

and may find applications in other systems because of the potential range they cover.

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**Registry No.** [Os(NH<sub>3</sub>)<sub>5</sub>O<sub>3</sub>SCF<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 83781-30-0; [Os(NH<sub>3</sub>)<sub>5</sub>CH<sub>3</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 109242-81-1; [Os(NH<sub>3</sub>)<sub>5</sub>C<sub>2</sub>H<sub>5</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>,

116232-04-3; [Os(NH<sub>3</sub>)<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>CCN](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 116232-06-5; [Os(NH<sub>3</sub>)<sub>5</sub>CH<sub>2</sub>=CHCN](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 116232-08-7; [Os(NH<sub>3</sub>)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 113161-74-3; [Os(NH<sub>3</sub>)<sub>5</sub>C<sub>6</sub>F<sub>5</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 113161-76-5; [Os(NH<sub>3</sub>)<sub>5</sub>(9-ACN)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 116232-10-1; [Os(NH<sub>3</sub>)<sub>5</sub>CH<sub>3</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 83781-33-3; [Os(NH<sub>3</sub>)<sub>5</sub>C<sub>2</sub>H<sub>5</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 116232-12-3; [Os(NH<sub>3</sub>)<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>CCN](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 116232-14-5; [Os(NH<sub>3</sub>)<sub>5</sub>CH<sub>2</sub>=CHCN](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 116232-16-7; [Os(NH<sub>3</sub>)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 116232-17-8; [Os(NH<sub>3</sub>)<sub>5</sub>C<sub>6</sub>F<sub>5</sub>CN](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 116232-19-0; [Os(NH<sub>3</sub>)<sub>5</sub>(9-ACN)](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, 116232-21-4.

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## Technetium Electrochemistry. 6.<sup>1</sup> Electrochemical Behavior of Cationic Rhenium and Technetium Complexes in Aqueous and Aqueous Micellar Solutions

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The behavior of the M(III/II) redox couple of a number of technetium(III) and rhenium(III) complexes of the general formula *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+</sup>, where D is 1,2-bis(diethylphosphino)ethane (depe) or 1,2-bis(dimethylphosphino)ethane (dmpe) and X is Cl or Br, has been investigated by cyclic voltammetry, chronocoulometry, and square-wave voltammetry in aqueous solution and in aqueous media that contain anionic (SDS), cationic (CTAB), or nonionic (Triton X-100) surfactants. In aqueous solution, insolubility of the electrogenerated *trans*-[M<sup>III</sup>D<sub>2</sub>X<sub>2</sub>]<sup>0</sup> complex results in adsorption at a glassy-carbon electrode for all complexes. However, ionic surfactants effectively solubilize the [M(dmpe)<sub>2</sub>X<sub>2</sub>]<sup>0</sup> species such that diffusion-controlled reversible cyclic voltammograms are observed in these media. In contrast, the more lipophilic [M(depe)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes behave differently in that while the solubility of the cationic M(III) complexes is enhanced in the surfactant media, the electrogenerated neutral M(II) complexes are adsorbed on the electrode surface. These observations are qualitatively discussed in terms of the net stabilization of the components of the M(III/II) redox pair in the various surfactant media. This stabilization is primarily dependent on (i) the formal charge on the electroactive complex (cationic vs neutral), (ii) the formal charge on the surfactant molecule that forms the micelle (anionic, cationic, or neutral), and (iii) the lipophilicity of the components of the redox couple (dmpe or depe) and somewhat dependent on the chemical nature of the ions from the supporting electrolyte.

### Introduction

Electrochemical techniques are important to the characterization of new inorganic complexes. Voltammetric methods allow for the assignment of oxidation states, assessment of chemical stability, and measurement of formal redox potentials, *E*<sup>o</sup>, of reversible redox couples. The development of cationic technetium-99m complexes as potential myocardial imaging agents<sup>2-5</sup> has especially benefited from applications of electrochemical and spectroelectrochemical techniques.<sup>3,6-9</sup> For example, several series of analogous technetium-99 and rhenium complexes that incorporate tertiary phosphine or arsine ligands have been synthesized in macroscopic amounts and characterized by physical methods,

including electrochemistry.<sup>3,6-9</sup> Systematic variation in the redox properties of these complexes is achieved by judicious choice of the donor properties of the coordinating ligands. The information obtained from the physical characterization of the <sup>99</sup>Tc and Re complexes, combined with complementary biodistribution studies, is useful in unraveling the complicated biological behavior of the analogous <sup>99m</sup>Tc species. In fact, such studies have shown that the *in vivo* redox fate of these complexes is an important criterion in determining their potential utility as organ imaging agents.<sup>8,9</sup> Thus, structure and redox reactivity studies in combination with biodistribution data form an important basis for the development of more effective technetium and rhenium radiopharmaceuticals.<sup>9</sup>

Previous electrochemical studies of technetium and rhenium complexes have focused on the characterization of their redox properties in nonaqueous solvents.<sup>3,10-14</sup> While chemically useful, the results of these nonaqueous studies are not directly relevant to the biological environment encountered by <sup>99m</sup>Tc myocardial imaging agents. In an effort to examine the redox behavior of cationic coordination complexes of the type *trans*-[M<sup>III</sup>D<sub>2</sub>X<sub>2</sub>]<sup>+</sup> (where D is a bidentate ditertiary phosphine ligand and X is a halide or pseudohalide ligand) in more biologically relevant media,

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**Table I.** Redox Potentials for the *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+0</sup> Couple in Aqueous and Aqueous Micellar Solutions<sup>a</sup>

	[M(dmpe) <sub>2</sub> Cl <sub>2</sub> ] <sup>+0</sup>		[M(dmpe) <sub>2</sub> Br <sub>2</sub> ] <sup>+0</sup>		[M(depe) <sub>2</sub> Cl <sub>2</sub> ] <sup>+0b</sup>	
	Re	Tc	Re	Tc	Re	Tc
0.5 M KNO <sub>3</sub> <sup>b,c</sup>	-0.516	-0.323	-0.408	-0.217	-0.404	-0.224
0.1 M SDS/0.1 M TEAP	-0.600	-0.396	-0.504	-0.300	-0.592	-0.404
32 mM CTAB/0.1 M NaCl	-0.472	-0.268	-0.364	-0.152	-0.428	-0.248
1.2% Triton X-100/0.1 M NaCl	-0.516	-0.308	-0.368	-0.188	-0.412	-0.216

<sup>a</sup> In V vs Ag/AgCl (3 M NaCl); peak potentials from square-wave voltammetry. Values are reproducible to ±5 mV. <sup>b</sup> Irreversible cyclic voltammetry; see text. <sup>c</sup> Technetium values taken from ref 12.

we have initiated a study of the electrochemical properties of these species in aqueous solution. The aqueous electrochemistry of *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+</sup> complexes is limited by the low solubility of the M(III) cationic complexes and insolubility of the electrogenerated M(II) neutral species. However, for many complexes aqueous surfactant media not only solubilize both forms of the *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+0</sup> redox couple but also allow facile analysis by conventional electrochemical methods. Furthermore, aqueous surfactant solutions are often considered to be biomimetic in that reactions on and within micelles may mimic reactions at biomembrane interfaces.<sup>15,16</sup>

In order to assess the redox properties of *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+</sup> complexes in a more biologically relevant milieu, we have undertaken the present studies, wherein surfactants are utilized to solubilize the components of the M(III/II) couples.

