J. Am. Chem. Soc. 1989, 111, 5091-5098

prior to the catalytic cycle the reacting species have been electrolytically generated.

In conclusion all the results obtained in this study may serve as a valuable basis for the interpretation of similar effects observed in other organometallic systems.

Acknowledgment. Financial support by the Baden-Württemberg Research Program (Radicals and One-Electron Transfers, FR-NW 31) and by the Fonds der Chemischen Ind. is gratefully acknowledged. J.S.F. is thankful for a Humboldt fellowship. We are indebted to F. Mallendorf for his assistance in electrochemical measurements.

Supplementary Material Available: Tables giving the experimental details of the synthesis reactions, the elemental analyses of the new compounds, and the NMR and IR data of the new compounds (4 pages). Ordering information is given on any current masthead page.

Electrochemistry and Electrocatalysis with Vitamin B_{12} in an AOT Water-in-Oil Microemulsion[1a]

Azita Owlia,[1b] Zhenghao Wang,[1c] and James F. Rusling*

Contribution from the Department of Chemistry (U-60), University of Connecticut, Storrs, Connecticut 06269-3060. *Received January 10, 1989*

Abstract: Vitamin B_{12a} solubilized in water pools of highly resistive water-in-oil (w/o) microemulsions of 0.2 M Aerosol OT (AOT, bis(2-ethylhexyl) sulfosuccinate)/4 M water/isooctane gave separate reductions of base-on cob(III)alamine to base-on cob(II)alamine ($E_{1/2} = -0.03$ V vs SCE) and base-on cob(II)alamine to base-off cob(I)alamine ($E_{1/2} = -0.87$ V). Diffusion coefficients suggested that vitamin B_{12} induces the formation of surfactant aggregates in w/o microemulsions that are larger than in solute-free systems. Relative reactivities toward reductions of three oil-soluble alkyl vicinal dihalides by electrochemically generated cob(I)alamine were modified in the microemulsion compared to isotropic water-acetonitrile. Changes in relative reactivity are not explained by simple partition of vicinal dibromides between isooctane and water and suggest specific interactions with surfactant aggregates or significant reaction in the bulk isooctane phase.

Clear, stable, water-in-oil (w/o) microemulsions[2] containing dynamic surfactant aggregates similar to inverted micelles can be prepared from hydrocarbon, water, and Aerosol OT [AOT, bis(2-ethylhexyl) sulfosuccinate].[3-5] Water is contained in the center of these aggregates. The anionic head groups face the "water pools", and the two hydrocarbon tails of AOT extend into the bulk hydrocarbon. Water in AOT w/o microemulsions with $w_0 = [\text{water}]/[\text{surfactant}] < 10$ is different from bulk water because it binds to head groups of the surfactant.[3,4] As w_0 increases, aggregate size increases and a smaller fraction of water is bound.[6]

In designing chemical systems for specific tasks, microemulsions offer the possibility of selecting reactant microenvironments as a means to control kinetics and reactivity.[4] Several reported kinetic effects of w/o microemulsions are quite dramatic. For example, the rate of aquation of tris(oxalato)chromium ion was 5×10^6 times faster in water pools of octadecyltrimethylammonium tetradecanoate than in bulk water. Rate enhancement could not be attributed simply to preconcentration of reactants in water pools.[7] Hydrolysis of *p*-nitrophenyl acetate catalyzed by imidazole decreased 50-fold in rate in AOT microemulsions because of unfavorable partitioning of reactants, i.e., catalyst resides predominantly in the water pools while *p*-nitrophenyl acetate favors the oil phase.[8a] The rate of thermocoloration of a water-soluble spiropyran was retarded 20-fold in AOT/hexane/0.6 M water. This was attributed to restricted mobility of the reactant in the water pool.[8b] Rates of axial ligand exchange of vitamin B_{12a} were enhanced up to 60 000-fold in water pools of dodecylammonium propionate or AOT in benzene.[9] Rate enhancements were amplified as w_0 decreased below 20.

The last example above is related to a specific concern of this paper, i.e., electrocatalysis with vitamin B_{12}, a naturally occurring cobalt corrin. In weakly acidic solutions, vitamin B_{12r} (cob(II)alamine) undergoes moderately fast reduction at carbon electrodes to its Co(I) form, vitamin B_{12s} or cob(I)alamine.[10,11] If an alkyl monohalide is present, it reacts with cob(I)alamine at the electrode to yield an alkylcob(III)alamine stable at the formal potential of the Co(II)/Co(I) redox couple.[11,12] However, if the alkyl halide has an appropriate activating group in the β position, the intermediate alkylcobalt complex is short lived and spontaneously decomposes to products. An example is the electrocatalytic reduction of alkyl vicinal dibromides by vitamin B_{12}, for which the pathway shown in Scheme I was proposed.[13] In Scheme I, cob(I)alamine formed at the electrode (eq 1) reacts rapidly with the vicinal dibromide RBr_2 (eq 2) to recycle cob(II)alamine at the

Scheme I

$$\text{Co(II)} + \text{e} = \text{Co(I)} \quad (k^\circ, \text{ at electrode}) \tag{1}$$

$$\text{Co(I)} + \text{RBr}_2 \xrightarrow{k_1} [\text{BrCo(III)RBr}] \xrightarrow{\text{fast}} \text{Co(II)} + \text{RBr}^\bullet + \text{Br}^- \tag{2}$$

$$\text{Co(I)} + \text{RBr}^\bullet \rightarrow \text{Co(II)} + \text{RBr}^- \quad \text{fast} \tag{3}$$

$$\text{RBr}^\bullet \rightarrow \text{alkene} + \text{Br}^- \quad \text{fast} \tag{4}$$

---

(1) (a) Part 7 of the series "Electrocatalysis in Organized Assemblies". (b) Present address: Mobay Corp., Baytown, TX. (c) On leave from Beijing Normal University, Beijing, China.

(2) The term microemulsion is used here for clear three-component systems of oil, water, and surfactant in which $w_0 = [\text{water}]/[\text{surfactant}] > 1$.

(3) Luisi, P. L.; Magid, L. *CRC Crit. Rev. Biochem.* **1987**, *20*, 409-474.

(4) (a) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982. (b) O'Connor, C. J.; Lomas, T. D.; Ramage, R. E. *Adv. Colloid Interface Sci.* **1984**, *20*, 21-97.

(5) Fendler, J. H. *Acc. Chem. Res.* **1976**, *9*, 153-161.

(6) (a) Raman spectroscopy indicated[6b] about 5% of the water bound to AOT head groups at $w_0 = 20$. (b) D'Aprano, A.; Lizzio, A.; Liveri, V. T.; Aliotta, F.; Vasi, C.; Migliardo, P. *J. Phys. Chem.* **1988**, *92*, 4436-4439.

(7) O'Connor, C. J.; Fendler, E. J.; Fendler, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 600-602.

(8) (a) Menger, F. M.; Donohue, J. A.; Williams, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 286-288. (b) Sunamoto, J.; Iwamoto, K.; Akutagawa, M.; Nagase, M.; Kondo, H. *J. Am. Chem. Soc.* **1982**, *104*, 4904-4907.

(9) Fendler, J. H.; Nome, F.; Van Woert, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 6745-6753.

(10) *B_{12}*; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. I.

(11) Scheffold, R. In Scheffold, R., *Modern Synthetic Methods*; Ed.; Wiley: New York: 1983; Vol. 3, pp 355-439.

(12) Lexa, D.; Saveant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* **1979**, *100*, 159-172.

0002-7863/89/1511-5091$01.50/0

electrode and increase the cathodic current. The RBr$^\bullet$ radical resulting from spontaneous decomposition of the assumed alkylcob(III)alamine intermediate is reduced by Co(I) (eq 3), again recycling Co(II) at the electrode. Alkene results according to Scheme I from elimination of bromide from RBr$^-$ (eq 4). An alternative pathway not ruled out by kinetic studies is β elimination from the intermediate alkylcob(III)alamine. However, the rate-determining step (rds) for both pathways is the reaction of cob(I)alamine with RBr_2, eq 2. Spectroelectrochemistry showed that the rds is energetically downhill, and cyclic voltammetry (CV) gave $k_1 = 6 \times 10^6$ M^{-1} s^{-1} for 1,2-dibromobutane (DBB).[13] The two-electron electrocatalytic cycle decreased overpotentials for reduction of DBB and ethylene dibromide (EDB) by 0.8-0.9 V compared to direct charge transfer at the electrode.

