NMR[14] ($C_6D_6$) 66.48 (d, $OCH_2$, $^2J_{PC}$ = 7.33 Hz), 50,34 (d, $NCH_2CH_2Cl$, $^2J_{PC}$ = 2.44 Hz), 49.31 (d, $N(CH_2CH_2Cl)_2$, $^2J_{PC}$ = 4.89 Hz), 47.57 (s, $NCH_2CH_2Cl$), 42.32 (s, $N(CH_2CH_2Cl)_2$), 41.48 (d, $NCH_2CH_2CH_2O$, $^2J_{PC}$ = 3.66 Hz), 26.04 ppm (d, $NCH_2CH_2CH_2O$, $^3J_{PC}$ = 3.66 Hz) and (+)-**3** from diastereomer B (64.4% yield; $[\alpha]^{25}_{589}$ +30.1° (*c* 3.535, MeOH)). The $^{31}P$ NMR ($C_6D_6$) and $^{13}C$ NMR ($C_6D_6$) spectra of (+)-**3** are identical with those of (−)-**3** and both enantiomers are colorless oils. The chemical purity of the enantiomers is demonstrated by the NMR data and a single TLC spot using a 2:1 ratio of $CH_2Cl_2$–$Me_2CO$ as a development solvent ($R_f$ 0.53). The enantiomers are optically pure according to FT $^{31}P$ NMR spectroscopy. Thus a 1:1 molar ratio of (±)-**3** to EuOpt-I (Willow Brook Laboratories) shift reagent as a 0.2 M solution in $C_6D_6$ exhibited two well-defined peaks at −107.21 and −108.73 ppm. Under the same conditions, the enantiomers gave only the −108.73-ppm peak for (+)-**3** and the −107.21-ppm peak for (−)-**3**.

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(13) $^{31}P$ chemical shifts are relative to 85% $H_3PO_4$ as external standard.

(14) $^{13}C$ chemical shifts are measured relative to the solvent and calculated relative to tetramethylsilane.

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## Electrochemistry in Ordered Systems. 1. Oxidative Electrochemistry of 10-Methylphenothiazine in Anionic, Cationic, and Nonionic Micellar Systems

*Sir:*

Electron-transfer reactions of phenothiazine derivatives of interest in physiological[1] and photoionization studies[2] have been examined in both aqueous[3] and nonaqueous[4] media. We report herein the effects on the redox properties of 10-methylphenothiazine (MPTH) resulting from solubilization of this substrate in anionic, cationic, and nonionic surfactants.[5] Relative to voltammetric behavior in aqueous media,[6] the addition of either cationic or nonionic surfactants causes no significant shift in the differential pulse voltammetric (DPV) peak potentials for the one-electron oxidation of MPTH to the corresponding cation radical ($MPTH^{+\cdot}$).[7] This invariance of peak potential indicates the absence of preferential interactions[9] between either MPTH or $MPTH^{+\cdot}$ and surfactant in both cationic and nonionic micellar systems.[10]

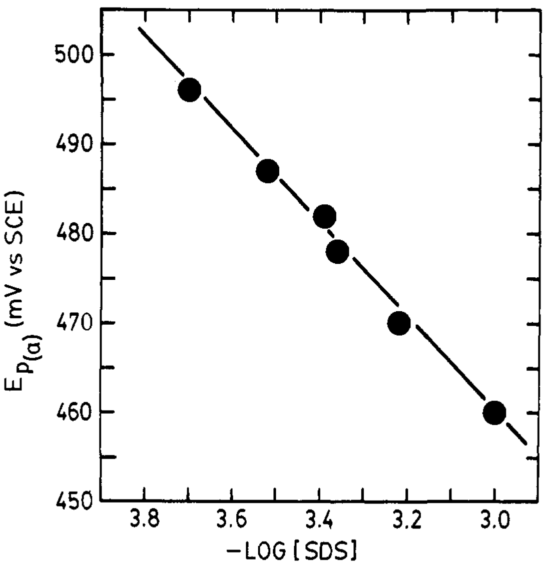

**Figure 1.** Dependence of DPV peak potential for the oxidation of 20 μM MPTH on SDS concentration in 0.05 M $LiClO_4$: slope = −53 (±3) mV; intercept = 303 (±7) mV; coefficient of correlation = 0.9962.

In anionic SDS systems, however, the DPV peak potential for the oxidation of MPTH to $MPTH^{+\cdot}$ was found to vary linearly with the logarithm of the SDS concentration up to the cmc (Figure 1) and to remain invariant at surfactant concentrations in excess of this value. Alterations of the peak potential can be expected as a result of preferential interaction between the medium and one member of the redox couple.[9] For an oxidation process, a cathodic shift reflects increased ease of oxidation and is attributable to stabilization of the oxidized member of the couple (i.e., $MPTH^{+\cdot}$). Below the cmc, the extent of surfactant aggregation is minimal and such solutions may be viewed as being comprised of free monomeric surfactant species.[8] Hence the variation of peak potential with surfactant concentration *below* the cmc points to an interaction between monomeric dodecyl sulfate anion ($DS^-$) and $MPTH^{+\cdot}$. Above the cmc, monomer concentration remains essentially unchanged with newly added surfactant resulting in increased numbers of micelles.[8a] That the DPV peak potential above the cmc is unaltered by added surfactant reflects invariance of the microenvironment experienced by the solubilized MPTH and resulting $MPTH^{+\cdot}$

To assess the relative stability of $MPTH^{+\cdot}$ in the surfactant systems addressed in this work, the rates of decay of $MPTH^{+\cdot}$ in $H_2O$, $H_2O$-$LiClO_4$, $H_2O$-KBr, SDS-$LiClO_4$, Brij-$LiClO_4$, and CTAB-KBr were measured. The half-lives for the solvolyses of $MPTH^{+\cdot}$ in these media (Table I) show that of the cation radical in the anionic surfactant system to be ca. twice that observed in comparable aqueous medium. Grätzel et al.[2c] reported $MPTH^{+\cdot}$ to be extremely stable in SDS micelles, decaying <20% in 24 h. The more rapid decay of $MPTH^{+\cdot}$ in SDS described here may be a manifestation of supporting electrolyte ($LiClO_4$) on micelle structure.[8a] Indeed, in the

**Table I.** Half-Life of $MPTH^{+\cdot}$ in Media of Interest to This Work[a]

| medium | $t_{1/2}$, h[b] |
|---|---|
| $H_2O$ | 8.8 (±0.3)[c] |
| $LiClO_4$ (0.05 M) | 9.9 (±0.6) |
| KBr (0.05 M) | 7.2 (±0.8) |
| CTAB (4.9 mM)-KBr (0.05 M) | 1.4 (±0.2) |
| Brij-35 (2020 mg %)-$LiClO_4$ (0.05 M) | 2.5 (±0.5) |
| SDS (20 mM)-$LiClO_4$ (0.05 M) | 17.2 (±0.6) |

[a] $[MPTH^{+\cdot}]_0 \simeq 5 \times 10^{-5}$ M, introduced as perchlorate salt.[11] Decay kinetics monitored spectrophotometrically at 516 nm. [b] Mean of triplicate determinations at 25 °C. [c] Average deviation.

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