### Experimental Section

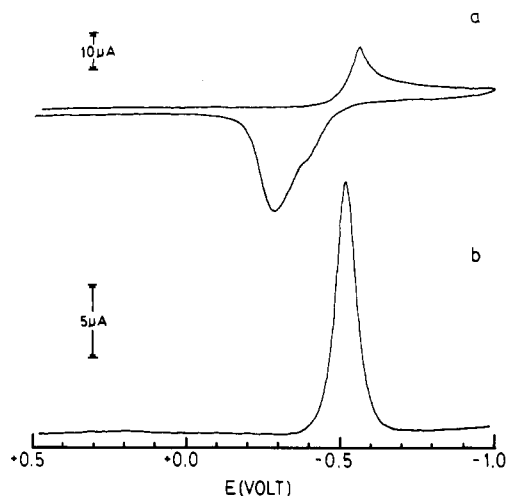
**General Considerations.** Technetium-99 emits a low-energy (0.292-MeV) β-particle with a half-life of 2.12 × 10<sup>5</sup> years. When this isotope is handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but standard radiation safety procedures must be used at all times to prevent contamination.

**Materials.** The technetium and rhenium complexes were available from previous studies.<sup>3,10</sup> Their preparation was accomplished by literature procedures: *trans*-[Tc(dmpe)<sub>2</sub>Cl<sub>2</sub>]Cl,<sup>3</sup> *trans*-[Tc(dmpe)<sub>2</sub>Br<sub>2</sub>]Br,<sup>3</sup> *trans*-[Tc(depe)<sub>2</sub>Cl<sub>2</sub>]Cl,<sup>3</sup> *trans*-[Re(dmpe)<sub>2</sub>Cl<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub>,<sup>8</sup> *trans*-[Re(dmpe)<sub>2</sub>Br<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub>,<sup>8</sup> and *trans*-[Re(depe)<sub>2</sub>Cl<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub>.<sup>8</sup> The ligand abbreviations dmpe and depe represent 1,2-bis(dimethylphosphino)ethane and 1,2-bis(diethylphosphino)ethane, respectively.

Hexadecyltrimethylammonium bromide (CTAB) was purchased from Mallinckrodt, while Triton X-100 was obtained from Rohm and Haas. Triton X-100 is the common name for the neutral surfactant polyoxyethylene (9.5) *p*-1,1,3,3-tetramethylbutylphenol. Both surfactants were used as received. Sodium dodecyl sulfate (SDS) was purchased from MC/B, recrystallized from ethanol, and dried in vacuo for 5 h. Polarographic grade tetraethylammonium perchlorate (TEAP) was obtained from G. F. Smith Chemical Co. and used as received. All solutions were prepared with water purified by a Barnstead Organicpore filtration system. All other chemicals were of reagent grade quality.

**Instrumentation.** Electrochemical measurements were made with a Bioanalytical Systems Inc. BAS-100 electrochemical analyzer. Voltammograms were recorded on a Houston Instruments DMP-2 digital plotter. The working electrode for the electrochemical measurements was a glassy-carbon electrode (GCE (BAS)) with an effective surface area of 0.071 cm<sup>2</sup> as determined by chronocoulometry of a standard potassium ferricyanide solution.<sup>17</sup> The working electrode for determination of the critical micelle concentration, cmc, of 0.1 M SDS/0.1 M TEAP was a PAR Model 303 static-mercury-drop electrode interfaced to the BAS-100. An aqueous Ag/AgCl (3 M NaCl) electrode (BAS) and a platinum wire were used as the reference and auxiliary electrodes, respectively. All potentials are reported versus the Ag/AgCl (3 M NaCl) electrode. Absorption measurements were obtained by using a Perkin-Elmer Lambda 5 UV-vis spectrophotometer.

**Methods.** Surfactant solutions were prepared by dissolving the surfactant and electrolyte in water to give solutions with micelle concentrations, [M], between 0.5 and 2.0 mM. The surfactant, supporting electrolyte, and approximate micelle concentrations were as follows: 0.1 M SDS, 0.1 M TEAP, [M] ≈ 1.6 mM; 0.1 M SDS, 0.1 M NaCl, [M] ≈ 1.6 mM; 32 mM CTAB, 0.1 M NaCl, [M] ≈ 0.5 mM; 1.2% (vol %)



**Figure 1.** Electrochemical behavior of 0.9 mM [Re(dmpe)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in 0.5 M KNO<sub>3</sub>/H<sub>2</sub>O at a GCE: (a) cyclic voltammogram at 100 mV/s; (b) Osteryoung square-wave voltammogram.

Triton X-100, 0.1 M NaCl, [M] ≈ 1.0 mM.<sup>18</sup> The micelle concentrations were approximated by using literature and measured values for the cmc and aggregation numbers.<sup>19-21</sup> The cmc value for a solution of 0.1 M SDS/0.1 M TEAP was determined by phase-selective ac voltammetry using the method of Emons et al.<sup>22</sup> and was found to be 0.1 mM. The error in the micelle concentrations is estimated to be ±25% since both the cmc and aggregation numbers are influenced by the addition of supporting electrolyte.<sup>21</sup> Knowledge of the exact micelle concentration is not necessary to this study; solutions were prepared so that the ratio of inorganic complex to micelle is approximately 1.

The GCE working electrode was routinely polished with alumina between electrochemical measurements to ensure a reproducible surface. Deoxygenation was accomplished by an argon purge. Osteryoung square-wave voltammograms were obtained by scanning a potential window from +0.500 to -1.000 V. Typical parameters were as follows: square-wave amplitude, 25 mV; step frequency, 15 Hz; potential step, 4 mV.

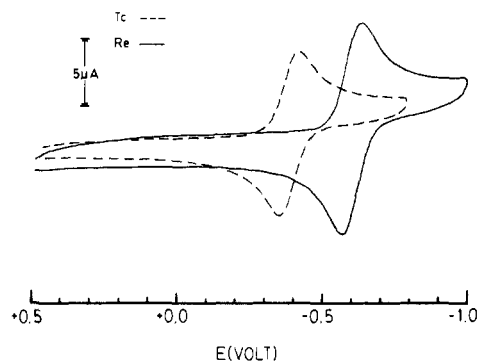
### Results and Discussion

**Electrochemistry of *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+</sup> (M = Tc, Re) Complexes.** The *trans*-[MD<sub>2</sub>X<sub>2</sub>]<sup>+</sup> complexes exhibit a rich electrochemistry in nonaqueous solvents.<sup>10-14</sup> The predominate redox processes are two successive one-electron reductions described by eq 1 and 2.



