

# Bicontinuous Microemulsions as Media for Electrochemical Studies

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**Bicontinuous microemulsions of didodecyldimethylammonium bromide (DDAB)/dodecane/water were explored as media for voltammetric reductions and oxidations of ruthenium(III) hexaammine, ferrocyanide, ferrocene, cob(II)alamin, and several polycyclic aromatic hydrocarbons (PAHs). These clear microemulsions are conductive and are believed to contain a dynamic extended network of interconnected water tubules. Agreement of simulated and experimental voltammetric data shows that electrochemical theory for homogeneous media is followed to a good approximation in DDAB microemulsions. Diffusion of electroactive solutes did not reflect the high bulk viscosities of the microemulsions. Nonpolar molecules and ions diffuse as if they were in neat oil or aqueous media, respectively, and voltammograms with good signal to noise ratio are obtained. Reductions of PAHs in the microemulsions occurred by an ECE-type pathway, with nearly reversible one-electron reductions achieved at high scan rates.**

Water and hydrocarbon oils do not mix at normal ambient temperature and pressure. Addition of surfactant to water and oil can lead to a clear, thermodynamically stable, macroscopic phase which has come to be known as a microemulsion (1-3). In some cases, salt and cosurfactants such as alcohols are used in such systems. Microemulsions, though homogeneous to the eye, are microscopically heterogeneous. The continuous liquid "phase" in the system may be water, with surfactant solubilizing most of the oil in globular aggregates resembling swollen micelles. These are oil-in-water (o/w) microemulsions. Conversely, the oil phase may be continuous, with the surfactant forming inverted aggregates having water in their centers. These are water-in-oil (w/o) microemulsions. Bicontinuous microemulsions are a third type of system, in which both oil and water are continuous throughout with surfactant residing at extended oil-water interfaces. Microemulsions are used widely in domestic and industrial applications ranging from detergency to cosmetics and pharmaceuticals to tertiary oil recovery (1-3).

Among the important properties of microemulsions is their ability to dissolve significant amounts of solutes of different types. Thus, a microemulsion can be used as a medium to bring together ionic and nonpolar reactants. Control of the structural aspects of microemulsions offers the possibility of selecting reactant microenvironments to control chemical kinetics and reactivity for specific applications (1-4). A case in point for electrochemistry is electrocatalysis, which can be used to amplify analytical sensitivity. In this technique, electrons are transferred between an electrode and a substrate whose electrode reaction is slow via a chemical mediator (catalyst). We recently reported catalytic reduction of oil-soluble vicinal dihalides mediated by water-soluble vitamin B<sub>12</sub> in a w/o microemulsion. Because of the high resistivity

of the isooctane-based w/o microemulsion, ultramicroelectrodes were needed for voltammetry in this system (5).

In contrast to w/o microemulsions, o/w and bicontinuous microemulsions conduct electricity. In principle, they should be usable in electrochemical studies with electrodes of any size. Bicontinuous microemulsions might offer unique properties for electroanalytical studies in addition to those discussed above, including the chance to study reductions and oxidations of nonpolar compounds in a continuous oil phase of nearly pure hydrocarbon with conventional-sized electrodes. Several reports have appeared in which steady-state voltammetric methods were used to study diffusion of probe molecules in o/w microemulsions (6-11). In a few of these, measurements were extended to bicontinuous microemulsions (9-11). However, fundamental studies of electrochemical reactions in such systems are lacking. Thus, we began a systematic investigation of the electrochemistry of a series of ionic and nonionic redox couples in a model bicontinuous microemulsion of didodecyldimethylammonium bromide (DDAB)/dodecane/water.

Phase diagrams and physical properties of three-component bicontinuous microemulsions of DDAB, water, and oils have been thoroughly investigated by Evans, Ninham, and co-workers (12-18) with the aim of determining factors controlling microstructure. DDAB is insoluble in water and oil and resides almost entirely at the interface between the two. Its microemulsions can be prepared by titrating DDAB/oil suspensions with water. Conducting bicontinuous microemulsions can be prepared with as little as 7% water if hexane is the oil or 2% water if cyclohexane is used. Bulk viscosities of these microemulsions are usually considerably larger than that of the neat oil. Addition of more water eventually results in a transition to a nonconducting, less viscous w/o microemulsion. This transition becomes less sharp as chain length of the oil is increased. On the basis of physical properties and NMR self-diffusion studies, microstructure of conducting, bicontinuous microemulsions of DDAB is believed to feature a dynamic, interconnecting network of water tubules surrounded by surfactant with head groups facing the water (16).

In this paper, we report the cyclic voltammetry (CV) of water-soluble ferrocyanide, ruthenium(III) hexaammine, and vitamin B<sub>12</sub> and oil-soluble ferrocene, pyrene, perylene, and 9-phenylanthracene in bicontinuous microemulsions of DDAB/water/dodecane. Glassy carbon was chosen as the working electrode because of its wide potential window. Comparisons of experimental data with computer-simulated CVs showed that to a good approximation, the electrode reductions and oxidations behaved as if the solutes were diffusing in a homogeneous medium. The polycyclic aromatic hydrocarbons (PAHs) were reduced by ECE-type mechanisms.

