cal mol^{-1}), and k_o(PMBD) $= 5.33 \times 10^{-4}$ s^{-1} ($E_A = 27\,500$ cal mol^{-1}). We found that k_o values in water for OMBD, MMBD, and PMBD are essentially independent of added electrolytes[22,41] such as HCl (0–1.0 M), NaCl (0–1.0 M), or CuCl$_2$ (0–0.01 M), in agreement with published results for other diazonium ions.

We have also investigated the effect of counterion exchange by adding NaCl to the reaction mixture. Figure 3 shows that, for a fixed SDS concentration, k_o values in the presence of 1.0 M NaCl are the same as those obtained in its absence within experimental error. The variation of k_o with increasing SDS follows a similar pattern of behavior in the presence and absence of NaCl, suggesting that a substantial fraction of diazonium ions is located in the Stern layer even at high NaCl concentrations. When adding NaCl to Cu(SD)$_2$ micelles, Table 4, one expects that Cu^{2+} ions exchange with Na$^+$, so dediazoniation takes place in the now essentially SDS micelles and consequently k_o variation with increasing Cu(SD)$_2$ is similar to that found with SDS micelles.

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(40) Brower, K. R. *J. Am. Chem. Soc.* **1960**, *82*, 4535–4537.
(41) Pazo-Llorente, R.; Rodriguez-Sarabia, M. J.; Gonzalez-Romero, E.; Bravo-Díaz, C. *Int. J. Chem. Kinet.*, in press.

stant, k_o. **Effects of SDS and Cu(SD)2 Micelles on k_o and Effect of Counterion Exchange.** Figure 3 and Tables 3 and 4 show the effects of SDS and Cu(SD)$_2$ micelles on k_o. All runs were done using fixed amounts of HCl and in the presence and absence of NaCl, keeping total chloride ion concentration constant, to hold the relative amount of chloro complexes in the medium constant[35–37] when using Cu(SD)$_2$ surfactant and to make them comparable. All runs showed first-order behavior.

Figure 3 and Tables 3 and 4 show that, in the absence of NaCl, k_o for OMBD does not change but it decreases slightly for MMBD and PMBD. We could not follow dediazoniation at higher Cu(SD)$_2$ concentrations spectrophotometrically because of the absorbance of the Cu(II) chloro complexes.[35–37] k_o values in absence of surfactant

Table 5. Values of k_o for ArOH Formation (obtained by HPLC) and k_o for the Loss of Diazonium Salt (obtained spectrophotometrically monitoring and azo dye formation) in the Presence of Anionic Micelles[g]

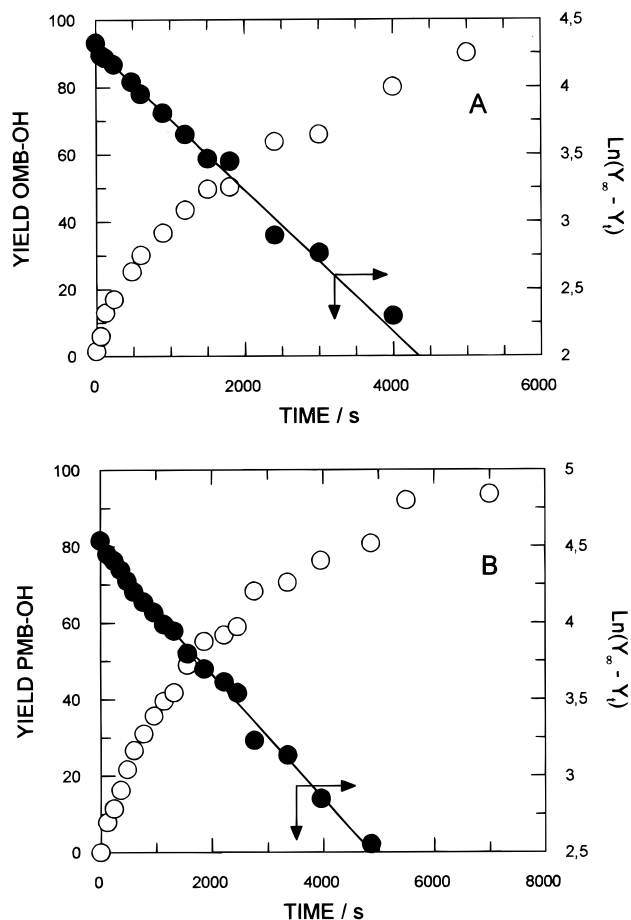| $10^4\,k_o$(OMBD)	$10^4\,k_o$(MMBD)	$10^4\,k_o$(PMBD)
9.92[a,b]	5.30[a,b]	4.35[a,b]
9.96[a,c]	5.40[a,c]	4.42[a,c]
9.80[e]	5.54[e]	4.45[e]
9.84[b,d]	6.52[b,d]	5.10[b,d]
9.82[f]	6.89[f]	5.00[f]