Analytical applications of Scheme I feature amplification of cathodic current from rapid cycling of Co(II) at the electrode. We used this reaction to estimate ethylene dihalides in conductive emulsions of AOT in isooctane/water (ca. 60/40) and in gasoline/AOT emulsions.[14]

We wished to explore the influence of reactant segregation in w/o microemulsions on the kinetics of the reaction in Scheme I. This required development of an understanding of heterogeneous charge-transfer reactions of vitamin B_{12a} in this unusual medium. Resistance of microemulsions with discrete water pools is high, precluding the use of electrodes with millimeter dimensions because of large ohmic (*iR*) drop. However, ultramicroelectrodes with micrometer dimensions provide a means to study electrochemistry in highly resistive media.[15,16] Only small currents (*i*) are passed during faradaic events at these electrodes (henceforth simply called microelectrodes), making ohmic drop (*iR*) small even if cell resistance (*R*) is large.

In this paper, we report the use of microdisk electrodes to study electron-transfer reactions of vitamin B_{12a} (cob(III)alamine) solubilized in water pools of AOT w/o microemulsions. We assigned the observed two-electrode reactions to reductions of base-on cob(III)alamine and base-on cob(II)alamine. Microelectrode studies of reduction of three oil-soluble alkyl vicinal dibromides by cob(I)alamine showed that relative reactivities were modified in the microemulsion compared to isotropic water–acetonitrile.

Experimental Section

Chemicals. Acetonitrile was Baker UV grade. Isooctane was Burdick and Jackson HPLC grade. Vitamin B_{12a} was hydroxocob(III)alamine hydrochloride (99%) from Sigma Chemical Co. Sodium dodecyl sulfate (99+%) was from Fisher Scientific. 1,2-Dibromoethane (99+%), 1,2-dibromobutane (97%), (±)-*trans*-1,2-dibromocyclohexane, and deuterium oxide (99.8 at. % D) were from Aldrich. Distilled water was purified with a Barnstead Nanopure system to a specific resistance >15 MΩ cm. Aerosol OT, bis(2-ethylhexyl)sulfosuccinate sodium salt (99%), was from Sigma (lot no. 67F-0267). UV spectroscopy and titrations of AOT with HCl and NaOH indicated the absence of significant impurities.[18] All other chemicals were ACS reagent grade.

Apparatus. Carbon microdisks were made by sealing P55-s grade VSB-32 carbon fibers (Union Carbide) in Corning 7740 glass.[17,18] The quality of the seal was confirmed by microscopy. Microdisks were polished once with SiC paper grit no. 600 on a polishing wheel under cold water. Disk radii (*r*) were estimated from the limiting current (i_l) of a 1.0 mM solution of ferrocene in acetonitrile/0.2 M $LiClO_4$ via the relation[16]

$$i_l = 4FDC^*r \qquad (5)$$

where *F* is Faraday's constant, *D* is the diffusion coefficient of ferrocene[19] (2.5×10^{-5} cm^2 s^{-1}), and C^* is its concentration. Average *r* was 6.3 μm.

Table I. Specific Resistance of Selected w/o Microemulsions

AOT/water/isooctane	[AOT], M	w_0	specific resistance, 10^{-9} Ω cm
5.4/9.9/84.7	0.10	45	0.017
12.2/9.8/78	0.20	20	4.69
12.2/9.9/78[a]	0.20	20	3.57
17.1/15.1/67.8	0.35	20	2.35

[a] Water contained pH 3 phosphate buffer (17 mM).

A BAS-100 electrochemical analyzer with lab-built amplifier[20] was used for voltammetry. A two-electrode cell was used in a Faraday cage. The aqueous saturated calomel (SCE) reference employed an aqueous saturated KCl salt bridge ending in an agar/KCl plug.

NMR was done with a Brucker WH270 spectrometer at 109.35 MHz, with spectral width 10^7, repeat time 0.61 s, pulse width 13.3 μs. A Hewlett-Packard 5890 gas chromatograph with electron capture detector, capillary column DB-624, 0.53-mm o.d. × 30 m, oven 200 °C, detector 300 °C, and injector 200 °C was used to determine alkyl dibromides. Helium (5 mL min^{-1}) was the carrier gas.

Procedures. Water/oil microemulsions (w_0 = 20) were made by adding AOT/isooctane solutions to water or buffer. Dissolution of solutes in microemulsions was done on the day of experiment. Media for electrochemistry were deoxygenated with purified nitrogen saturated with the medium used in the experiment. The electrochemical cell was thermostated at 25 ± 0.2 °C.

Electrode pretreatments necessary to obtain reproducible results with carbon microdisks depended on the system studied, as is typical of carbon electrodes.[21] The procedures used were as follows: (i) ferrocene in acetonitrile, electrode held at 800 mV for 60 s followed by 0 mV for 90 s; (ii) vitamin B_{12} in acetonitrile/water, electrode ultrasonicated in methanol for 1 min following each scan and then held at −400 mV for 30 s; (iii) ferrocene in AOT microemulsions, ultrasonication in methanol for 2 min, rinsing with pure water and then held for 10 s at 0 mV; (iv) vitamin B_{12a} in AOT microemulsions, polishing on a clean billiard cloth on a polishing wheel for 30 s in a stream of pure water, ultrasonication in methanol for 2 min and then held at 300 mV for 10 s. Pretreatments preceded each scan. Limiting currents were determined from steady-state *i–E* curves by drawing tangents to base line, plateau, and at the half-wave potential ($E_{1/2}$). Limiting currents were measured as the vertical difference in current between the intersection of plateau and $E_{1/2}$ tangents and the extrapolated base line. Limiting currents in microemulsions were reproducible to about ±10% and $E_{1/2}$ to ±15 mV.

Distribution of alkyl dibromides was measured after equilibration in isooctane/water overnight at 25 °C. The two phases were separated and dibromide was measured by GC in the isooctane phase. Analyses of dibromide in the water phase were done after extraction with fresh isooctane.[18]

Results

1. General Characterization of Microemulsions. Resistivity. Conductivity measurements confirmed the high resistivity of AOT microemulsions with $w_0 \leq 45$ (Table I). Phosphate in the water pools caused a small decrease in resistivity. Although smaller resistivity was found for systems with larger w_0, we chose w_0 = 20 as the smallest value practical for quantitative electrochemical studies.

Acidity of the Water Pools. Phosphorus-31 NMR peaks for phosphate are pH dependent and were used previously to estimate pH in water pools of microemulsions containing up to 0.1 M AOT.[22] The method is less sensitive to pH changes at pH below 5. We hoped to use pH ≤3 so that the benzimidazole side chain would be dissociated from cob(II)alamine. This "base-off" form accepts an electron faster from the electrode than the base-on form.[23] Phosphorus-31 resonances of aqueous phosphate standards shifted +10.0 Hz as pH increased from 1.8 to 5.5. However, their peak positions were 50-56 Hz more negative than the phosphorus-31 chemical shifts found in AOT microemulsions

---

(13) Connors, T. F.; Arena, J.; Rusling, J. F. *J. Phys. Chem.* **1988**, *92*, 2810-2816.

(14) Rusling, J. F.; Connors, T. F.; Owlia, A. *Anal. Chem.* **1987**, *59*, 2123-2127.

(15) Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1125A-1130A.

(16) Fleischmann, M.; Pons, S.; Rolinson, D. R.; Schmidt, P. P. *Ultramicroelectrodes*; Datatech Systems: North Carolina, 1987.

(17) Owlia, Azita; Rusling, J. F. *Electroanalysis* **1989**, *1*, 141-149.