## EXPERIMENTAL SECTION

**Chemicals and Solutions.** Ferrocene, perylene, pyrene, 9-phenylanthracene, and 4,4'-dichlorobiphenyl were obtained from Aldrich Chemical Co. in >98% purities. Potassium ferrocyanide and *n*-dodecane were ACS certified grade from Fisher Scientific. Didodecyldimethylammonium bromide (DDAB, 99+%) was from Eastman Kodak. Vitamin B<sub>12</sub> was hydroxocob(III)alamin hy-

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**Table I. Composition and Properties of DDAB/Dodecane/Water Systems**

surfactant	wt %		viscosity, cP	$10^3 \kappa$ , $\Omega^{-1} \text{ cm}^{-1}$
	water	oil		
		100	1.35	
13 <sup>a</sup>	28	59	19	0.11
21 <sup>a</sup>	39	40	38	1.05
24 <sup>b</sup>	14	62	27	1.79

<sup>a</sup> Microemulsion. <sup>b</sup> Emulsion.

drochloride (99%) from Sigma Chemical Co. Ruthenium(III) hexaammine was from Strem Chemicals. Distilled water was purified with a Sybron-Barnstead Nanopure system to a specific resistance  $>15 \text{ M}\Omega \text{ cm}$ . All other chemicals were reagent grade.

Microemulsions were prepared by titrating a mixture of DDAB and dodecane with pure water until a clear solution with a suitably high conductance was obtained. The initial mixture of DDAB and oil was made such that the titration would bring the composition into the microemulsion region of the three-component phase diagram (15). Microemulsions prepared in this way were optically clear and stable at room temperature for several months. The one emulsion used was prepared in the same way. Its final composition was slightly out of the microemulsion region of the phase diagram, toward the surfactant corner. This emulsion appeared opaque immediately after vigorous shaking, but two phases separated within an hour. Emulsions were brought to the opaque condition immediately before each experiment.

**Apparatus and Procedures.** Cyclic voltammetry was done with a Bioanalytical Systems BAS-100 electrochemistry system and a three-electrode cell containing a glassy carbon disk ( $A = 0.071 \text{ cm}^2$ ) working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. The SCE was connected to the cell by a salt bridge containing microemulsion. Glassy carbon was prepared and polished on a metallographic wheel with successively smaller particles of SiC, diamond paste, and alumina (smallest  $0.05 \mu\text{m}$ ), and subsequent ultrasonication in pure water, as described previously (19). Before each scan, the electrode was polished for 2 min with  $0.3\text{-}\mu\text{m}$  alumina, ultrasonicated for 2 min in purified water, polished with  $0.05 \mu\text{m}$  alumina, and finally ultrasonicated again in pure water. Ohmic drop of the cell was fully compensated in all CV experiments. All electrochemical experiments were thermostated at  $25.0 \pm 0.1^\circ \text{C}$ .

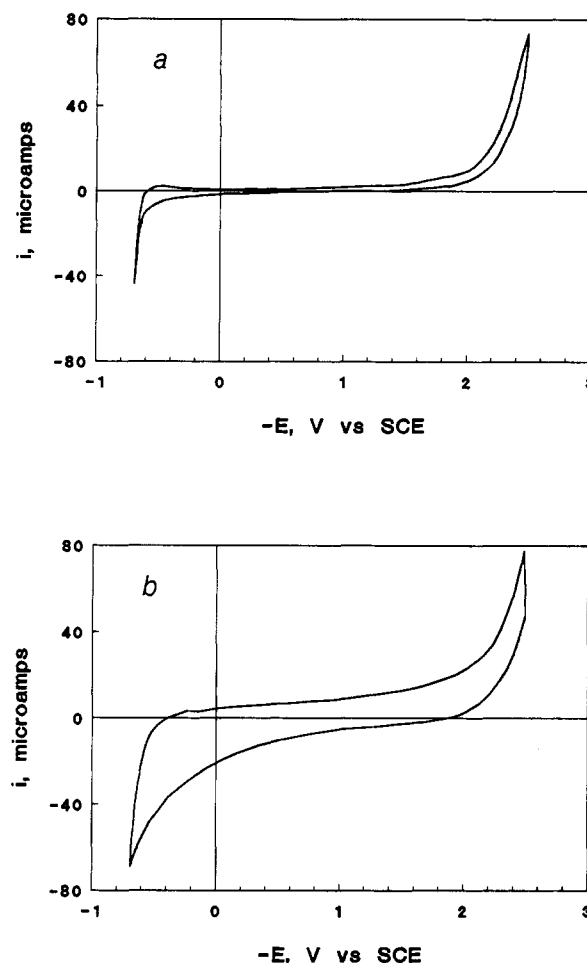
Conductance was measured with a YSI Model 3400 conductivity cell calibrated with  $0.1 \text{ M KCl}$  and a YSI Model 31 conductivity bridge. Bulk viscosities were measured at  $25.00 \pm 0.01^\circ \text{C}$  with an Ostwald viscometer calibrated with pure water.