For all combinations of D and X ligands that have been studied,

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**Figure 2.** Cyclic voltammograms of 1.47 mM  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  (—) and 1.62 mM  $[\text{Tc}(\text{dmpe})_2\text{Cl}_2]^+$  (---) in 0.1 M SDS/0.1 M TEAP/ $\text{H}_2\text{O}$ . The scan rate is 100 mV/s.

the M(III/II) couple (eq 1) is electrochemically and chemically reversible; however, the chemical stability of the anionic  $\text{trans-}[\text{MD}_2\text{X}_2]^-$  species depends on the nature of the D and X ligands and in some cases results in a chemically irreversible M(II/I) couple (eq 2).

In this study, electrochemical measurements have been performed in aqueous solution and aqueous solutions modified with anionic (SDS), cationic (CTAB), and nonionic (Triton X-100) surfactants. Attention is focused on the M(III/II) couple since this comprises the basis of the biologically relevant redox process.<sup>8,9</sup> Analogous complexes of technetium and rhenium yield qualitatively similar voltammograms in a given surfactant solution, so discussion of the electrochemical behavior is applicable to both metal centers. Most of the mechanistic studies have been performed on the nonradioactive rhenium complexes; any differences between the technetium and rhenium systems are noted in the following discussions. Table I summarizes the electrochemical data for all combinations of complexes and media that were investigated.

(i) **In 0.5 M  $\text{KNO}_3/\text{H}_2\text{O}$ .** The electrochemistry of the M(III/II) couple in aqueous solution is complicated by the insolubility of the electrogenerated neutral species (eq 1). Figure 1a illustrates the cyclic voltammogram of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  in 0.5 M  $\text{KNO}_3$ . A negative potential scan initiated at +0.500 V with a scan rate of 100 mV/s reveals non-Nernstian behavior in the cyclic voltammogram. This behavior can be explained by deposition of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^0$  onto the electrode surface during reduction. The peak potential for the reduction is -0.560 V. On the reverse scan, a broad oxidation wave that drops to residual current after the peak potential (-0.285 V) is observed for the stripping of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^0$  off the electrode by reoxidation to the cationic complex. In order to effect the oxidation of Re(II) to Re(III), a greater oxidizing potential is required. Thus, a peak separation of 275 mV is observed in 0.5 M  $\text{KNO}_3$ , compared to the Nernstian value of 59 mV expected for a one-electron diffusion-controlled reversible process. This behavior is typical for adsorbed species that are stabilized by interaction with the electrode surface.<sup>23</sup> The shoulder on the oxidation wave (ca. -0.380 V) may reflect the stripping of multilayers of the adsorbed neutral species off the electrode or possibly stripping of adsorbed species in different orientations.

Square-wave voltammetry was also used to study the electrochemistry of the  $\text{trans-}[\text{MD}_2\text{X}_2]^+$  complexes. Figure 1b shows the square-wave voltammogram of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  in 0.5 M  $\text{KNO}_3$ . A single peak is observed with a peak potential of -0.516 V. In aqueous solution, all of the  $\text{trans-}[\text{MD}_2\text{X}_2]^+$  complexes show behavior analogous to that obtained for  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  and thus were studied by square-wave voltammetry in addition to cyclic voltammetry. The peak potentials from square-wave voltammetry are used for comparison of the redox potentials of the different complexes and media and are summarized in Table I.

**Table II.** Effect of Scan Rate on  $E^\circ$  and  $i_p$  for  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  in 0.1 M SDS/0.1 M TEAP Solution<sup>a,b</sup>

$v$ , mV/s	$i_{pc}$ , $\mu\text{A}$	$i_{pa}$ , $\mu\text{A}$	$i_{pc}/i_{pa}$	$E^\circ$ , V
20	3.48	3.48	1.00	-0.601
50	5.56	5.70	1.03	-0.602
100	7.65	7.87	1.03	-0.602
150	9.32	9.60	1.03	-0.602
200	10.62	11.00	1.04	-0.603
300	12.84	13.32	1.04	-0.602
400	14.79	15.34	1.04	-0.602
500	16.43	17.04	1.04	-0.603

<sup>a</sup>  $[\text{Re}] = 1.5 \text{ mM}$ . <sup>b</sup>  $i_{pa}$  vs  $v^{1/2}$ : slope 22.7  $\mu\text{A s}^{1/2}/\text{V}^{1/2}$ ; y intercept 0.41  $\mu\text{A}$ ;  $R = 0.999$ .  $i_{pc}$  vs  $v^{1/2}$ : slope 23.8  $\mu\text{A s}^{1/2}/\text{V}^{1/2}$ ; y intercept 0.29  $\mu\text{A}$ ;  $R = 0.999$ .

**Table III.** Electrochemical Parameters from Cyclic Voltammetry for the  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+/0$  Couple as a Function of SDS Concentration<sup>a</sup>

[SDS], M	$E^\circ$ , V <sup>b</sup>	$\Delta E_p$ , V <sup>b</sup>	$i_{pc}$ , $\mu\text{A}$	$i_{pc}/i_{pa}$	$10^{-7}D$ , $\text{cm}^2/\text{s}^c$
0.005 <sup>d</sup>	-0.570	0.060	3.62	1.02	
0.05	-0.591	0.064	7.85	1.00	7.5
0.1	-0.597	0.066	7.45	0.99	6.1
0.15	-0.601	0.070	7.13	0.99	5.3
0.20	-0.610	0.067	6.83	0.98	4.1
0.25	-0.608	0.070	6.10	0.98	3.2

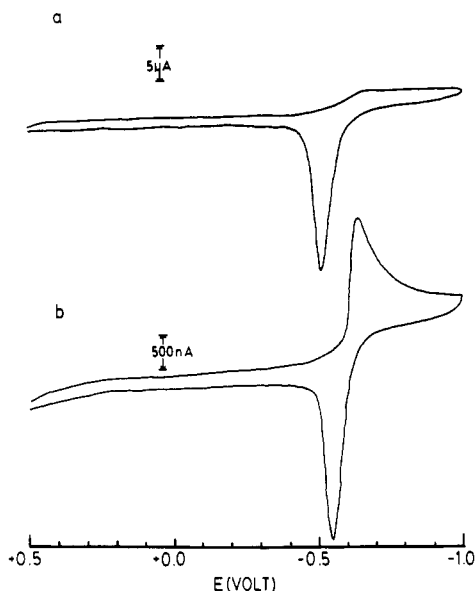
<sup>a</sup> Conditions: scan rate 100 mV/s;  $[\text{Re}] = 1.5 \text{ mM}$ ;  $[\text{TEAP}] = 0.1 \text{ M}$ . <sup>b</sup>  $E^\circ = (E_{pc} + E_{pa})/2$  and  $\Delta E_p = E_{pc} - E_{pa}$  vs Ag/AgCl (3 M NaCl). <sup>c</sup> Determined at each surfactant concentration from the slope of a plot of  $i_{pc}$  vs  $v^{1/2}$ . <sup>d</sup>  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  is not completely solubilized at this surfactant concentration.