(18) Owlia, Azita, Ph.D. Thesis, University of Connecticut, Storrs, CT, 1988.

(19) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 219.

(20) Huang, H. J.; He, P.; Faulkner, L. R. *Anal. Chem.* **1986**, *58*, 2889-2890.

(21) Kamau, G. N. *Anal. Chim. Acta* **1988**, *207*, 1-16.

(22) Smith, R. E.; Luisi, P. L. *Helv. Chim. Acta* **1980**, *63*, 2302-2311.

(23) (a) The pK_a for protonation of the benzimidazole side chain of cob(II)alamine is 2.9.[23b] This protonation yields the "base-off" form of cob(II)alamine. (b) Lexa, D.; Saveant, J. M. *Acc. Chem. Res.* **1983**, *16*, 235-243.

Table II. Phosphorus-31 NMR Chemical Shifts in AOT w/o Microemulsions[a]

pH_{st}[b]	w_0	chem shift,[c] Hz
1.8 (H_3PO_4)	20	-278.0
3.0 + 1 mM B_{12a}	20	-275.3
2.3	20	-275.9
3.0	20	-272.7
5.3	20	-271.7

[a] All contained 0.2 M AOT. [b] pD of starting D_2O buffer 17 mM in total phosphate. [c] Relative to trimethyl phosphate chemical shift.

made with phosphate buffers of the same starting pH (pH_{st}). At these concentrations of AOT, changes in the pK_a of phosphoric acid and/or specific interaction of the trimethyl phosphate standard with AOT may invalidate this type of analysis.

However, since water pool pH was previously found to be within 0.4 units of pH_{st},[22] NMR data yield a rough estimate for the apparent pH range of the water pools (Table II). Phosphorus-31 peaks became more positive by 6.3 Hz as pH_{st} was increased. Addition of 1 mM vitamin B_{12a} to the pH_{st} 3.0 microemulsion caused a negative shift of 2.6 Hz, suggesting a small increase in acidity. Thus, an estimated pH range for water pools containing vitamin B_{12a} with pH_{st} 3.0 is about 2-3.4.

Absorption Spectrum of Vitamin B_{12a}. The spectrum of 1 mM vitamin B_{12a} in 17 mM aqueous phosphate buffer (Figure 1a) showed α, β, and γ bands at 554, 520, and 350 nm, respectively. This spectrum is characteristic of cob(III)alamine with water and the benzimidazole side chain as axial ligands.[24] Subtle changes are observed for vitamin B_{12a} in 0.2 M AOT with $w_0 = 20$ (Figure 1b). Although the γ band is still at 350 nm, the β band is broadened, its lower wavelength shoulder is less pronounced, and the α band is absent or overlapped with the β band. However, the β band at 520 nm in the microemulsion suggests a polarity of the microenvironment similar to water when compared to a correlation of β-band wavelengths of cob(III)alamine in solvents with different polarities.[9,24]

2. Characterization by Microelectrode Voltammetry. Ohmic Resistance. Voltammograms are broadened by ohmic drop (iR_u) according to

$$E = V + iR_u \qquad (6)$$

where E is the actual potential at the working electrode, V is applied voltage, R_u is uncompensated cell resistance, and i is current (cathodic currents taken as positive). Substituting eq 6 into the expression for a steady-state i-E curve of a one-electron, reversible electrode reaction yields

$$i = i_l B\{1 + \exp[(V + iR_u - E^{\circ\prime})(F/RT)]\}^{-1} \qquad (7)$$

where i_l is the limiting current, $E^{\circ\prime}$ is the formal potential, B accounts for observed difference in slope between baseline and plateau,[17] and the other terms have their usual electrochemical meanings.

Twenty-two voltammograms at 10 mV s^{-1} at four concentrations of ferrocene between 0.1 and 1 mM in the 0.2 M AOT microemulsion, $w_0 = 20$, were analyzed[17] by nonlinear regression onto eq 7. The average R_u was $(1.49 \pm 0.35) \times 10^8\ \Omega$, 43 times larger than for acetonitrile[17] without purposely added electrolyte.

Microviscosity. The effective viscosity for a species diffusing in the bulk phase of a microemulsion is known as the microviscosity. Diffusion coefficients (D) of bulk-phase probes can be used[25] to estimate microviscosity (η') from the Stokes–Einstein equation:

$$D = kT/6\pi\eta' r_h \qquad (8)$$

where k is Boltzmann's constant and r_h is the hydrodynamic radius of the probe. Assuming that ferrocene with bulk concentration C^* travels exclusively in the isooctane, D is found from

$$D = i_l/4FC^*r \qquad (9)$$

where r is electrode radius. Limiting currents for ferrocene in 0.2 M AOT from 22 voltammograms gave an average $D = (1.77 \pm 0.19) \times 10^{-5}$ cm^2 s^{-1}. Taking r_h of ferrocene (2.64 Å) to be the same as in acetonitrile,[25b] an average microviscosity of 0.47 ± 0.05 cP was found, about the same as that of pure isooctane at 25 °C.[26]

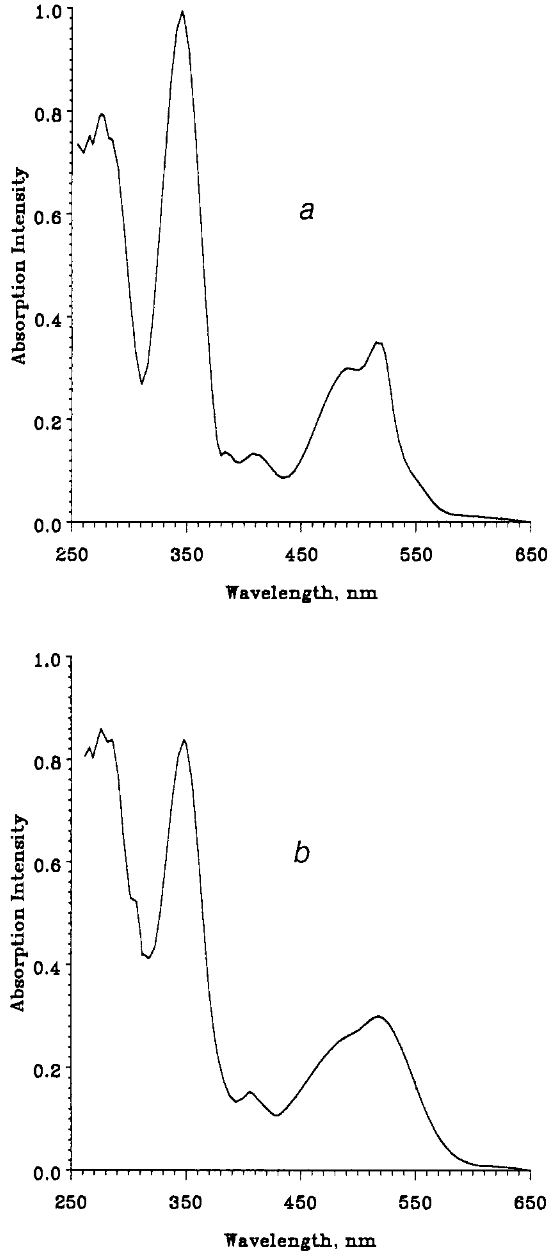

Figure 1. UV-visible absorption spectra of 1 mM vitamin B_{12a} in a 2-mm path-length cell: (a) pH 2.3 (17 mM) phosphate buffer; (b) microemulsion in isooctane with 0.2 M AOT, 4 M water with 17 mM phosphate, pH_{st} = 3.

3. Electrochemistry of Vitamin B_{12} at Carbon Microdisk Electrodes. Electrochemistry in Water. SWV of vitamin B_{12a} at low frequencies in water with no purposely added supporting electrolyte showed two peaks of equal height at about -60 and -920 mV vs SCE at the carbon microdisk electrodes (Figure 2). Forward and reverse i-E curves revealed characteristics[27] expected

---

[24] Gianotti, C. In *B_{12}*; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 1, pp 393-430.