**Analysis of Data.** Apparent diffusion coefficients ( $D'$ ) were obtained from the cyclic voltammetric (CV) peak currents by using the Randles-Ševčík equation. For quasireversible redox couples, peak currents at scan rates ( $\nu$ ) below  $1 \text{ V s}^{-1}$  were regressed vs  $\nu^{1/2}$  and the slope of this line extrapolated to  $0 \text{ V s}^{-1}$  was used to estimate  $D'$ . This provides an approximate correction for nonlinearity caused by quasireversible charge transfer (20). Formal potentials ( $E^\circ$ ) were taken as the midpoint between the cathodic and anodic peak potentials of the same CVs. Apparent standard heterogeneous rate constants ( $k^\circ$ ) were estimated from anodic-cathodic peak potential differences (21, 22) of CVs over a range of scan rates where these differences exceeded about 65 mV, assuming equal diffusion coefficients of reduced and oxidized forms of the redox couple and electrochemical transfer coefficients of 0.5.

Simulations of cyclic voltammograms were done by a previously described (23) expanding space grid explicit digital simulation program compiled in Turbo Basic on a PC-AT type microcomputer. Simulations assumed equal diffusion coefficients of both halves of the redox couples and electrochemical transfer coefficients of 0.5.

## RESULTS

**Physical Properties.** Two microemulsion compositions and an emulsion showed good conductivities (Table I) for electrochemical studies. Their bulk viscosities were much

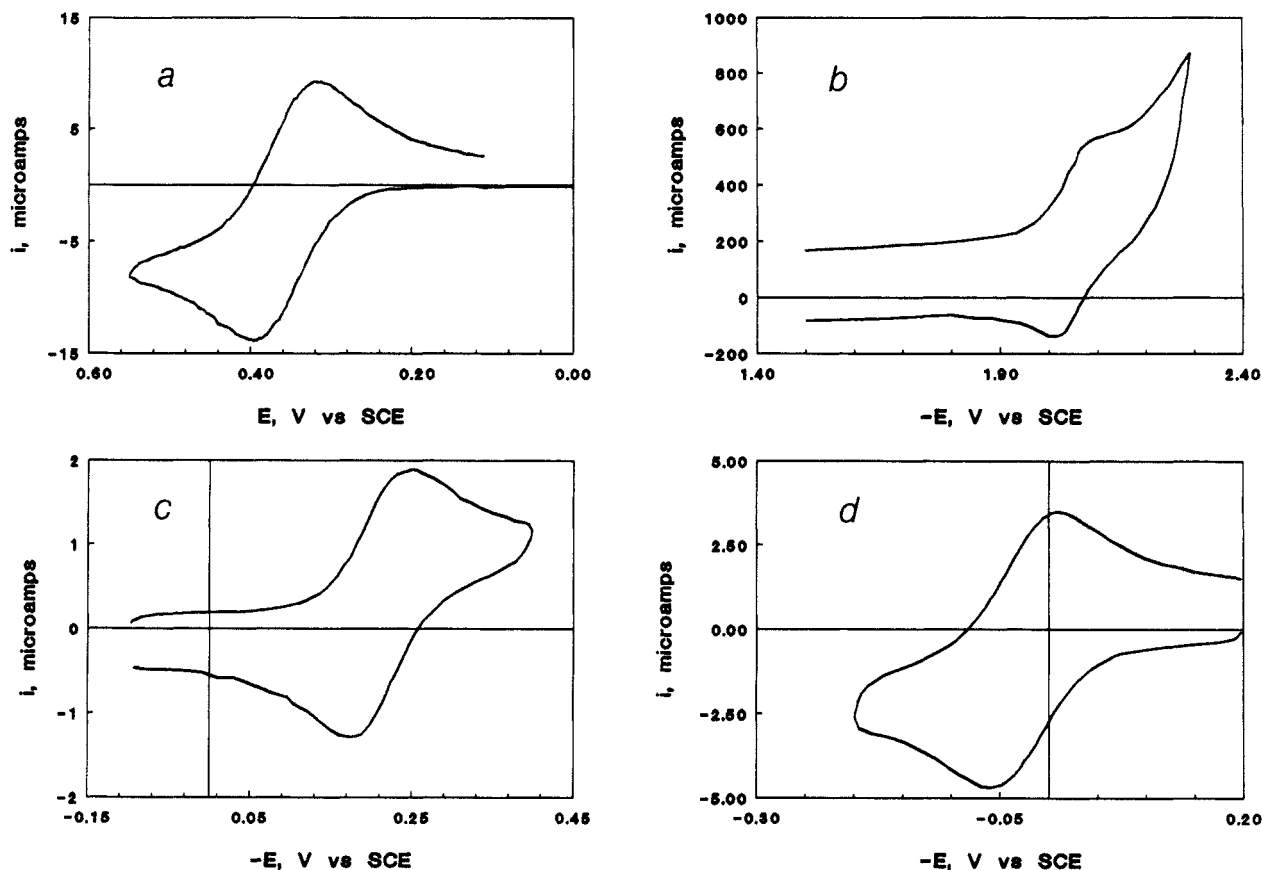


**Figure 1.** Cyclic voltammograms of DDAB/dodecane/water (21/40/39) at glassy carbon electrode: (a)  $0.10 \text{ V s}^{-1}$ ; (b)  $2.0 \text{ V s}^{-1}$ .

higher than either the oil or water from which they were made. Values of conductivity and viscosity for the microemulsions are in agreement with previously reported measurements (13).