(ii) **In 0.1 M SDS/0.1 M TEAP/ $\text{H}_2\text{O}$ .** All of the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes exhibit similar behavior in 0.1 M SDS/0.1 M TEAP solution. Figure 2 illustrates typical cyclic voltammograms for  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  and  $[\text{Tc}(\text{dmpe})_2\text{Cl}_2]^+$ . Unlike the situation in pure aqueous solution, electrochemistry in 0.1 M SDS/0.1 M TEAP is uncomplicated by deposition of the neutral species. Addition of SDS effectively solubilizes the  $\text{trans-}[\text{M}(\text{dmpe})_2\text{X}_2]^0$  complexes and leads to reversible M(III/II) redox couples. Establishment of the reversibility of the metal-centered reduction is based on the following observations made from the representative electrochemical data in Table II for the cyclic voltammetry of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  (Figure 2). The ratio of the peak currents is approximately unity and, within experimental error, is independent of scan rate. Furthermore, the cathodic and anodic peak currents are linearly proportional to the square root of the scan rate as defined by the Randles-Sevcik equation. All three conditions indicate the M(III/II) redox process is a diffusion-controlled reversible electron transfer. The average  $E^\circ$  values and peak-to-peak separations derived from cyclic voltammograms of the technetium and rhenium complexes in Figure 2 are -0.393 V with  $\Delta E = 63 \text{ mV}$  and -0.599 V with  $\Delta E = 66 \text{ mV}$ , respectively.

$E^\circ$ ,  $i_{pc}$ , and  $i_{pa}$ , however, are dependent on the concentration of SDS when monitored at a constant scan rate and M(III) concentration. Table III summarizes these data, as well as the diffusion coefficients for  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$ , as a function of SDS concentration. At 0.005 M, SDS only partially solubilizes  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$ , but even so, reversible electrochemistry is observed. For the remaining solutions, the peak current and the corresponding diffusion coefficient decrease as the SDS concentration increases. The dramatic difference in electrochemical behavior between 0.5 M  $\text{KNO}_3$  and 0.1 M SDS/0.1 M TEAP indicates that the metal complex is associated with the micellar environment. As a result, the rate-determining step of the electrochemical reaction reflects the diffusion of the micelle-solubilized molecule to the electrode. The data of Table III show that the diffusion coefficient decreases in the presence of SDS micelles relative to the value observed in aqueous solution ( $D = 3.4 \times 10^{-6} \text{ cm}^2/\text{s}$ ).<sup>24</sup> Kaifer and Bard<sup>25</sup> have observed similar decreases in diffusion

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(24) Determined by chronocoulometry<sup>17</sup> of a 1.02 mM solution in 0.1 M (TEA)Cl/ $\text{H}_2\text{O}$ ; average of five trials. (TEA)Cl was substituted for TEAP since  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  precipitates as the  $\text{ClO}_4^-$  salt.

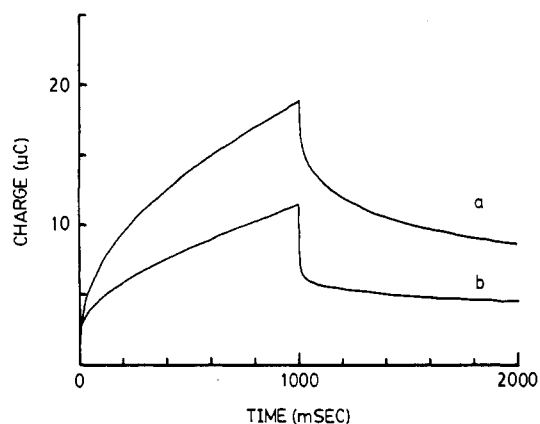


**Figure 3.** Cyclic voltammograms of 1.53 mM  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  in 0.1 M SDS/0.1 M TEAP/ $\text{H}_2\text{O}$  as a function of scan rate: (a) 100 mV/s; (b) 5 mV/s.

coefficients for the reduction of water-soluble methylviologen in SDS micellar solution and attribute this phenomenon to the increase in effective size of the micelle-solubilized methylviologen. The micelle-solubilized molecule diffuses to the electrode more slowly and results in lower peak currents. Further addition of surfactant increases the viscosity of the solution,<sup>26</sup> which in turn retards diffusion and accounts for the further decrease in  $i_p$ ,  $i_{pa}$ , and  $D$  as the SDS concentration is increased. These data also show that  $E^{\circ'}$  shifts to more negative potentials with increasing SDS concentration. Analogous behavior has been reported for the oxidation of  $[\text{Os}(5\text{-dmbpy})_3]^{2+}$ <sup>27</sup> (where 5-dmbpy is 5,5'-dimethyl-2,2'-bipyridine) in aqueous and aqueous SDS solutions.

The  $[\text{M}(\text{depe})_2\text{Cl}_2]^+$  complexes behave quite differently from their dmpe analogues. Figure 3 illustrates the cyclic voltammogram of  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  as a function of scan rate. At 100 mV/s (Figure 3a), the reduction of Re(III) to Re(II) occurs without the well-defined peak potential that was observed for the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes. However, at slow scan rates (Figure 3b, 5 mV/s), a more typical current response is observed. On the reverse scan, a sharp oxidation wave appears at both scan rates. Presumably, the solubility of  $[\text{Re}(\text{depe})_2\text{Cl}_2]^0$  is not enhanced significantly in SDS solution and deposition of the neutral complex occurs on the electrode surface. The sharp wave results from oxidative stripping of this neutral species off the electrode. Double-potential-step chronocoulometry experiments provide further evidence that  $[\text{Re}(\text{depe})_2\text{Cl}_2]^0$  adsorbs onto the electrode. Figure 4 illustrates comparative chronocoulograms of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  (Figure 4a) and  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  (Figure 4b). For  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$ , a charge ( $Q$ ) vs time ( $t$ ) response typical for a diffusion-controlled reversible process is observed, whereas for  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  the sharp decrease in charge on the reverse step clearly indicates a surface-active electrochemical process. If  $[\text{Re}(\text{depe})_2\text{Cl}_2]^0$  is adsorbed, a plot of  $Q$  vs  $t^{1/2}$  for the reverse step should be within experimental error a straight line with a nonzero intercept.<sup>28</sup> Analysis of the data yield an intercept (background corrected) of 2.8  $\mu\text{C}$  for  $[\text{Re}(\text{depe})_2\text{Cl}_2]^0$  as compared to 0.2  $\mu\text{C}$  for  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^0$ .