[25] (a) Mackay, R. A. In *Microemulsions*; Robb, I. D., Ed.; Plenum Press: New York, 1982; pp 207-219. (b) Chen, J. W.; Georges, J. *J. Electroanal. Chem.* **1986**, *210*, 205-211.

[26] *Handbook of Chemistry and Physics*, 53rd ed.; CRC Press: Cleveland, 1972.

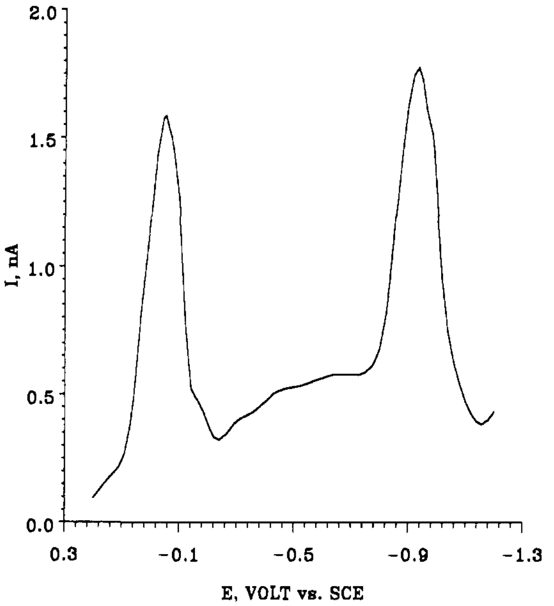

Figure 2. Square-wave voltammogram of 1 mM vitamin B_{12a} at a carbon microdisk electrode in water without purposely added electrolyte. SWV parameters: $f = 5$ Hz, step = 2 mV, amplitude = 50 mV.

Table III. SWV Results for Vitamin B_{12a} in Aqueous Media[a]

	Co(III)/Co(II)		Co(II)/Co(I)	
f, Hz	$-E_p$, V/SCE	$i_pf^{1/2}$	$-E_p$, V/SCE	$i_pf^{-1/2}$
	Water, No Added Electrolyte			
5	0.056	5.8	0.918	5.5
7	0.058	5.4	0.920	5.9
10	0.060	5.1	0.922	5.4
12	0.060	4.6	0.922	5.0
15	0.062	4.6	0.922	4.4
	0.1 M SDS in Water			
2	0.040	2.2	0.928	3.1
5	0.042	2.4	0.926	3.5
7	0.044	2.2	0.926	3.2
10	0.048	2.1	0.924	3.0
15	0.058	1.7	0.924	2.7

[a] Data for 2 mM vitamin B_{12a}. SWV parameters: step = 2 mV, amplitude = 50 mV.

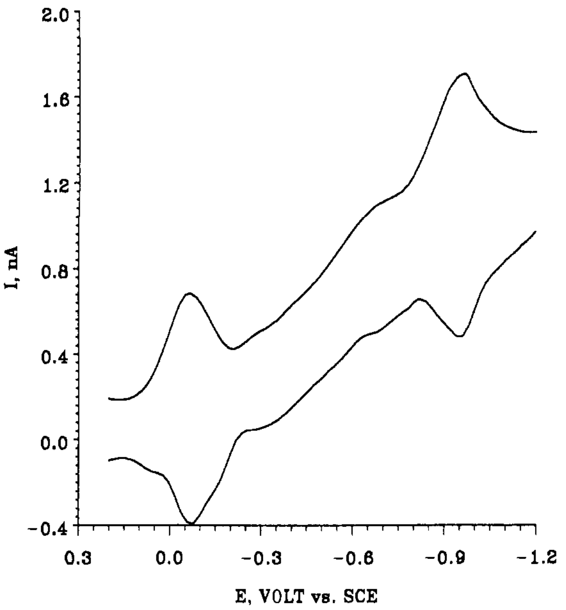

Figure 3. Forward (top) and reverse (bottom) current-potential curves from the square-wave voltammogram of 1 mM vitamin B_{12a} in water in Figure 2.

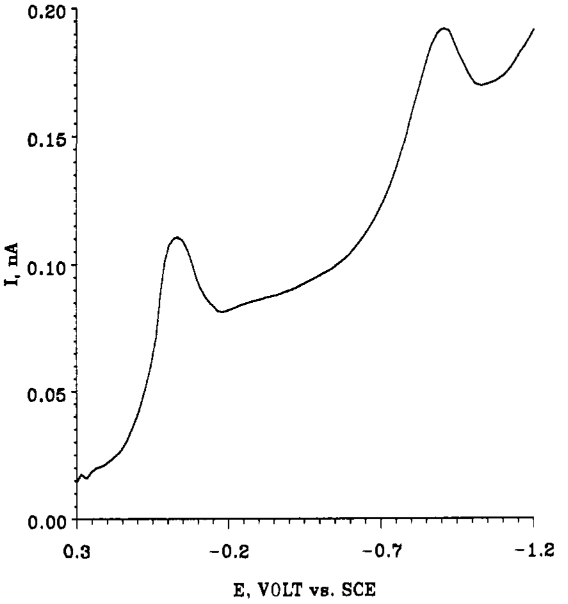

Figure 4. Square-wave voltammogram of 1 mM vitamin B_{12a} at a carbon microdisk electrode in microemulsion of 0.2 M AOT, 4 M water pH_{st} 3, and isooctane. SWV parameters: $f = 5$ Hz, step = 2 mV, amplitude = 50 mV.

for reversible redox couples, i.e., peaks of equal height at nearly equal potentials (Figure 3). Below a frequency (f) of 10 Hz, difference current peak potentials (E_p) and $i_p/f^{1/2}$ were independent of f for the two peaks (Table III). These results are also characteristic of reversible charge transfer from the electrode to Co(III) and Co(II) on the time scale of the experiment. An average D of 2.0×10^{-6} cm^2 s^{-1} for vitamin B_{12} calculated from difference peak currents was in good agreement with the average[23b] of 1.8×10^{-6} cm^2 s^{-1} in aqueous media pH 1-7. As f increased above 10 Hz for the Co(III) peak and 15 Hz for the Co(II) peak, E_p became more negative and $i_p/f^{1/2}$ decreased, characteristic of an electron transfer that is not fast enough to remain fully reversible at these frequencies.[27]

Electrochemistry in Aqueous 0.1 M SDS. Co(III) and Co(II) peaks were also readily observed in 0.1 M SDS at carbon microdisks by SWV at small f. The Co(III) peak was broader and smaller than the Co(II) peak. Changes in E_p and $i_p/f^{1/2}$ with increasing f (Table III) suggest that the Co(III)/Co(II) reaction is slower in the SDS solution than in water. The Co(II)/Co(I) redox couple retains the characteristics of a fast reversible redox couple at $f < 15$ Hz. An apparent diffusion coefficient of 1.1×10^{-6} cm^2 s^{-1} estimated from the reversible $i_p/f^{1/2}$ data for the Co(II) reduction was smaller than the value of 4.3×10^{-6} cm^2 s^{-1} for micelles in a 0.1 M SDS solution.[28] Peak potentials for Co(III) reduction at $f < 10$ Hz were shifted an average of +14 mV with respect to pure water, while those of Co(II) shifted -5 mV.

Electrochemistry in AOT Microemulsions. SWV of vitamin B_{12a} in 0.2 M or 0.35 M AOT with $w_0 = 20$ yielded two peaks with approximately equal heights (Figure 4). Forward and reverse currents show very broad Co(III)/Co(II) peaks (Figure 5), probably caused by a slow rate of electron transfer and the large ohmic drop. Shapes of the Co(II)/Co(I) forward and reverse peaks are more characteristic of a faster electron transfer under diffusion control at a microelectrode.[27] Nearly equal heights of the two difference current peaks suggest that they represent straightforward heterogeneous reductions from Co(III) to Co(II) to Co(I). High resistance and large background currents restricted

---

(27) Osteryoung, J.; O'Dea, J. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1986; Vol. 14, pp 209-308.

(28) Kratohvil, J. P.; Aminabhavi, T. M. *J. Phys. Chem.* **1982**, *86*, 1254-1256.