[a] [SDS] = 0.1 M. [b] Measured following ArOH formation. [c] Measured monitoring azo dye formation. [d] [Cu(SD)$_2$] = 0.01 M. [e] This work (value obtained spectrophotometrically monitoring diazonium salt decomposition at the closest SDS concentration, Table 3). [f] This work (value obtained spectrophotometrically monitoring diazonium salt decomposition at the closest Cu(SD)$_2$ concentration, Table 3). [g] Experimental conditions: [HCl] = 0.01 M; [NaCl] = 1.0 M; OMBD and MMBD, T = 35 °; PMBD, T = 60 °C.

Table 6. Yields of ArOH and ArCl in the Presence and Absence of Surfactants at Two Different NaCl Concentrations

10^4 [OMBD]/ M	[HCl]/ M	[Cl$^-$]/ M	[SDS]/ M	Y_{ArOH}	Y_{ArCl}
1.00	0.01	0.01		95.67	<3
1.00	0.01	1.0		90.41	4.1
2.30	0.01	0.01	0.02	93.67	<3
2.30	0.01	1.0	0.02	94.64	<3

10^4 [MMBD]/ M	[HCl]/ M	[Cl$^-$]/ M	[SDS]/ M	Y_{ArOH}	Y_{ArCl}
0.97	0.01	0.01		94.93	<3
0.97	0.01	1.00		89.9	4.3
1.34	0.01	0.01	0.03	95.2	<3
1.34	0.01	1.00	0.03	93.4	<3

10^4 [PMBD]/ M	[HCl]/ M	[Cl$^-$]/ M	[SDS]/ M	Y_{ArOH}	Y_{ArCl}
1.15	0.01	0.01		94.94	<3
1.15	0.01	1.0		92.94	<3
1.18	0.01	0.01	0.05	93.10	<3
1.23	0.01	1.0	0.08	93.00	<3

(2b) Determination of k_o by HPLC and Quenching and Effects of Surfactants on Product Yields. Chromatograms showed no extraneous peaks that may be attributed to products from radical pathways (like toluene, biaryls, etc.), from the nucleophilic participation of the SDS itself or from acid-catalyzed surfactant hydrolysis,[13,42] i.e., dodecanol; thus hydrolysis of SDS is not important under our experimental conditions. Selectivity values, S_w^{Cl}, for OMBD, MMBD, and PMBD have been reported as S_w^{Cl} = 2.7 (OMBD), S_w^{Cl} = 2.6 (MMBD), and S_w^{Cl} = 1.7 (PMBD). Consequently, low ArCl yields, even at high NaCl concentrations, are expected (Table 6). ArCl was detected in the presence of micelles, suggesting that co-ions such as chloride ions are not completely excluded from the Stern layer, in agreement with literature data.[43]