(iii) In 32 mM CTAB/0.1 M NaCl/ $\text{H}_2\text{O}$ . For all complexes studied, the electrochemical behavior in 32 mM CTAB/0.1 M NaCl solution is qualitatively similar to the behavior observed



**Figure 4.** Charge vs time response for double-potential-step chronocoulometry of 1.50 mM  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  (a) and 1.47 mM  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  (b) in 0.1 M SDS/0.1 M TEAP/ $\text{H}_2\text{O}$ . The potential step was from -200 to -900 mV with a pulse width of 1000 ms.

**Table IV.** Visible Absorption Maxima for  $[\text{ReD}_2\text{X}_2]^+$  Complexes in Aqueous and Aqueous Micellar Solutions<sup>a</sup>

	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , $\text{M}^{-1} \text{cm}^{-1}$ )		
	$\text{H}_2\text{O}$	SDS/ $\text{H}_2\text{O}$ <sup>b</sup>	CTAB/ $\text{H}_2\text{O}$ <sup>c</sup>
$[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$	411 (2700) 439 (2500)	409 (3100) 437 (2900)	411 (2700) 439 (2500)
$[\text{Re}(\text{dmpe})_2\text{Br}_2]^+$	466 (3000)	465 (3500)	466 (3400)
$[\text{Re}(\text{depe})_2\text{Cl}_2]^+$	413 (d) 443 (d)	408 (2800) 436 (2500)	410 (2700) 438 (2400)

<sup>a</sup> Molar absorptivities are  $\pm 10\%$ . <sup>b</sup> Contains 0.1 M TEAP. <sup>c</sup> Contains 0.1 M NaCl. <sup>d</sup> Low solubility limits accurate determination.

in 0.1 M SDS/0.1 M TEAP solution. Reversible M(III/II) redox couples are observed for the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes, while irreversible voltammograms are obtained for the  $[\text{M}(\text{depe})_2\text{Cl}_2]^+$  complexes. Comparison of the SDS and CTAB electrochemical data listed in Table I indicates that the M(III/II) reduction potential is dependent on the nature of the surfactant. This dependence, which presumably reflects the difference in the formal charge of the surfactant molecule, is discussed in a following section.

**Solution Properties.** The *trans*- $[\text{MD}_2\text{X}_2]^+$  complexes exhibit low solubility in pure aqueous solution; however, solubilization can be somewhat enhanced by utilization of halide or  $\text{CF}_3\text{SO}_3^-$  counterions instead of  $\text{BF}_4^-$  and  $\text{PF}_6^-$ . Alternatively, millimolar concentrations of these complexes can be obtained in surfactant solutions, independent of the counterion employed.

Ionic surfactants aggregate into micellar assemblies in which the hydrophobic tails and polar head groups of the monomeric units align in such a way to give a nonpolar interior and a polar interface with the bulk aqueous solution.<sup>21,26,29,30</sup> Because of the variety of microenvironments present within the micellar structure, slightly modified complexes can be solubilized in different ways. Several different solute/micelle interactions are possible depending on the nature of the surfactant and solute molecules. The solute can be either situated in the hydrophobic interior, radially at various depths, or adsorbed at the micelle surface.<sup>21</sup> Coulombic interactions and the hydrophobicity of the complexes are the dominant factors that affect solubilization. Since all of the M(III) complexes studied in this work are monovalently charged, it is reasonable to assume the Coulombic interactions between each M(III) complex and a given ionic surfactant are similar. Evidence for the affect of the hydrophobicity of the complex on the mode of micellar solubilization can be inferred from comparisons of visible absorption maxima in  $\text{H}_2\text{O}$  and surfactant solutions. Table IV lists the absorption maxima for the rhenium complexes in these

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media.  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  exhibits a slightly greater shift in peak maxima (in 0.1 M SDS/0.1 M TEAP and 32 mM CTAB/0.1 M NaCl vs  $\text{H}_2\text{O}$ ) than do  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  and  $[\text{Re}(\text{dmpe})_2\text{Br}_2]^+$ ; i.e.,  $\Delta\lambda_{\text{max}} = 0.8 \pm 1.0 \text{ nm}$  ( $n = 6$ ) for dmpe complexes and  $\Delta\lambda_{\text{max}} = 5.0 \pm 1.6 \text{ nm}$  ( $n = 4$ ) for depe complexes. This may suggest that, within the micelles,  $[\text{Re}(\text{depe})_2\text{Cl}_2]^+$  exists in a less polar environment than the analogous dmpe complexes.  $[\text{M}(\text{depe})_2\text{Cl}_2]^+$  complexes, by virtue of the ethyl substituents, are more hydrophobic than are  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes, and therefore they are presumably situated further into the hydrophobic core of the micelle. This deeper penetration of the depe complexes into the micelle interior could contribute to the scan-rate dependence (Figure 3) observed for these complexes.

**Electrochemical Mechanism in Ionic Micellar Solutions.** The electrochemical results obtained in ionic surfactant solutions imply that the mechanistic details of the reduction of the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  and  $[\text{M}(\text{depe})_2\text{Cl}_2]^+$  complexes are different. Within the bulk solution, aggregation of the surfactant monomers forms the micellar structures that solubilize the metal complex. Partitioning between the aqueous and micellar phases of the bulk solution is possible, but the enhanced solubility and dramatic difference in electrochemistry from that observed in 0.5 M  $\text{KNO}_3$  indicate the complexes are largely situated within the micellar environment. At the 1:1 ratio of solute molecules to micelles utilized in these studies, the number of solute molecules that reside in a micelle can be described by Poisson statistics.<sup>31</sup>

The results of Table III indicate that it is the micelle-solubilized cation which diffuses to the electrode surface. If both forms of the redox couple are solubilized and, therefore, stabilized within the micellar environment, diffusion-controlled reversible electrochemistry is observed. This is apparently the case for cyclic voltammetry of the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes, where fast, uninhibited electron transfer is observed between the electrode and the solubilized reactant. However, this is not the case for the cyclic voltammetry of the  $[\text{M}(\text{depe})_2\text{Cl}_2]^+$  complexes. For the more lipophilic depe complexes, the scan-rate dependence of the cyclic voltammogram (Figure 3) indicates that movement of the complex to the outer surface of the micellar environment may be a necessary prerequisite for electron transfer. This reorganization presumably is required because the depe complexes are solubilized further into the hydrophobic microenvironment of the micelle. At 5 mV/s, the reorganization occurs on a time scale comparable with the scan rate and results in a cathodic peak corresponding to the reduction of M(III) to M(II) (Figure 3b). A further driving force for this reorganization step may be related to the observation that  $[\text{M}(\text{depe})_2\text{Cl}_2]^0$  adsorbs onto the electrode even in micellar solution. Thus, the electrogenerated neutral complex is stabilized by adsorption onto the electrode rather than by solubilization within the micelle.