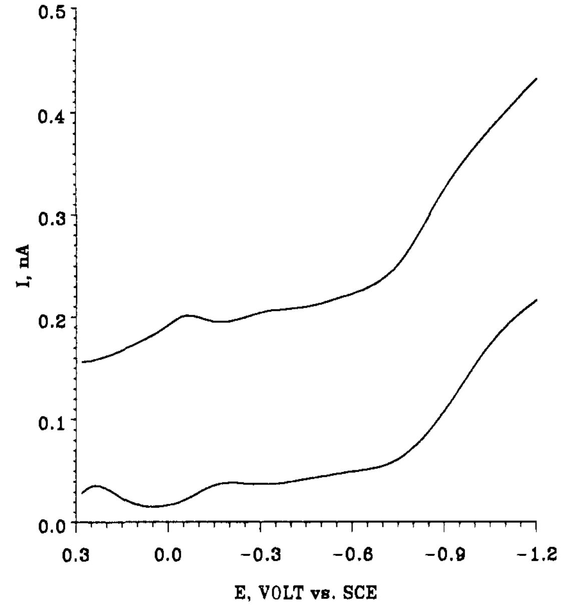

Figure 5. Forward (top) and reverse (bottom) current-potential curves from square-wave voltammogram of 1 mM vitamin B_{12a} in microemulsion in Figure 4.

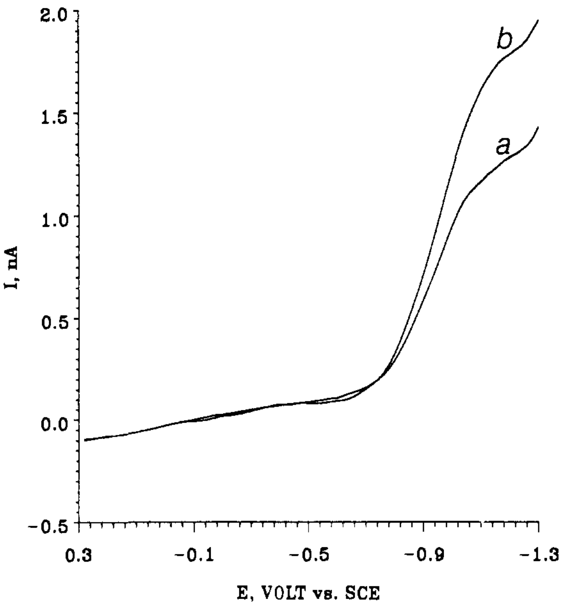

Figure 6. Linear sweep voltammograms at 10 mV s^{-1} at carbon microdisk electrode in microemulsion of 0.2 M AOT, 4 M water pH_{st} 3, and isooctane: (a) 0.5 mM vitamin B_{12a}; (b) 0.5 mM vitamin B_{12a} and 2 mM ethylene dibromide.

studies to very low f. However $i_p/f^{1/2}$ estimated for the Co(II) peak was independent of f below 5 Hz. When microdisk electrodes were placed in a microemulsion containing vitamin B_{12a} for up to 24 h, washed with microemulsion, and then scanned by SWV in microemulsion free of electroactive solute, a i-E curve similar to the background for a fresh electrode was found. This suggests the absence of strong adsorption of vitamin B_{12} on carbon microdisks.

Linear sweep voltammograms (LSV) of vitamin B_{12a} in AOT microemulsions with $pH_{st} = 3$ gave a very poorly defined Co(III) wave and a well-defined Co(II) wave (Figure 6a). Nineteen LSVs of the Co(II) wave gave an average $E_{1/2}$ corrected[17] for ohmic drop of -0.874 ± 0.017 V vs SCE. Similar voltammograms were found in AOT microemulsions with $pH_{st} = 1.9$, where the corrected $E_{1/2}$ was -0.81 V, a shift of -58 mV/pH_{st}.

When air was purposely introduced into microemulsions containing vitamin B_{12a}, a catalytic wave for reduction of oxygen was observed about 50 mV positive of the Co(II) wave. Thus, catalytic reduction of traces of oxygen in the microemulsion do not contribute to the Co(II) wave. Catalytic reduction of hydrogen ion[29] might also influence the height of the Co(II) wave. LSVs for vitamin B_{12a} in homogeneous solutions of pH between 1 and 4 containing phosphate buffer, phosphoric acid, or perchloric acid revealed (i) relatively broad waves for Co(III) reduction, even though ohmic resistance was much lower than in the microemulsions, and (ii) a positive shift in the final rise in current as pH decreased, but retention of a distinct Co(II) peak positive of this current rise. This suggests that catalytic hydrogen evolution probably does not occur at the Co(II) $E_{1/2}$ in microemulsions with $pH_{st} = 3$. The possibility that the disproportionation reaction[23b]

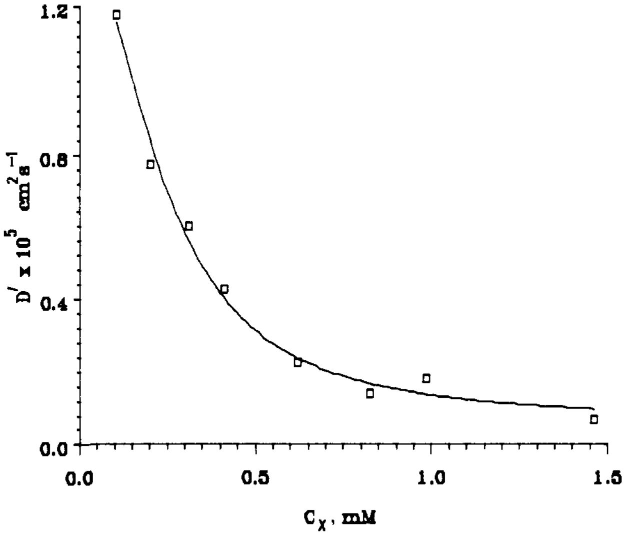

Figure 7. Influence of concentration of vitamin B_{12a} on apparent diffusion coefficient in microemulsion of 0.2 M AOT, 4 M water, pH_{st} 3, and isooctane. Squares are experimental data; line is best fit by nonlinear regression onto eq 12 for $n = 3$. Parameters given in text.

$$\text{Co(III)} + \text{Co(I)} = 2\text{Co(II)}$$

contributes to the height of the second wave cannot be ruled out from present data. However, this would require[30] the diffusion coefficient of cob(III)alamine to be smaller than those of the Co(I) and Co(II) species.

Diffusion of Vitamin B_{12} in the Microemulsion. Assuming fast equilibrium with respect to the time scale of the diffusion measurement, the following equation[31,32] for the electrochemically measured apparent diffusion coefficient (D') applies in monodisperse aggregate systems:

$$D' = f_a D_0 + f_b D_1 \tag{10}$$

where $f_a = 1 - f_b$ is the fraction of free probe, f_b is the fraction of bound probe, D_1 is the aggregate diffusion coefficient, and D_0 is the diffusion coefficient of unbound probe. A micelle (M) is considered capable of binding n molecules of X in the overall equilibrium

$$\text{M} + n\text{X} = \text{MX}_n \qquad K^n = [\text{MX}_n]/\{[\text{M}][\text{X}]^n\} \tag{11}$$

In terms of total concentrations of micelles (C_M) and probe (C_X), if $[X] \ll C_X$, i.e., if the probe is tightly bound

$$D' = D_0/(1 + C_M K^n C_X^{n-1}) + D_1 C_M K^n C_X^{n-1}/(1 + C_M K^n C_X^{n-1}) \tag{12}$$

where K is an "apparent" binding constant per bound probe molecule.[33a] Since vitamin B_{12} is highly soluble in water and

---

(29) Birke, R. L.; Gu, R.-A.; Yau, J.-M.; Kim, M.-H. *Anal. Chem.* **1984**, *56*, 1716-1722.

(30) Eddowes, M. J.; Gratzel, M. *J. Electroanal. Chem.* **1983**, *152*, 143-155.