So, in Figures 4A, 4B, and 5A, chosen as representatives, we only show the variation of ArOH yields with time and the ln plots based on eq 1 for OMBD and PMBD (SDS) and MMBD (Cu(SD)$_2$). From the slopes of the ln plots we obtained k_o values for ArOH formation in the micellar medium. k_o values for loss of arenediazonium ions were also obtained from the variation of the absorbance of the azo dye with time and fitting the data to eq 1. Representative data are those for OMBD and PMBD (Figure 6, SDS) and MMBD (Figure 5B, Cu(SD)$_2$). Average k_o values

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Figure 4. Variation of yield of OMB−OH and PMB−OH with time in the presence of SDS and first-order plots (●) according to eq 8. The solid line is the theoretical curve obtained by least-squares fitting. OMBD: T = 35 °C, [OMBD] = 1.4 × 10^{-4} M, [NaCl] = 0.9 M, [HCl] = 0.1 M, [SDS] = 0.02 M PMBD: T = 60 °C, [PMBD] = 2.4 × 10^{-4} M, [NaCl] = 0.9 M, [HCl] = 0.1 M, [SDS] = 0.08 M.

are the same, within experimental error, as those obtained spectrophotometrically or chromatographically (Table 5).

Discussion

Location of diazonium salts in micellar structures determines their chemical reactivity in two ways: first, by governing their contact with other substrates incorporated in the micelle, with water or with ions present as counterions in the micellar Stern layer; second, by governing the polarity of their immediate environment, which can be decisive for unimolecular decomposition reactions. The former has been used by Romsted et al.[19,20] to estimate interfacial compositions in cationic micelles and to estimate the degree of ionization and counterion selectivity. The latter can induce changes in rates or in the mechanisms of dediazoniations[1] due to polarity changes.