While the above mechanistic discussion is both qualitative and oversimplified, it does adequately account for the experimental results. These results strongly imply that the hydrophobicity of the metal complex affects its solubilization in the micelle, which in turn influences the electrochemical response.

**Electrochemistry in Nonionic 1.2% Triton X-100/0.1 M NaCl/H<sub>2</sub>O.** The electrochemical behavior in the nonionic surfactant Triton X-100 offers some contrasts to that observed in the ionic surfactants. For the  $[\text{M}(\text{depe})_2\text{Cl}_2]^+$  complexes, the electrochemical response is the same as in the ionic surfactants, where adsorption and stripping govern the general shape of the voltammograms. On the other hand, differences occur for the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes. The cyclic voltammograms of the dichloro analogues  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  and  $[\text{Tc}(\text{dmpe})_2\text{Cl}_2]^+$  in 1.2% Triton X-100 are unique in that they reflect different electrochemistry for analogous technetium and rhenium complexes in an identical surfactant solution.  $[\text{Tc}(\text{dmpe})_2\text{Cl}_2]^+$  exhibits the typical diffusion-controlled reversible M(III/II) redox couple observed for the  $[\text{M}(\text{dmpe})_2\text{X}_2]^+$  complexes in SDS and CTAB. In marked contrast, the cyclic voltammogram of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$

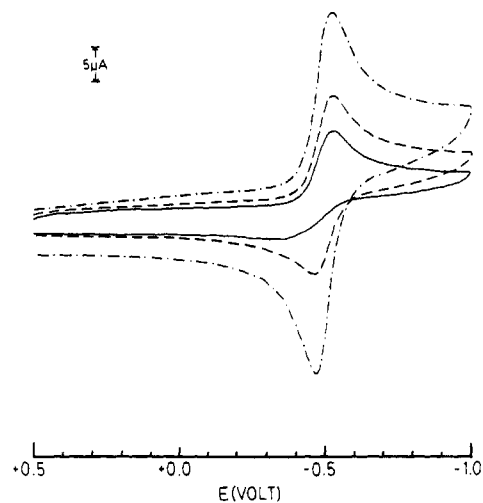


Figure 5. Cyclic voltammograms of 1.13 mM  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  in 1.2% Triton X-100/0.1 M NaCl/ $\text{H}_2\text{O}$  as a function of scan rate: (---) 300 mV/s; (-·-) 100 mV/s; (—) 50 mV/s.

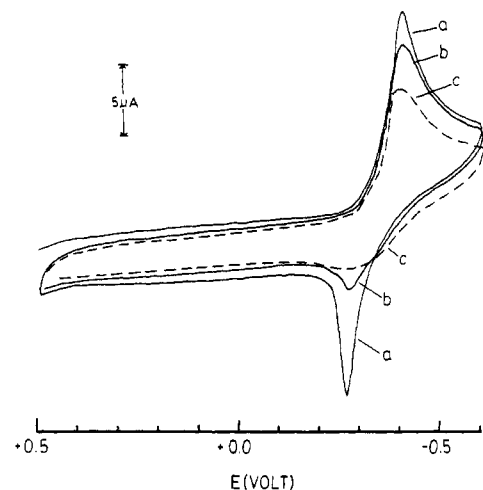


Figure 6. Repetitive cyclic voltammograms of 1.11 mM  $[\text{Re}(\text{dmpe})_2\text{Br}_2]^+$  in 1.2% Triton X-100/0.1 M NaCl/ $\text{H}_2\text{O}$ : (a) first cycle; (b) second cycle; (c) 20th cycle. The scan rate is 100 mV/s.

is dependent on the scan rate. As can be seen in Figure 5, the ratio of  $i_{\text{pc}}/i_{\text{pa}}$  is greater than unity at the slow scan rates but approaches unity at 300 mV/s. Scan-rate dependencies of this nature imply an EC mechanism is operative in which reduction of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  to  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^0$  is followed by a chemical reaction.<sup>32</sup> In view of the robust character of the *trans*- $[\text{MD}_2\text{X}_2]^+$  complexes and the large peak separations observed at slow scan rates, this chemical reaction most likely involves a reorientation of the complex within the micellar environment. The rate constant for this reorientation is estimated by the method of Nicholson<sup>33-35</sup> to be  $0.1 \text{ s}^{-1}$ .

Figure 6 illustrates repetitive cyclic voltammograms for  $[\text{Re}(\text{dmpe})_2\text{Br}_2]^+$  scanned at 100 mV/s (for clarity only the first, second, and 20th cycles are shown). On the initial cycle, cathodic and anodic peaks are observed. Subsequent cycles reveal that steady-state currents are achieved with loss of the well-defined peak for the oxidative process. Scan rates as high as 800 mV/s give voltammograms with the same general behavior in contrast to the well-behaved scan-rate dependence observed for the dichloro complex. Analogous behavior is observed for  $[\text{Tc}(\text{dmpe})_2\text{Br}_2]^+$ . Although chronocoulometry experiments are not definitive, it is

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likely that this behavior involves a mechanism which includes partial solubilization and adsorption of the  $[M(\text{dmpe})_2\text{Br}_2]^{0+}$  complexes. Decomposition by halide exchange with the supporting electrolyte can be ruled out on the basis that identical voltammograms are obtained when NaBr is substituted for NaCl.

In general, electrochemical behavior in Triton X-100 is not readily explained and does not follow regular trends. This behavior may result from the solubilization properties of this surfactant, which are dominated by relatively weak non-Coulombic interactions, or from changes in the electrode surface, which are induced by Triton X-100.

**Comparative Electrochemical Data for the  $\text{trans-}[M\text{D}_2\text{X}_2]^{+/0}$  Complexes.** (i) **Effect of Metal Center.** The  $\text{trans-}[^{99m}\text{TcD}_2\text{X}_2]^{+/0}$  complexes have been investigated as potential myocardial imaging agents.<sup>2-5</sup> A comparative biodistribution study of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^{+/0}$  and  $[\text{Tc}(\text{dmpe})_2\text{Cl}_2]^{+/0}$  has established that the Tc(III) agent is reduced in vivo whereas the Re(III) analogue is not.<sup>8</sup> Rhenium complexes are expected to be more difficult to reduce than their technetium analogues; a study of five  $\text{trans-}[M\text{D}_2\text{X}_2]^{+/0}$  pairs in *N,N*-dimethylformamide (DMF) has shown that the Re(III) center is  $219 \pm 15$  mV more difficult to reduce than is the Tc(III) center.<sup>10</sup> This same difference is also observed in the more biologically relevant aqueous and aqueous micellar media studied herein. For those systems that exhibit electrochemically reversible redox couples in surfactant media, the average potential difference between rhenium and technetium analogues is  $206 \pm 4$  mV ( $n = 5$ ). For the remaining complexes, a slightly smaller potential difference ( $187 \pm 7$  mV;  $n = 7$ ) is observed, presumably due to uncompensated effects that result from precipitation and adsorption of the neutral M(II) forms.