(31) Rusling, J. F.; Shi, C.-N.; Kumosinski, T. F. *Anal. Chem.* **1988**, *60*, 1260-1267, and references therein.

(32) (a) Evans, D. H. *J. Electroanal. Chem.*, in press. (b) The assumption of fast equilibrium seems justified since reported lifetimes for solutes in water pools of AOT microemulsions are 10^{-5}-10^{-8} s.[4,5]

Table IV. Characteristics of Catalytic Reduction of Vicinal Dibromides[a]

substrate	N^b	i_c/i_d	$-E_{1/2}$,[c] V vs SCE	$-E_{1/2}$,[d] V vs SCE	$10^{-6}k_1$, M^{-1} s^{-1}	rel k
			pH 2.3 Acetonitrile/Water[e]			
DBB	8	15.3 ± 1.2	0.776	0.723	1.3 ± 0.2	1
EDB	7	21.7 ± 1.8	0.776	0.744	2.6 ± 0.5	2
t-DBC	8	29.8 ± 3.6	0.767	0.734	5.1 ± 1.3	3.9
			0.2 M AOT/4 M Water/Isooctane[f]			
DBB	7	1.41 ± 0.11	0.869	0.814	0.31 ± 0.19[g]	1[h]
EDB	6	1.84 ± 0.05	0.894	0.870	1.34 ± 0.17[g]	4.3[h]
t-DBC	6	2.64 ± 0.16	0.860	0.847	6.2 ± 1.9[g]	20[h]

[a] By LSV at 10 mV/s at carbon microdisk electrodes. [b] Number of trials. [c] 0.5 mM vitamin B_{12} catalyst alone, corrected for ohmic drop. [d] Catalyst and substrate, corrected for ohmic drop. [e] 17 mM phosphate buffer, 0.5 mM vitamin B_{12}, 5 mM substrate. [f] 17 mM phosphate buffer (pH_{st} = 3) in water pools, total concentrations: 0.5 mM vitamin B_{12r}, 2 mM substrate. [g] $10^{-3}k_{obsd}$. [h] Relative k_{obsd}.

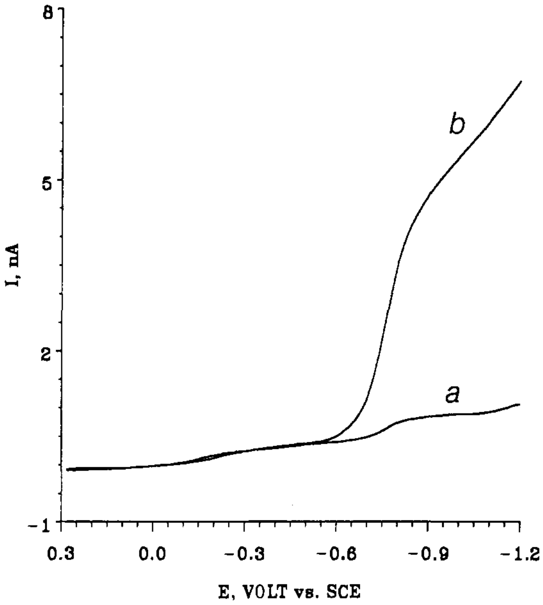

Figure 8. Linear sweep voltammograms at 10 mV s^{-1} at carbon microdisk electrode in pH 2.3 water/acetonitrile (1:1): (a) 0.5 mM vitamin B_{12a}; (b) 0.5 mM vitamin B_{12a} and 5 mM ethylene dibromide.

Table V. Partition Data and Relative Rate Comparisons

substrate	K_{ow}	$10^{-5}k_M$, M^{-1} s^{-1}	rel k_M	rel k(iso)[a]
DBB	5100	1.1	1	1
EDB	143	0.14	0.13	2
t-DBC[b]	50000	220	200	4

[a] Isotropic acetonitrile/water medium. [b] K_{ow} is only approximate here (±50%); difficultly in this measurement was caused by the extremely small water solubility of *t*-DBC.

insoluble in isooctane, the above model should apply. Values of D' obtained from limiting currents of the Co(II) wave decreased at constant composition of the microemulsion with increasing C_X (Figure 7), as predicted by eq 12 with $n > 1$. Parameters and standard errors found by nonlinear regression[33b] were $D_0 = (1.35 \pm 0.08) \times 10^{-5}$ cm² s⁻¹; $D_1 = (0.63 \pm 0.33) \times 10^{-6}$ cm² s⁻¹ and $C_M K^n = (1.68 \pm 0.11) \times 10^7$ M^{-2}.

Analysis of Cob(II)alamine *i–E* Data in Microemulsions. By using the ohmic resistance found from the ferrocene LSVs, E for cob(II)alamine was corrected to eliminate ohmic drop by using eq 7. The resulting "resistance free" voltammograms were analyzed by nonlinear regression onto an explicit form of an equation for microdisk electrodes:[34]

$$i = i_l\{1 + (k_m/k^{\circ\prime}) \exp[(E - E^{\circ\prime})(\alpha F/RT)] + \exp[(E - E^{\circ\prime})(F/RT)]\}^{-1} \quad (13)$$

where $k^{\circ\prime}$ is the apparent standard heterogeneous rate constant,[35a] α is the electrochemical transfer coefficient, and k_m was taken as the mean value for a microdisk: $(D/r)[(2/\pi) + (3\pi/16)]$.[35b] Averages for 10 *i–E* curves of 0.5 mM vitamin B_{12} in 0.2 M AOT/4 M water (pH_{st} 3)/isooctane were $E^{\circ\prime} = -0.80 \pm 0.01$, $\alpha = 0.33 \pm 0.04$, and $k^{\circ\prime} = 0.006 \pm 0.002$ cm s^{-1}.

4. Electrocatalytic Dehalogenation of Vicinal Dibromides. Isotropic Medium. Reduction of three vicinal dibromides in pH 2.3 acetonitrile/water (1:1) was investigated at carbon microdisks since they had been studied previously in this medium at conventional electrodes.[13] Addition of 1,2-dibromoethane (EDB), 1,2-dibromobutane (DBB), or *trans*-1,2-dibromocyclohexane (*t*-DBC) to a solution of vitamin B_{12a} resulted in a large increase in limiting current for cob(II)alamine (Figure 8). This indicates that cob(I)alamine formed at the electrode reacts with the vicinal dibromides in a catalytic cycle to regenerate cob(II)alamine at the electrode. The absence of changes in Co(III) waves after addition of substrate suggests that cob(II)alamine does not react with the dibromides on the LSV time scale.

For a large [substrate]/[catalyst] ratio, the rate-determining reaction of cob(I)alamine with vicinal dibromide (eq 2) is pseudo-first-order in catalyst. Assuming hemispherical diffusion at a microdisk electrode, the ratio of the limiting current of the catalytic reduction (i_c) to the diffusion-limited current of a one-electron catalyst alone (i_d) is[36]

$$i_c/i_d = 1 + r(\pi/4)(k'/D)^{1/2} \quad (14)$$

where k' is the pseudo-first-order rate constant for the rds. To account for the two-electron stoichiometry of vicinal dihalide reduction, we have $k' = 2C^*_s k_1$, where k_1 is the second-order rate constant (Scheme I) and C^*_s the bulk concentration of substrate. Equation 14 now yields

$$k_1 = (8D/\pi^2 r^2 C^*_s)[(i_c/i_d) - 1]^2 \quad (15)$$

Equation 15 was used to estimate k_1 from measured steady-state catalytic efficiencies (i_c/i_d) for the three vicinal dihalides.[37]

AOT Microemulsion. Addition of vicinal dibromides in 0.2 M AOT/4 M water (pH_{st} = 3)/isooctane also increased the current for the cob(II)alamine wave (Figure 6b). Concentrations of 2 mM substrate and 0.5 mM catalyst avoided phase separation. These are not pseudo-first-order conditions, and eq 15 is not strictly applicable. Thus, we digitally simulated a plot of catalytic efficiency vs log k_1 based on Scheme I, assuming a second-order

---

(33) (a) An expression for D' when two types of micelles are present was also described. These models were successful in describing D' vs C_X data for aqueous micelles.[31] (b) An extra-sum-of-squares F test (95% confidence level) showed that, compared to the two-micelle model,[33a] the monodisperse model for D' (eq 12) gave the best fit with $n = 3$.