^{1}H NMR experiments show that the benzene rings of the arenediazonium ions appear to be located near the micellar surface, suggesting that the −N$_2^+$ group is located in, or very close to the Stern layer, being these binding sites most likely average positions. In such a location, diazonium ions might form tight ion pairs with the surfactant monomer as observed for the *p*-methoxybenzenediazonium ion.[18] Conductivity data suggest that ion-pair formation between the methylbenzenediazonium ions and the SDS surfactant monomer seems not to be important. This conclusion is consistent with HPLC data,
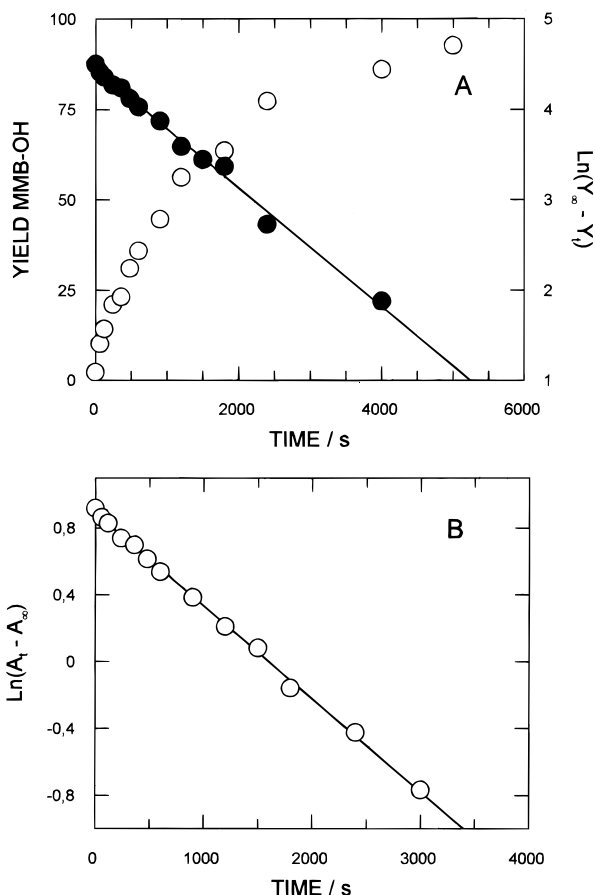
Figure 5. (A) Variation of yield of MMB−OH with time in the presence of Cu(SD)$_2$ and first-order plot (●) according to eq 8. The solid line is the theoretical curve obtained by least-squares fitting. Experimental conditions: T = 35 °C, [MMBD] = 9.5 × 10^{-5} M, [NaCl] = 0.9 M, [HCl] = 0.1 M. (B) First-order plot for the formation of azo dye in the presence of 0.01 M Cu(SD)$_2$ for MMBD. Experimental Conditions: T = 35 °C, [MMBD] = 3.4 × 10^{-4} M, [1NA] = 0.05 M, [NaCl] = 1 M, [SDS] = 4 × 10^{-3} M. Coupling reaction was done at pH ca. 7 with the aid of *Tris* buffer. Absorbance data were measured at λ = 484 nm after acidification of the reaction mixture (see Experimental Setup).
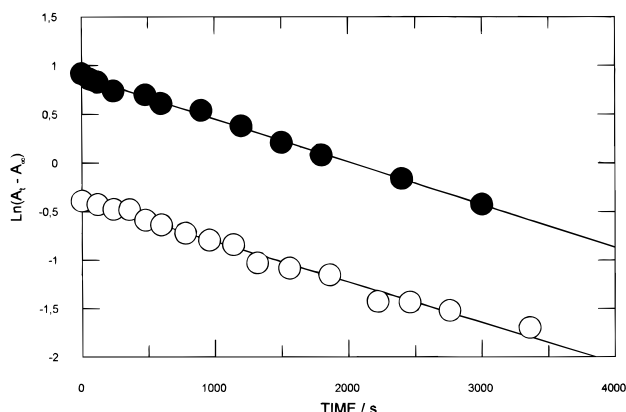
Figure 6. First-order plot for the formation of azo dyes in the presence of SDS surfactant. Experimental Conditions: ○, PMBD; ●, OMBD; T = 60 °C [PMBD] = 3.4 × 10^{-4} M, [OMBD] = 1.5 × 10^{-4} M, [1NA] = 0.05 M, [NaCl] = 1.0 M, [SDS] = 4 × 10^{-3} M. Coupling reaction was done at pH ca. 7 with the aid of TRIS buffer. Absorbance data were measured at λ = 529 nm (OMBD) and λ = 500 nm (PMBD) after acidification of the reaction mixture (see Experimental Setup).

since if diazonium salts were able to form strong ion pairs, they would not react with nucleophiles or substrates available in the Stern layer and yields of dediazoniation

products would probably decrease significantly. We obtained quantitative conversion within experimental error, <5%, Table 6 and Figures 4A, 4B and 5A. Values of K_s are not directly comparable since they were obtained with different methods,[13] but they suggest that a substantial fraction of the total arenediazonium ions are incorporated into the micelle even at low surfactant concentrations. Thus, dediazoniation is mainly taking place in the micellar Stern layer.

HPLC data indicate that conversion of diazonium salts to ArOH in the presence of SDS and Cu(SD)$_2$ micelles is quantitative, Table 6 and figures 4A, 4B and 5A), supporting the evidence that formation of ion pairs is not important for the three methylbenzenediazonium ions and that negligible amounts of other products, if any, are formed. These results contrast with those obtained in the presence of cationic micelles, where large amounts of aryl halides are formed at the expense of phenol.[16,19,20] HPLC kinetic data show that, in the presence of SDS or Cu(SD)$_2$, the rate of formation of ArOH (Figures 4 and 5A) is the same as the rate of disappearance of diazonium ion (Figures 5B and 6) and that both values are equal (within experimental error) to those obtained spectrophotometrically under the same experimental conditions (Table 5). These observations support the conclusion that the mechanism for the dediazoniation of these diazonium ions is the same as that in water, i.e., the formation of a highly reactive aryl cation in the rate-limiting step (Scheme 1b), and are in complete agreement with the results of Romsted et al.[19,20] using cationic CTABr micelles and Cuccovia et al. using SDS micelles.[44] Furthermore, formation of ArOH in the micellar aggregate is consistent with the current view of micelles as water-permeated structures.[45]