**Reversible and Quasireversible Redox Couples.** Cyclic voltammetry of DDAB microemulsions not containing solute revealed a region between about  $+0.7$  and  $-2.2 \text{ V}$  in which the background current is flat at glassy carbon electrodes (Figure 1). Charging current increased as scan rate ( $\nu$ ) was increased. Redox reactions of solutes reduced or oxidized within this potential window were easily observed. Well-defined cyclic voltammograms of both water-soluble and oil-soluble redox couples were obtained in this medium (Figure 2). At concentrations above about  $0.7 \text{ mM}$ , ionic solutes caused turbidity in the medium. However, solubility of nonpolar organic compounds in the microemulsion was good. For example, more than  $32 \text{ mmol}$  of 4,4'-dibromobiphenyl was solubilized in a liter of the 21% DDAB microemulsion (cf. Table I) at  $25^\circ \text{C}$  compared to equilibrium solubilities at  $30^\circ \text{C}$  of  $0.3 \text{ mM}$  in aqueous micelles of  $0.10 \text{ M}$  cetyltrimethylammonium bromide (CTAB)/ $0.1 \text{ M KBr}$ , and about  $10^{-4} \text{ mM}$  in pure water.

Peak currents in the DDAB microemulsions were linearly dependent on concentration of solute up to about  $0.7 \text{ mM}$  for ionic solutes and about  $2 \text{ mM}$  for the nonpolar molecules. In contrast to behavior in some aqueous micellar media (24),  $D'$  values estimated by CV were independent of solute concentration for all solutes. To test the data against voltammetric theory, values of  $D'$ ,  $k^\circ$ , and  $E^\circ$  (Table II) obtained from CV in the 21% DDAB microemulsion for ferrocyanide, ferrocene, and ruthenium(III) hexaammine were used in computer simulations of a series of CVs. Simulated and experimental CVs were similar in appearance. Comparisons of simulated and



**Figure 2.** Cyclic voltammograms at glassy carbon electrodes in 21% DDAB microemulsion for (a) 1 mM ferrocene at  $0.1 \text{ V s}^{-1}$ , (b) 1 mM pyrene at  $51 \text{ V s}^{-1}$ , (c) 0.5 mM ruthenium(III) hexaammine at  $0.050 \text{ V s}^{-1}$ , and (d) 0.58 mM ferrocyanide at  $0.20 \text{ V s}^{-1}$ .

**Table II. Apparent Electrochemical Parameters at Glassy Carbon Electrodes in DDAB/Dodecane/Water Systems**

species	% DDAB <sup>a</sup>	$10^6 D'$ , $\text{cm}^2 \text{ s}^{-1}$	$k^\circ$ , $\text{cm s}^{-1}$	$E^\circ$ , V vs SCE
ferrocyanide	21	1.0	0.027	0.027
	13	0.79	0.017	0.022
	24	1.0	0.019	0.030
$\text{Ru}^{\text{III}}(\text{NH}_3)_6$	21	0.68	0.016	-0.213
cob(II)alamin	21	0.3	0.0002	-0.87
ferrocene	21	6.3	0.010	0.34
	13	5.6	0.004	0.38
	24	3.1	0.009	0.41
perylene	21	5	0.2	-1.64
pyrene	21	6	0.1	-2.06
9-PA	21	8	0.2	-1.95

<sup>a</sup> Compositions of microemulsions (13% and 21% DDAB) and emulsion (24% DDAB) as in Table I.

experimental peak currents, peak potentials, and anodic-cathodic peak separations (Figures 3–5) showed that theory developed for diffusion-kinetic controlled voltammetry in homogeneous solutions is obeyed quite well for these three quasireversible redox couples in bicontinuous DDAB microemulsions. Scatter in the data is attributed mainly to normal variance in electrode polishing (19).

CVs of similar quality were obtained for ferrocene and ferrocyanide in a microemulsion with 13% DDAB, as well as an emulsion (Table II). Only small differences were observed in  $D'$ ,  $E^\circ$ , and  $k^\circ$  values from those found in the 21% DDAB microemulsion.

**Polycyclic Aromatic Hydrocarbons.** PAHs such as perylene, pyrene, and 9-phenylanthracene yield anion radicals as products of their one-electron reductions. Water can rapidly donate a proton to these aromatic anion radicals (25–28). The resulting free radical is more easily reduced than its parent hydrocarbon. It is usually reduced as soon as it is formed at

the electrode. Thus, transfer of two electrons to PAHs may be achieved by the well-known ECE (electron transfer-chemical step-electron transfer) mechanism. If the anion radical is used up by protonation and reduction, it will not be detected on the reverse CV scan. For perylene, CVs in the 21% DDAB microemulsion showed an anodic peak current a significant fraction of the cathodic peak height at scan rates as low as  $1.0 \text{ V s}^{-1}$ , with nearly equal heights at  $41 \text{ V s}^{-1}$  (Figure 6). This suggests stability of the anion radical greater than that in aqueous CTAB micelles, in which a partial anodic peak is found at Hg electrodes only at  $\nu > 40 \text{ V s}^{-1}$  (29). For pyrene, an anodic peak about 50% of the height of the cathodic peak was found at  $10 \text{ V s}^{-1}$ . For 9-PA, at  $\nu > 41 \text{ V s}^{-1}$  an anodic peak only a small fraction of the cathodic peak height was observed.