(34) Galus, Z.; Golas, J.; Osteryoung, J. *J. Phys. Chem.* **1988**, *92*, 1103–1107.

(35) (a) This expression assumes constant concentration across the microdisk,[16,34] and thus the analysis provides only an average apparent k°. (b) The difference in $k^{\circ\prime}$ when using the mean k_m as opposed to either limiting value corresponding to constant flux or constant concentration is <2.5%.[17]

(36) Fleischmann, M.; Lasserre, F.; Robinson, J. Swan, D. *J. Electroanal. Chem.* **1984**, *177*, 97–114.

(37) An average D for catalyst and substrates was used. Since average molecular dimensions of the other vicinal dibromides are within 20–30% of DBB, all were assumed to have similar diffusion coefficients. This was taken as 10-fold larger than vitamin B_{12r} (2.8×10^{-6} cm² s⁻¹), as found for DBB.[13] Values used for estimating k_1 were $D = 1.54 \times 10^{-5}$ cm² s⁻¹ and $r = 6.37 \times 10^{-4}$ cm. Models with unequal diffusion coefficients are not yet available for microelectrodes.

Table VI. Formal Potentials and Apparent Kinetic Constants for Cobalamines in Selected Media

		Co(III)/Co(II)		Co(II)/Co(I)		
medium (electr)[a]	$10^6 D$, cm^2/s	$-E_0'$, V vs SCE	$k°$, cm/s	$-E_{\circ}'$, V vs SCE	$k°$, cm/s	ref
pH 2.3/aq MeCN (GC)	2.8	0.0	0.001	0.766	0.02	13
$1 \leq pH \leq 2$ (Hg)	1.7[b]	<0.04		0.74	0.1	32b
$4 \leq pH \leq 7.8$ (GC)	1.9[b]	0.04	8×10^{-6}	0.85	0.0002	32b
0.001 M H_3PO_4 or $HClO_4$ (CFD)				0.76		tw[d]
pH 2.3/aq MeCN (CFD)				0.77		tw
AOT emulsion[c] (GC)	2.0	0.05	0.0025	0.90	0.0056	14
water, no salt[e] (CFD)	2.0	0.056		0.918		tw
0.1 M SDS[e] (CFD)	1.1	0.041		0.926		tw
0.2 M AOT/isooctane/4 M water (CFD)						
$pH_{st} = 3$	0.63	0.03[e]		0.80[f] (0.874)[g]	0.006	tw
$pH_{st} = 1.9$				(0.81)[g]		

[a] Electrodes: GC, glassy carbon; CFD, carbon fiber microdisk. [b] Average of CV and capillary method. [c] 3.4% AOT/41% water/54% isooctane, saturated with TEAP. [d] tw = this work. [e] Estimated by SWV at $f \leq 5$ Hz. [f] Formal potential estimated from nonlinear regression of corrected LSVs at ≤10 mV/s onto eq 13 (see text). [g] Half-wave potentials obtained from LSV at 10 mV/s.

rds (eq 2), equal diffusion coefficients,[38] and the hemispherical diffusion approximation.[16] This working curve was used to estimate k_1 from measured catalytic efficiencies.

Smaller rate constants (Table IV) were observed in the microemulsions because of unfavorable partition of vicinal dibromides into the oil phase. Relative reactivities of the vicinal dibromides were different in the microemulsions than in isotropic acetonitrile/water.[39] Partition coefficients (K_{ow}) between isooctane and water (Table V) yield a rough estimate of the concentrations of dibromides in the water pools. Assuming that the surfactant has no effect on the partition, that all the vitamin B_{12r} resides in the water pools, and that the predominant kinetic influence is fast catalytic reduction in the water pools, the following expression[4a] can be written:

$$k_M(C^*_{B12}/V_w)C^*_s/K_{ow} = k_{obsd}C^*_{B12}C^*_s \tag{16}$$

where V_w is the volume fraction of the water pools (0.071 in this system), C^*_{B12} is the bulk concentration of catalyst, and k_M is the rate constant for the catalytic reaction in the water pools. From eq 16

$$k_M = V_w K_{ow} k_{obsd} \tag{17}$$

Relative values of k_M were very different from those in water–acetonitrile (Table VI). Thus, this simple model does not explain the change in relative reactivity in the microemulsion.

Discussion

Diffusion in the Microemulsion. D' vs C_X data for vitamin B_{12} yielded D_1, the AOT micelle diffusion coefficient. With use of eq 8, the D_1 value, and the estimated microviscosity, a hydrodynamic radius of 75 Å is found for the AOT aggregate containing cob(II)alamine. This is larger than the radius of 50 Å found for solute-free AOT aggregates in isooctane with $w_0 = 20$ by photon correlation spectroscopy.[40] It is consistent with an earlier finding[9] that vitamin B_{12} induced formation of large aggregates of dodecylammonium propionate in benzene.

Electrochemistry of Vitamin B_{12}. Electron transfer to vitamin B_{12a} is associated predominantly with its central cobalt atom. If the benzimidazole side chain is unprotonated, it can act as an axial ligand for cob(III)alamine and cob(II)alamine (base-on forms). Protonation of the benzimidazole nitrogen produces "base-off" forms which are more rapidly reduced at electrodes.[23b] In the pH range relevant to this work, the following redox reactions are likely to be important:

$$H^+ + [LL'Co(III)] + e \rightarrow [LCo(II)]{\sim}L'H^+ \qquad E°' > -0.04 \text{ V} \tag{18}$$

$$[LL'Co(III)] + e \rightarrow [L'Co(II)] + L \qquad E°' = -0.04 \text{ V} \tag{19}$$

$$[Co(II)]{\sim}L'H^+ + e = [Co(I)]{\sim}L'H^+ \qquad E°' = -0.74 \text{ V} \tag{20}$$

$$H^+ + [L'Co(II)] + e \rightarrow [Co(I)]{\sim}L'H^+ \qquad -0.74 \text{ V} < E°' < -0.85 \text{ V} \tag{21}$$

$$[L'Co(II)] + e \rightarrow [Co(I)]{\sim}L' \qquad E°' = -0.85 \text{ V} \tag{22}$$

In eq 18–22, L′ represents the benzimidazole side chain, L is the other axial ligand, probably water in most cases discussed here, $[\,]{\sim}L'$ represents a base-off species, [L′Co(II)] is a base-on form, and formal potentials are in aqueous buffers from ref 23b.

The pK_a of the benzimidazole of cob(III)alamine[23b] is −2.4, so that its base-on form predominates in our systems. In water, 0.1 M SDS, and the AOT microemulsion, formal potentials for the Co(III)/Co(II) reaction support this claim; they are very close to the $E°'$ found for eq 19 in aqueous systems of pH 2.9–7.8 (Table VI).

Formal potentials for the Co(II)/Co(I) reaction at carbon microdisks in water and 0.1 M SDS (Table VI) are considerably more negative those at glassy carbon at pH < 3, even when a possible small error from sluggish charge transfer is considered. These potentials are more in line with eq 22, i.e., reduction of base-on cob(II)alamine to base-off unprotonated cob(I)alamine, which occurs in water between pH 4 and 7.8. On the other hand, in the microemulsion at pH_{st} 3, the $E°'$ of −0.80 V suggests predominance of eq 21, featuring protonated cob(I)alamine as product. The −58 mV/pH_{st} shift in $E_{1/2}$ is consistent with participation of a proton in this reaction.

Comparison of the $E°'$ of Co(II)/Co(I) with the formal potential-pH diagram[23b] for vitamin B_{12} suggests an apparent pH of about 3.7 for microemulsion water pools with pH_{st} 3. This is only slightly larger than the upper limit of 3.4 estimated by phosphorus-31 NMR. Above pH 3 in aqueous media (Table VI), eq 19 and 21 tend to predominate as in the microemulsion.