Tables 3 and 4 show that k_0 values for OMBD and MMBD in the absence of surfactant are close to each other, but they are significantly different from that of PMBD. As might be expected, substituents in the aromatic ring have a marked effect on the stability of diazonium salts; their effects can be explained on the basis of the Swain−Lupton[46] dual substituent parameter equation. Similar effects of the methyl group have been reported under different experimental conditions.[1]

In the presence of monovalent (SDS) and divalent (Cu(SD)$_2$) anionic surfactants, k_0 decreases slightly (about 30%) for MMBD and PMBD with increasing surfactant concentration, but no changes have been detected for OMBD (Figure 3 and Tables 3 and 4), both in the presence and absence of NaCl. Micellar effects on unimolecular reactions involving carbocations are usually small[47−49] compared to the effects on bimolecular ones, and they are not readily explained. They have generally been interpreted in terms of the reduced polarity of the micellar pseudophase or the reactivity of water in the medium[49,50] or by micellar perturbation of the solvation sphere of the carbocations.[49,50] Since our data indicate that the rate-

(44) In recent dediazoniation work with SDS micelles employing 2,6-dimethyl-4-hexadecylbenzenediazonium tetrafluoroborate, Cuccovia et al.[43] found that an unknown product was formed. Although this is not the case, our results confirm their assumption about the competitive reaction of the corresponding aryl cation.

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determining step is the formation of an aryl cation, the observed variation in k_0 can be attributed to changes in the polarity of the medium where arenediazonium ions are located in the Stern layer, a very anisotropic region with properties between those of water and hydrocarbon (alcohol-like).[14,51] This assumption is consistent with literature data that indicate that rates of decomposition of arenediazonium ions are remarkably constant when changing the polarity of the solvent, although dediazoniation products may vary widely: rates of heterolytic dediazoniation of a number of arenediazonium ions vary by a factor of only 9 in 19 solvents,[52,53] but no definitive conclusions can be drawn. The observed variation in k_0 for the three arenediazonium ions suggests a significant orientational effect of the methyl group in the presence of micelles. Investigation of this effect is part of future work.

Conclusions

We have studied the effects of SDS and Cu(SD)$_2$ surfactants on the reactivity of three arenediazonium ions. ^{1}H NMR results suggest that diazonium salts are incorporated into micelles and that their preferential location is very close to the micellar surface. Association constant values indicate that a significant fraction of the diazonium salt is incorporated into the micellar aggregate. No evidence of formation of tight ion-pairs between diazonium salts and anionic micelles was found.

Our results show that dediazoniations in the presence of anionic surfactants proceed via heterolytic, i.e., rate-determining, formation of a very reactive aryl cation that traps weakly basic nucleophiles competitively, because no products associated with radical pathways (like toluene or biphenyls) are formed and because k_0 for the formation of ArOH in the presence of surfactants is the same as that for the disappearance of diazonium salt. Rates of decomposition of PMBD and MMBD decrease with increasing SDS or Cu(SD)$_2$ concentrations reaching a constant value about 25−30% lower than those in water. Conversion to ArOH in the presence of anionic surfactants is almost quantitative. ArOH formation in the micellar aggregate is consistent with the current view of water-permeated micelles, and formation of ArCl suggests that Cl$^-$ ions are not excluded completely from the micellar surface.

The methodology employed allowed us to monitor dediazoniation reactions in the presence of micellar aggregates by simultaneous monitoring of the concentration and rates of product formation and loss of starting material. The basis of this methodology is the use of a quenching reaction using a suitable coupling agent followed by HPLC analysis, and we believe that it can be employed to study dediazoniations in colloidal systems.

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