Cathodic peak currents ( $i_p$ ) of perylene, pyrene, and 9-PA in the DDAB microemulsion expressed as the peak current function  $i_p/\nu^{1/2}$  increased with decreasing scan rate. For perylene the current function at  $\nu < 0.5 \text{ V s}^{-1}$  was about twice its value at  $\nu > 1 \text{ V s}^{-1}$  (Figure 7). 9-PA and pyrene did not show full 2-fold changes in current function over the  $\nu$ -range studied, but similar trends were found. At  $\nu < 0.5 \text{ V s}^{-1}$ , the cathodic peak for perylene shifted to more positive potentials as scan rate decreased. These results are consistent with occurrence of a two-electron ECE-type electrode reaction at lower scan rates as found for reduction of PAHs in organic solvents in the presence of proton donors (27–30). At higher scan rates, the chemical step, presumably protonation, does not have time to occur and the reaction becomes a nearly reversible one-electron process. Electrochemical parameters were estimated under the latter conditions from CV data (Table II).

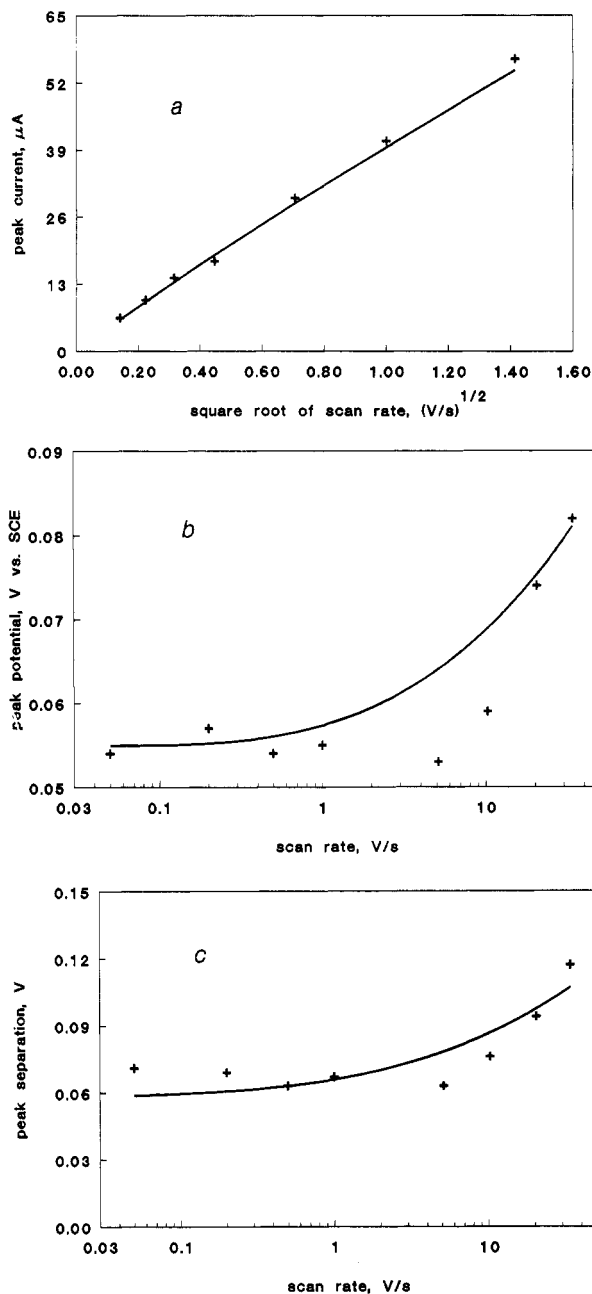
## DISCUSSION

**Electrochemical Parameters of Redox Couples.** Figures 3–5 show that voltammetric behavior in the DDAB microemulsion is similar to that in homogeneous solutions. Formal