(ii) **Effect of Surfactant.** Heterogeneous electrochemical reactions of solution species involve a complex series of steps, which include mass transport, electron transfer, and adsorption. Each of these steps can be influenced by the addition of surfactant molecules not only by changes in solubilization of the species but also by changes that occur at the electrode/solution interface due to surfactant adsorption. The net effect of the surfactant on the electrochemical reaction results from a complicated interplay among several, often opposing, thermodynamic and kinetic factors. The data of Table I show that the peak potential of the M(III/II) couple is strongly dependent on the nature of the surfactant. While the kinetic contributions to this variation in peak potential are not easily inferred, some generalizations can be made on the basis of thermodynamic considerations. (i) Solubilization, and thus stabilization, of the neutral M(II) form within the micelle occurs to various degrees for all surfactants. This phenomenon makes it easier to reduce M(III) complexes in the presence of surfactants. (ii) Solubilization, and thus stabilization, of the poorly soluble cationic M(III) salts can also occur, and this phenomenon makes reduction of M(III) more difficult. (iii) Electrostatic interactions of the M(III) cations with the ionic micelles, and dipolar interactions of the M(III) cations with the nonionic micelles, can make reduction of the M(III) complexes either easier or more difficult.

**SDS.** All the M(III) cations are harder to reduce in SDS media than they are in water, which implies the net stabilization of the M(III) cations in the negatively charged SDS micelles is greater than the stabilization of the neutral M(II) complexes. This is not surprising since metal cations are known to bind strongly to anionic micelles,<sup>36</sup> and the ionic strength in the Stern layer has been estimated to be 3–5 M. The average potential shift for the four dmpe complexes is  $-84 \pm 9$  mV, whereas for the two more lipophilic depe complexes it is  $-184 \pm 6$  mV. This greater stabilization of the depe M(III) cations is understood on the basis that the depe M(III) cations are considerably less soluble in water than are the dmpe M(III) cations and thus gain more stabilization in the SDS micelles. (Both the depe and dmpe M(II) neutral species are essentially insoluble in water.)

**CTAB.** For all four of the dmpe M(III) cations the results are opposite to those observed in SDS; i.e., it is easier to reduce M(III) to M(II) in the presence of CTAB than in pure water. The

**Table V.** Differences in Peak Potential between  $\text{trans-}[M(\text{dmpe})_2\text{Cl}_2]^{+/0}$  and  $\text{trans-}[M(\text{depe})_2\text{Cl}_2]^{+/0}$  ( $M = \text{Tc, Re}$ ) in Various Media<sup>a</sup>

medium	$E_p(\text{depe}) - E_p(\text{dmpe}), \text{V}$	
	Re	Tc
0.5 M TEAP/DMF <sup>b</sup>	-0.029	-0.027
0.1 M SDS/0.1 M TEAP	+0.008	+0.008
32 mM CTAB/0.1 M NaCl	+0.044	+0.020
1.2% Triton X-100/0.1 M NaCl	+0.104	+0.092
0.5 M KNO <sub>3</sub>	+0.122	+0.099

<sup>a</sup>  $E_p$  values taken from Table I unless noted. <sup>b</sup> From ref 10.

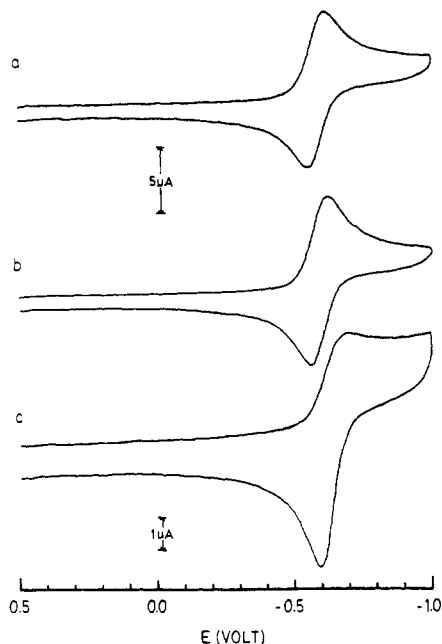
average potential shift is  $+52 \pm 10$  mV ( $n = 4$ ). Thus, for the positively charged CTAB micelles, it appears as though solubilization of the neutral M(II) form within the micelles constitutes the predominate stabilization factor. Not surprisingly, the positively charged dmpe M(III) cations do not appear to undergo significant stabilization in the positively charged Stern layer of the CTAB micelles.

However, this situation does not hold for the two more lipophilic depe complexes. For the depe M(III) cations it is slightly more difficult to reduce M(III) to M(II) in the presence of CTAB than in water; the potential shift is  $-24$  mV ( $n = 2$ ). This result can be rationalized on the basis that since the depe cations are essentially insoluble in water, both the M(III) and M(II) forms achieve significant solubility stabilization in the CTAB micelles. It appears that, for the depe M(III) cations, solubility stabilization overrides the potentially unfavorable Coulombic interactions within the Stern layer; this may occur because the more lipophilic depe complexes are solubilized deeper into the hydrophobic core of the micelle (vide infra).

**Triton X-100.** Of the three surfactants studied, the nonionic Triton X-100 generates the most complicated electrochemistry, and many of the observations made in this medium are not readily explicable. In general, the differences in reduction potential between water and aqueous Triton X-100 are smaller than the differences observed for the ionic surfactants, and these differences are not consistently positive or negative. It appears that the various forces stabilizing M(III) cations and M(II) neutral species within the Triton X-100 micelles are approximately balanced, and small changes in the nature of the complex can alter this balance.