The shape of the UV spectrum of cob(III)alamine in the microemulsion suggests a weak interaction with AOT. Results in aqueous SDS provide indirect evidence for interactions of vitamin B_{12} species with anionic surfactants. A D' value in 0.1 M SDS nearly 10-fold smaller than in water and 4-fold smaller than for SDS micelles is indicative of binding. Small shifts in formal potential for the vitamin B_{12} redox couples in 0.1 M SDS solutions suggest binding[41] of reduced vitamin B_{12} species to the micelles.

---

(38) Assuming that catalytic reduction occurs after diffusion to the electrode of reactants in the same water pool implies equal diffusion coefficients for catalyst and substrate. The assumption appears reasonable because of high intrinsic reaction rates which are probably larger than intermicellar rates for exchange of solute.[4,5] Also, measured catalytic efficiencies in microemulsions fall well within the range computed by digital simulations with equal diffusion coefficients whereas catalytic efficiencies in acetonitrile/water were much larger than predicted by simulations with equal diffusion coefficients.

(39) Although eq 15 does not strictly hold for catalytic experiments in microemulsions, it gave k_1 values of 0.5, 2, and 7.6×10^3 M^{-1} s^{-1} for DBB:EDB:*t*-DBC, a ratio of 1:4:15 (cf. Table IV).

(40) (a) Zulauf, M.; Eicke, H.-F.; *J. Phys. Chem.* **1979**, *83*, 480–486. (b) The value of r_h was independent of AOT concentration[40a] above about 0.02 M. (c) The difference between r_h of 75 Å from D_1 in the microemulsion containing vitamin B_{12} and the solute-free value of 50 Å was significant at the 88% confidence level as shown by *t* tests.

(41) Kaifer, A. E.; Bard, A. J. *J. Phys. Chem.* **1985**, *89*, 4876–4880.

J. Am. Chem. Soc. **1989**, *111*, 5098-5101

Electrocatalytic Reduction of Vicinal Dibromides. Kinetics of reduction of vicinal dibromides in pH 2.3 acetonitrile–water at carbon microdisk electrodes were similar to those obtained at larger electrodes. The observed k_1 for reduction of DBB with cob(I)-alamine was 6×10^6 M^{-1} s^{-1} at glassy carbon[13] and 1.3×10^6 M^{-1} s^{-1} at carbon microdisks (Table IV) at a lower buffer concentration. The difference may be due to the use of an average diffusion coefficient in eq 16 for the latter estimate. A more exact model with separate diffusion coefficients for substrate and catalyst was used to analyze the glassy carbon data. Comparison of the $E^{\circ\prime}$ of the Co(II)/Co(I) couple to a correlation[42] of k_1 vs $E^{\circ\prime}$ of outer-sphere catalysts reacting with *t*-DBC predicts a k_1 of 0.02 M^{-1} s^{-1}, whereas the observed value is 5×10^6 M^{-1} s^{-1}. Thus, catalysis by vitamin B_{12r} is much more efficient than expected for an outer-sphere reaction, supporting an inner-sphere mechanism.

Apparent rate constants in the AOT microemulsion were about 3 orders of magnitude smaller than in acetonitrile/water. The k_1 measured in both media is for reaction of base-off cob(I)alamine with vicinal dibromide. Attenuation of rates is caused by the large unfavorable partition of the vicinal dihalides into isooctane (Table V), while vitamin B_{12} remains predominantly in water pools.

Relative k_1 values in water/MeCN for DBB:EDB:*t*-DBC were 1:2:4 as opposed to 1:4:20 in the microemulsion. The difference cannot be explained totally by partition of the substrate between isooctane and water. While the relative reactivity of EDB may increase because it partitions into water better than the other substrates, *t*-DBC is very poorly partitioned into water but has the largest relative rate. There are two possible explanations: (i) neglect of the reaction in isooctane is not justified; (ii) partition may be counterbalanced by specific interactions of the alkyl dibromides with AOT aggregates. Both factors may favor increased relative reactivity for *t*-DBC in the microemulsion since it is the most reactive in MeCN/water and also the most hydrophobic of the three substrates.

Conclusions

This work illustrates the possibilities of quantitative studies with microelectrodes in highly resistive w/o microemulsions. Analysis of diffusion coefficient data provided the microviscosity of the system and confirmation that vitamin B_{12} induces formation of larger surfactant aggregates in w/o microemulsions than in its absence. Comparisons of standard potentials with those in isotropic solutions led to identification of species involved in the electrode reactions of vitamin B_{12}. Relative reactivity for reductions of vicinal dibromides by cob(I)alamine was found to be modified in the microemulsion compared to an isotropic medium.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and partly by U.S. PHS Grant ES03154 awarded by the National Institute of Environmental Health Sciences. We thank Union Carbide for the carbon fibers, Alan Brown for preparing the microelectrodes, Thomas Leipert for help with NMR experiments, Dennis Evans for a preprint of ref 32a, and Shili Liu and the Environmental Research Institute, University of Connecticut, for access to electron-capture gas chromatography.

Supplementary Material Available: Details of calculations and figures showing voltammograms and plots of simulated steady-state catalytic efficiency vs log k_1 (8 pages). Ordering information is given on any current masthead page.

---

[42] Lexa, D.; Saveant, J. M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 6464–6470.

Calculation of Correlation Times for the γ-Alumina-Supported Molybdenum Subcarbonyl, $Mo(CO)_3$(ads)

George W. Wagner and Brian E. Hanson*

Contribution from the Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.

Received July 11, 1988

Abstract: The theory of carbon-13 NMR line widths in the solid state for molecules with large chemical shift anisotropies is applied to the adsorbed molybdenum subcarbonyls $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads). Correlation times for the rotation of the molybdenum subcarbonyl groups $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads) on partially dehydroxylated alumina are calculated. Good agreement is obtained between data reported at observation frequencies of 15 to 75.5 MHz for carbon-13 for $Mo(CO)_3$(ads). The correlation time for this adsorbed species is calculated to have a lower limit of 4.6 ± 0.5 ms. The presence of broad lines in the room temperature spectra for $Mo(CO)_3$(ads) is thus explained by a slow molecular motion. An alternative explanation for the broad lines observed at room temperature is a distribution of overlapping isotropic chemical shifts for different adsorption sites. This explanation, however, does not account for the variation of line width (in Hz) with observation frequency. Data for $Mo(CO)_5$(ads) are available at observation frequencies of 15 to 90.5 MHz. A good fit to the experimental data is obtained assuming either long or short correlation times for this species. Thus literature estimates of $<10^{-6}$ s for the correlation time for this species cannot be confirmed with certainty from the analysis presented here.

After the initial detection of γ-alumina-supported molybdenum subcarbonyls by CP-MAS ^{13}C NMR, it was suggested that the surface species, $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads), are involved in motional processes which average the carbonyl ligands.[1] This argument was used to explain the simple spectra in the carbonyl region under CP-MAS conditions. More recent broad-line and CP-MAS NMR studies[2,3] on the molybdenum carbonyl/alumina system have refined the understanding of the dynamic behavior of the subcarbonyls. In this manuscript we show that all the published work on these subcarbonyls and previously unpublished spectra from our laboratory can be used to obtain correlation times for $Mo(CO)_3$(ads).

The CP-MAS ^{13}C NMR work of Shirley noted that the chemical shift anisotropy (CSA) of $Mo(CO)_3$(ads) is very large (390 ± 50 ppm).[2] Thus, it was proposed that any motion involving

---

[1] Hanson, B. E.; Wagner, G. W.; Davis, R. J.; Motel, E. *Inorg. Chem.* **1984**, *23*, 1635.

[2] Shirley, W. M. *Z. Phys. Chem.* **1987**, *152*, 41.

[3] Walter, T. H.; Thompson, A.; Keniry, M.; Shinoda, S.; Brown, T. L.; Gutowsky, H. S.; Oldfield, E. *J. Am. Chem. Soc.* **1988**, *110*, 1065.