Table III. Electrochemical Parameters of Redox Couples in Homogeneous Media

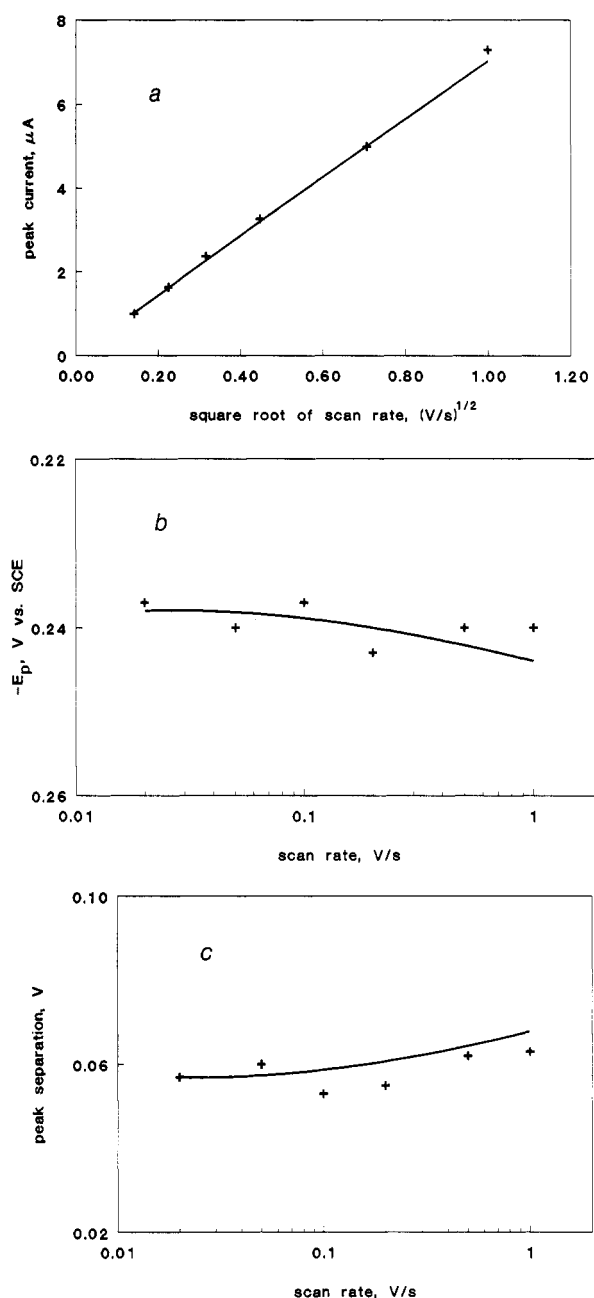
species	medium (elec) <sup>a</sup>	$10^6 D, \text{cm}^2 \text{s}^{-1}$	$k^\circ, \text{cm s}^{-1}$	$E^\circ, \text{V vs SCE}$	ref
ferrocyanide	0.5 M $\text{KNO}_3$ , pH 6.3 (GC)	7.0	0.098	0.204	19
$\text{Ru}^{\text{III}}(\text{NH}_3)_6$	pH 6.2 phosphate (GC)	3.4	0.03	-0.261	tw <sup>a</sup>
cob(II)alamin	aq pH 4-7 (GC)	1.8	0.0002	-0.85 <sup>b</sup>	31
ferrocene	MeCN (GC, CMD)	24	>0.8	0.311	19, 34
perylene	DMF (Hg)	5.7	5	-1.62	32
9-PA	DMF (Hg)	8	>0.8	-1.855	33
pyrene	DMF (Hg)			-2.09	25

<sup>a</sup> Abbreviations: GC, glassy carbon; CMD, carbon microdisk; tw, this work. <sup>b</sup> Reduction of base-on cob(II)alamin to base-off cob(I)alamin.



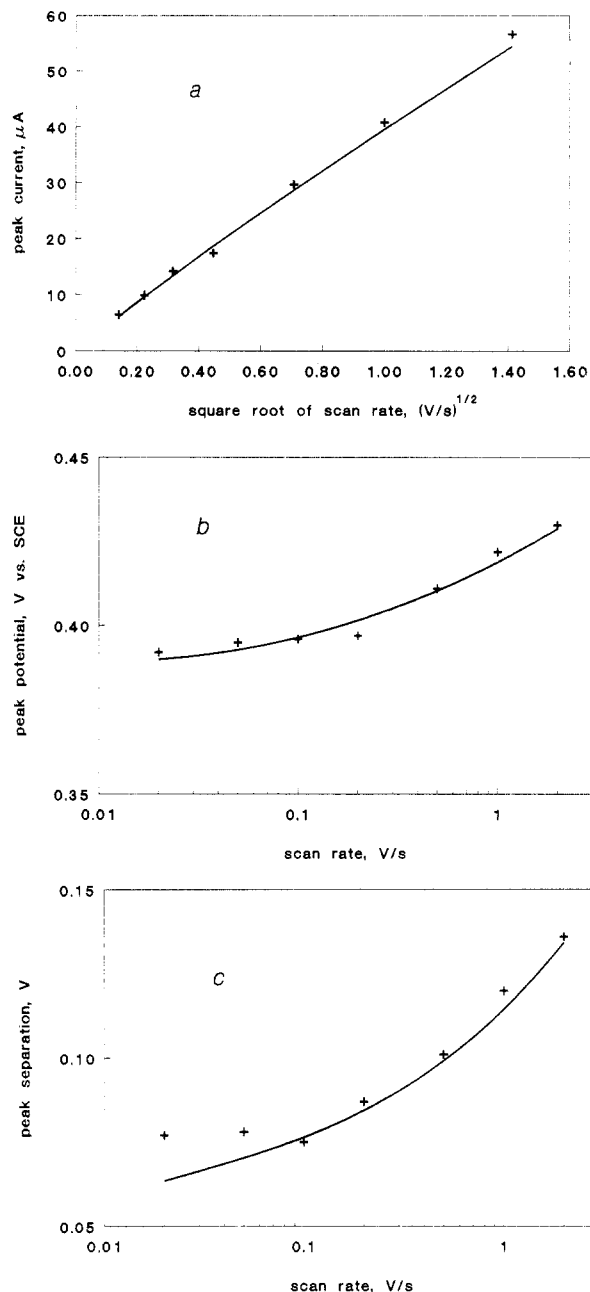
**Figure 3.** Comparison of simulated (—) and experimental (+) results for cyclic voltammetry of 0.58 mM ferrocyanide ion in 21% DDAB microemulsion for the influence of scan rate on (a) anodic peak current, (b) anodic peak potential, and (c) separation between anodic and cathodic peaks. Simulation parameters  $D = 1 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ ,  $k^\circ = 0.027 \text{ cm s}^{-1}$ , and  $E^\circ = 0.027 \text{ V}$ .