**SDS vs CTAB vs Triton X-100.** The difference in reduction potentials between  $[M(\text{dmpe})_2\text{Cl}_2]^{+/0}$  and  $[M(\text{depe})_2\text{Cl}_2]^{+/0}$  in a given medium provides a measure of how well that medium stabilizes the cationic and neutral forms of these complexes. In DMF, the cationic and neutral complexes of the  $[M\text{D}_2\text{Cl}_2]^{+/0}$  couple are soluble. As a result, the difference in reduction potential is  $-30$  mV (Table V) because depe is a better  $\sigma$  electron donor than is dmpe.<sup>10</sup> However, in aqueous media the neutral M(II) forms are not stabilized by the medium, and these electrogenerated species are adsorbed onto the electrode, which leads to a more positive reduction potential for the depe complex relative to the potential for the dmpe complex. The difference in reduction potentials in 0.5 M KNO<sub>3</sub> is about  $+100$  mV. These two cases provide the extremes for stabilization by the medium: a difference of  $-30$  mV corresponds to complete stabilization, while a difference of  $+100$  mV corresponds to very little stabilization. The data of Table V show that, by this measure, stabilization of the redox components decreases in the order DMF > SDS > CTAB > Triton X-100, H<sub>2</sub>O. Since both the dmpe and depe M(II) species are completely insoluble in water, and the dmpe M(III) cations are reasonably soluble in water, it is likely that this series reflects primarily solubilization of the depe M(III) cations in the various media.

(iii) **Effect of Supporting Electrolytes.** While supporting electrolytes do not directly participate in electrochemical processes, they can affect the micellar properties and structure,<sup>19-21</sup> which in turn can have electrochemical consequences. For instance voltammograms obtained in 0.1 M SDS are dramatically different when 0.1 M NaCl is used as a supporting electrolyte instead of 0.1 M TEAP (Figure 7). Specifically, the use of NaCl causes



**Figure 7.** Cyclic voltammograms of  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  in aqueous solution: (a) 0.1 M SDS/0.1 M TEAP,  $[\text{Re}] = 1.51 \text{ mM}$ ; (b) 0.1 M SDS/0.1 M (TEA)Cl,  $[\text{Re}] = 1.50 \text{ mM}$ ; (c) 0.1 M SDS/0.1 M NaCl,  $[\text{Re}] = 1.61 \text{ mM}$ . The scan rate is 100 mV/s.

a reduction in Faradaic current for all complexes; in fact, the current is reduced to such an extent that reliable voltammetric information can be obtained only for  $[\text{Re}(\text{dmpe})_2\text{Cl}_2]^+$  and  $[\text{Re}(\text{dmpe})_2\text{Br}_2]^+$ , which exhibit peak potentials of  $-0.608$  and

$-0.548 \text{ V}$ , respectively. The replacement of TEAP by tetraethylammonium chloride has no significant effect on voltammograms obtained in 0.1 M SDS (Figure 7), and thus the effect induced by NaCl clearly results from the replacement of the tetraethylammonium cation by the sodium cation. This effect on the electrochemistry in SDS micellar solution is attributed to changes induced in the micellar environment by the cations from the supporting electrolyte; the cmc values of 0.1 M SDS in the presence of 0.1 M NaCl and 0.1 M TEAP are 1.5 and 0.1 mM, respectively. The 15-fold decrease in cmc reflects a greater tendency for surfactant aggregation in the presence of the tetraethylammonium cation. The larger tetraethylammonium cation presumably ion-pairs more effectively with the dodecyl sulfate anion than does the smaller, more hydrophilic, sodium cation. The effect of this tetraethylammonium ion-pairing on the structure of the SDS micelles should be similar to the effect engendered by the incorporation of heptanol,<sup>37</sup> i.e., increased distances between the anionic SDS head groups, which result in a tighter, more closely packed, micellar environment. The more tightly packed TEAP/SDS micelles apparently allow for more efficient electron transfer between the electrode and solubilized complexes than do the more loosely packed Na/SDS micelles.

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## Structural and Kinetic Investigations of a Tc(III)/Tc(II) Redox Couple. X-ray Crystal Structures of *trans*- $[\text{Tc}^{\text{II}}(\text{DPPE})_2\text{Cl}_2]$ and *trans*- $[\text{Tc}^{\text{III}}(\text{DPPE})_2\text{Cl}_2]\text{NO}_3 \cdot \text{HNO}_3$ , Where DPPE = 1,2-Bis(diphenylphosphino)ethane<sup>1</sup>

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The components of a reversible Tc(III/II) redox couple have been characterized by single-crystal X-ray analysis. The Tc(II) complex *trans*- $[\text{Tc}(\text{DPPE})_2\text{Cl}_2]$  (fw = 966.67) crystallizes in the monoclinic space group  $P2_1/a$  with  $a = 17.821(4) \text{ \AA}$ ,  $b = 11.187(2) \text{ \AA}$ ,  $c = 23.572(4) \text{ \AA}$ ,  $\beta = 103.55(1)^\circ$ , and  $Z = 4$ ; 4945 observed reflections were refined to a weighted  $R$  factor of 0.029. The Tc(III) salt *trans*- $[\text{Tc}(\text{DPPE})_2\text{Cl}_2]\text{NO}_3 \cdot \text{HNO}_3$  (fw = 1091.69) crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 10.083(2) \text{ \AA}$ ,  $b = 11.119(4) \text{ \AA}$ ,  $c = 12.767(1) \text{ \AA}$ ,  $\alpha = 71.80(1)^\circ$ ,  $\beta = 73.68(1)^\circ$ ,  $\gamma = 69.35(1)^\circ$ , and  $Z = 1$ ; 5697 observed reflections were refined to a weighted  $R$  factor of 0.035. Oxidation of the Tc(II) complex to the Tc(III) form causes a shortening of the Tc-Cl bond by 0.105(2)  $\text{ \AA}$ , consistent with the ionic nature of this interaction. Conversely, oxidation from Tc(II) to Tc(III) causes a lengthening of the Tc-P bond by 0.072(2)  $\text{ \AA}$ , consistent with the domination of this interaction by  $\pi$ -back-bonding from Tc to P. The magnitudes of these bond length changes are used to predict the inner-sphere reorganizational barrier to electron transfer of the *trans*- $[\text{Tc}(\text{DPPE})_2\text{Cl}_2]^{+0}$  couple to be only ca. 2.6 kcal/mol. Preliminary kinetic studies in nonaqueous media confirm that *trans*- $[\text{Tc}^{\text{II}}(\text{DPPE})_2\text{X}_2]$  (X = Cl, Br) complexes are facile electron-transfer partners for a variety of 1-equiv oxidants. The rate of reduction of  $[(\text{en})_2\text{Co}(\text{S}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$  by *trans*- $[\text{Tc}^{\text{II}}(\text{DPPE})_2\text{Cl}_2]$  in acetonitrile (25  $^\circ\text{C}$ ;  $\mu = 0.10 \text{ M}$ ) is  $3.0(7) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

### Introduction

Redox-active technetium complexes are of considerable interest for nuclear medicine applications.<sup>5,6</sup> Technetium(III/II) com-

plexes of the general formula *trans*- $[\text{TcD}_2\text{X}_2]^{+0}$  (where D represents a chelating bis(tertiary phosphine or arsine) ligand and X represents a halide or pseudohalide ligand) are of special interest since some of the Tc(III) cations are taken up by the heart<sup>7-10</sup>

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