potentials and  $k^\circ$ 's of ruthenium(III) hexaamine were similar in water and the microemulsion (cf. Tables II and III). The same is true for cob(II)alamin (the Co(II) form of vitamin B<sub>12</sub>), assuming that electrochemical reduction in the microemulsion



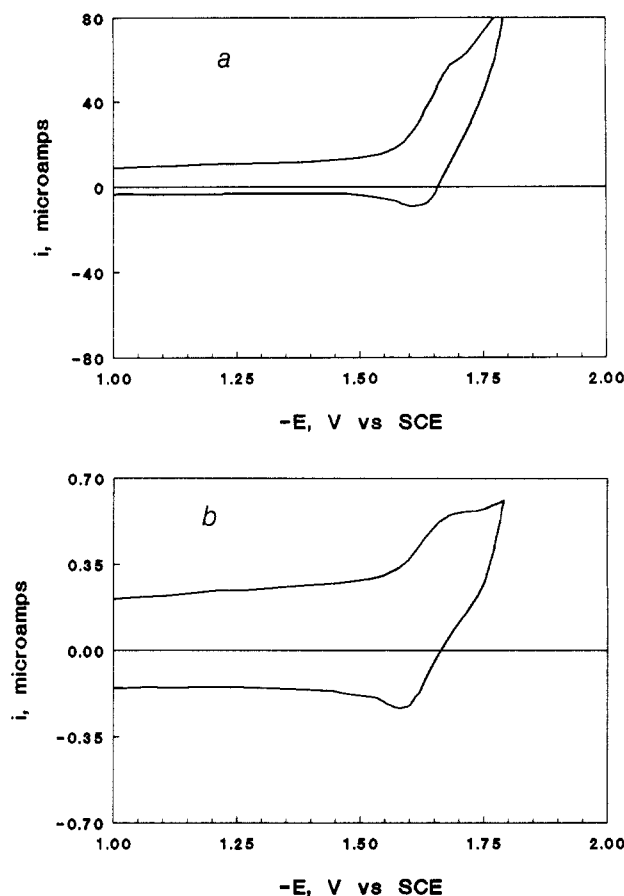
**Figure 4.** Comparison of simulated (—) and experimental (+) results for cyclic voltammetry of 0.5 mM ruthenium(III) hexaamine in 21% DDAB microemulsion for the influence of scan rate on (a) cathodic peak current, (b) cathodic peak potential, and (c) separation between anodic and cathodic peaks. Simulation parameters  $D = 0.68 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ ,  $k^\circ = 0.016 \text{ cm s}^{-1}$ , and  $E^\circ = -0.213 \text{ V}$ .

corresponds to electron transfer from the five-coordinate base-on cob(II)alamin to yield base-off, four-coordinate cob(I)alamin as in pH 4-7 homogeneous aqueous solutions (31). For ferrocyanide, the formal potentials in microemulsions and

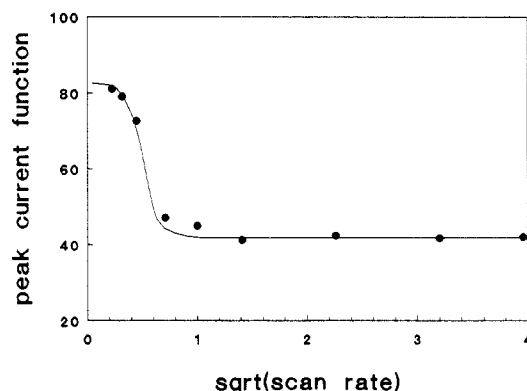


**Figure 5.** Comparison of simulated (—) and experimental (+) results for cyclic voltammetry of 1.0 mM ferrocene in 21% DDAB microemulsion for the influence of scan rate on (a) anodic peak current, (b) anodic peak potential, and (c) separation between anodic and cathodic peaks. Simulation parameters  $D = 6.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $k^0 = 0.01 \text{ cm s}^{-1}$ , and  $E^{0'} = 0.336 \text{ V}$ .

the emulsion are about 175 mV more negative than in water. Negative shifts of about 100 mV were also found in formal potentials of ferrocyanide at Pt and pyrolytic graphite electrodes in micellar solutions of 0.1 M hexadecyltrimethylammonium bromide (CTAB) (35). Such shifts could possibly reflect interaction of ferrocyanide(−4) anion with the positively charged head groups of the surfactants. Indeed, at concentrations below 0.01 M, CTAB formed an insoluble precipitate with potassium ferrocyanide (35), also suggesting interactions between ferrocyanide and cationic head groups. Ferrocyanide  $k^0$ 's were similar in microemulsions of different composition and in the emulsion and were slightly smaller than that in pH 6.3 aqueous potassium nitrate solution. Such small differences in  $k^0$  may be caused by variable surface preparations of the glassy carbon, by a higher pH (36) at the electrode surface in the unbuffered microemulsion, or by inhibition of hetero-



**Figure 6.** Cyclic voltammograms at glassy carbon electrodes in 21% DDAB microemulsion for 1.0 mM perylene at (a) 1.0  $\text{V s}^{-1}$  and (b) 41  $\text{V s}^{-1}$ .



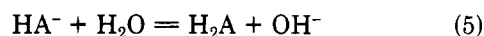
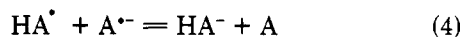
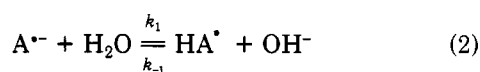
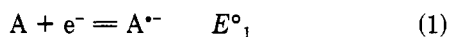
**Figure 7.** Influence of scan rate on cathodic peak current function ( $i_p/v^{1/2}$ ) for cyclic voltammograms of 1.0 mM perylene at glassy carbon electrodes in 21% DDAB microemulsion.

geneous electron transfer by microemulsion components adsorbed on the electrode.

Diffusion coefficients of ferrocyanide, ruthenium(III) hexaammine, and cob(II)alamin in the 21% DDAB microemulsion were 5–7 times smaller than in water (cf. Tables II and III). This is in line with a self-diffusion coefficient of water in conductive DDAB microemulsions that is 5-fold smaller than in bulk water (15). These results are consistent with residence of these ions almost entirely in the water phase.

The  $D'$  value of ferrocene in the microemulsions is about one-fourth that of its value in acetonitrile. Assuming that ferrocene resides entirely in the oil phase, this diffusivity ratio follows from the 4-fold greater viscosity of dodecane (Table I) over acetonitrile (37), as is consistent with the inverse Stokes–Einstein proportionality between  $D$  and viscosity. The  $D'$  values found are similar to the average of  $6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

## Scheme I



found for self-diffusion of dodecane in its microemulsions with DDAB and water (15). Ferrocene's electrochemical parameters (Table II) do not change much at different compositions of the microemulsion. Its  $k^\circ$  was smaller in the microemulsions than in acetonitrile.

Values of  $k^\circ$  for PAHs in DDAB microemulsions were somewhat smaller than at Hg electrodes in dry organic solvents, but still reflected rather fast charge transfer at the electrode.  $E^\circ$ 's were similar to those in organic solvents. These compounds, soluble mainly in the oil phase, also had  $D'$  values similar to that of dodecane in the DDAB microemulsions.

**Electroreduction of PAHs.** Data for perylene, pyrene, and 9-PA in DDAB microemulsions are consistent with their reduction in an ECE-type pathway at low scan rates. Such a mechanism resulting in hydrogenation of PAHs ( $A = \text{PAH}$ ) can be formulated (28) as shown in Scheme I. Equations 1–3 are the classical ECE pathway. If  $E^\circ_2 \gg E^\circ_1$ ,  $HA^\cdot$  will be reduced as soon as it is formed. Provided the rate of formation of  $HA^\cdot$  is fast with respect to the experimental time scale controlled by scan rate in CV, a two-electron cathodic peak will be observed. Increasing the scan rate may lead to "tuning out" of the chemical step in eq 2 such that only a one-electron reversible CV characteristic of eq 1 is observed. This happens for perylene, and to a partial extent for pyrene and 9-PA as well. However, where electrode reactions of PAHs in the presence of proton donors have been studied in sufficient detail, notably for anthracene and naphthalene (27, 28), the alternative DISP1 pathway has been demonstrated. DISP1 (eqs 1, 2, and 4) is an ECE variant featuring eq 2 as the chemical step following initial charge transfer but substituting homogeneous (eq 4) for heterogeneous charge transfer (eq 3) as the source of the second electron.

Analysis of CV current function or anodic/cathodic peak ratio vs scan rate data leads to slightly different values of the rate parameter  $k = k_1[H_2O] + k_{-1}$  for the ECE and DISP1 pathways (38). Thus, precise estimates of  $k$  by comparing the data to published working curves relating current function to  $\log(k/\nu)$  requires a knowledge of the exact electrode reaction mechanism, the analysis of which is beyond the scope of the present work. However, consideration of both mechanisms leads, after neglect of  $k_{-1}$ , to a range of lifetimes for the PAH anion radicals in the 21% DDAB microemulsion. Half-lives of 15–40 ms for perylene, 2–4 ms for pyrene, and <1 ms for 9-PA were estimated from the CV data. These lifetimes are smaller than those obtained in dry  $N,N$ -dimethylformamide in which reversible one-electron CVs found (39) at scan rates as low as 50 mV s<sup>-1</sup> suggest half-lives on the order of a second or more for these anion radicals.

## CONCLUSIONS

Conductive bicontinuous microemulsions are microheterogeneous fluids with interesting properties for electrochemical studies. Decreases of similar magnitude in diffusion coefficients of electroactive ions and water (self-diffusion) suggest that ions dissolved in the water phase diffuse with  $D$  values characteristic of that phase. Molecules dissolved in the oil

phase have diffusion coefficients characteristic of the oil phase. Even though DDAB/dodecane/water microemulsions have viscosities 20–40 times that of bulk water (Table I), diffusion of electroactive species is not greatly influenced by bulk viscosity and voltammetric signals with good signal to noise ratio are obtained. Charge transfer reactions controlled by mass transport and kinetics in DDAB microemulsions behave as if they occurred in homogeneous solutions.

Results for the PAHs suggest that water is accessible to ions formed by reduction of oil-soluble molecules. Stability of the anion radicals in the 21% DDAB microemulsion is less than in dry organic solvents, but greater than expected in the presence of large amounts of water.

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