

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77204-5641, and Laboratoire de Synthèse et d'Electrosynthèse Organometallique, Associé au CNRS (UA 33), Faculté des Sciences "Gabriel", University de Dijon, 21100 Dijon, France

Micellar Effects on the Aggregation of Tetraanionic Porphyrins. Spectroscopic Characterization of Free-Base *meso*-Tetrakis(4-sulfonatophenyl)porphyrin, (TPPS)₂, and (TPPS)M (M = Zn(II), Cu(II), VO²⁺) in Aqueous Micellar Media

K. M. Kadish,^{*,1a} G. B. Maiya,^{1a} C. Araullo,^{1a} and R. Guillard^{*,1b}

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UV-visible, ¹H NMR, and ESR characterization of free-base tetraanionic *meso*-tetrakis(4-sulfonatophenyl)porphyrin, (TPPS)₂, and (TPPS)M (M = Zn(II), Cu(II), VO²⁺) were carried out in water and in aqueous solutions containing either the cationic surfactant cetyltrimethylammonium bromide (CTAB), the anionic surfactant sodium dodecyl sulfate (SDS), or the neutral surfactant Triton X-100 (TX-100). (TPPS)₂ and (TPPS)M are monomeric in aqueous solutions containing neutral and cationic surfactants over a porphyrin concentration range of 10⁻⁷-10⁻² M but are aggregated both in neutral aqueous solutions and in the presence of SDS. ESR data indicate a solubilization of (TPPS)Cu and (TPPS)VO in cationic and neutral micelles, and this is attributed to Coulombic as well as hydrophobic interactions between the porphyrin and the micelle. This micellar interaction brings about the monomerization of the porphyrins in aqueous solutions of cationic and neutral surfactants.

Introduction

The aggregation and/or dimerization of porphyrins and metalloporphyrins in aqueous solutions is well-known,²⁻¹¹ and attempts are often made to minimize these effects in order to study properties of a specific monomeric complex under a given set of solution conditions. For example, Simplico et al.¹²⁻¹⁴ have shown that ferric protoporphyrin IX complexes are dimeric in aqueous media but can be solubilized and stabilized as monomers when intercalated in aqueous detergent micelles. Pasternack et al.⁷ and Kano et al.^{8,9} reported ¹H NMR, UV-visible, and fluorescence spectral properties of the tetracationic free-base *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin, (TMPyP)₂, in sodium dodecyl sulfate (SDS) solutions and compared these data to data for the same complex in aqueous solutions where an aggregation of the compound is shown to occur.

Tetraanionic *meso*-tetrakis(4-sulfonatophenyl)porphyrin, (TPPS)₂, and its metal(II) derivatives (TPPS)M are aggregated in neutral buffered and unbuffered aqueous solutions as well as in unbuffered aqueous media containing univalent salts.^{2,5,6,10} Dimerization constants for these complexes range between 10² and 10⁶ M⁻¹ depending upon the solution conditions,^{2,10,11} and a monomer-dimer equilibrium exists at porphyrin concentrations as low as 10⁻⁶ M.

It was not known whether aggregation of (TPPS)M and (TPPS)₂ complexes would occur in micellar solutions. This is investigated in the present work, which presents a study of tetraanionic porphyrin interaction with cationic, anionic, and neutral surfactants in aqueous media. The surfactants used were cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and Triton X-100 (TX-100). The investigated porphyrins were (TPPS)₂, (TPPS)VO, (TPPS)Cu, and (TPPS)Zn, whose

structures are shown in Figure 1.

An additional interest in examining the properties of (TPPS)₂ and (TPPS)M in micellar media comes from the compounds' possible use in photodynamic therapy and magnetic resonance imaging. (TPPS)₂ is known to localize in certain tumors to a high absolute concentration with favorable tumor to other tissue ratios. It is also known that a direct interaction and a strong binding of (TPPS)₂ with tubulin is involved in the biochemical mechanism for its selective uptake.¹⁵ In addition, (TPPS)M (M = Fe(III), Mn(III), Cu(II)) are being tried as contrast agents for NMR imaging of solid tumors.¹⁶ In this regard, it is important to examine the spectroscopic and aggregation properties of (TPPS)₂ and (TPPS)M in membrane mimetic media such as micelles.

Experimental Section

Instrumentation. UV-visible spectra were recorded on an IBM Model 9430 spectrophotometer. ¹H NMR spectra were taken on a QE-300 spectrometer, and chemical shifts are reported with respect to external tetramethylsilane.¹⁷ ESR spectra were taken with an IBM Model 100D electron spin resonance system. DPPH (*g* = 2.0036) was used as the ESR standard.

Chemicals. (TPPS)₂ (sodium salt, 99.1% pure) from Alfa Inorganics was used as received. (TPPS)VO, (TPPS)Cu, and (TPPS)Zn were prepared according to reported procedures.¹⁸ SDS (99.5% pure) and CTAB (99% pure) were obtained from Aldrich Chemical Co., while TX-100 was purchased from Malinkrodt, Inc. Each detergent was used without further purification. Water, which was twice distilled over KMnO₄, was used for the UV-visible and ESR measurements. D₂O (99.8 atom % D) was purchased from Aldrich Chemical Co. and was used as a solvent for ¹H NMR spectroscopic measurements.

Methods. The micellar solutions were prepared as follows: Appropriate amounts of surfactants were weighed and dissolved in water or D₂O by ultrasonication the solution for 2-3 min, after which the solution was stirred for 30 min. The concentrations of the monomeric surfactants were above the critical micelle concentration (cmc)¹⁹ and gave concentrations of the micelles that ranged from 0.5 to 3.0 mM. The porphyrin solid (or aliquots from stock solutions of 0.1-0.001 M) was then added to the micellar solution, and stirring was continued for an additional

- (1) (a) University of Houston. (b) Université de Dijon.
- (2) White, W. I. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5, Chapter 7.
- (3) Margalit, R.; Rotenberg, M. *Biochem. J.* **1984**, *219*, 445.
- (4) Shellnutt, J. A. *J. Phys. Chem.* **1984**, *88*, 4988.
- (5) Satterlee, J. D.; Shellnutt, J. A. *J. Phys. Chem.* **1984**, *88*, 5487.
- (6) Chandrashekar, T. K.; van Willigen, H.; Ebsersole, M. H. *J. Phys. Chem.* **1984**, *88*, 4326.
- (7) Pasternack, R. F.; Gibbs, E. J.; Gaudemer, A.; Antebi, A.; Bassner, S.; DePoy, L.; Turner, D. H.; Williams, A.; Laplace, F.; Lansard, M. H.; Merriene, C.; Perree Fauvet, M. *J. Am. Chem. Soc.* **1985**, *107*, 8179.
- (8) Kano, K.; Miyake, T.; Uomoto, K.; Sato, T.; Ogawa, T.; Hashimoto, S. *Chem. Lett.* **1983**, 1867.
- (9) Kano, K.; Nakajima, T.; Takei, M.; Hashimoto, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1281.
- (10) Corsini, A.; Hermann, O. *Talanta* **1986**, *33*, 335.
- (11) Krishnamurthy, M.; Sutter, J. R.; Hambricht, P. *J. Chem. Soc., Chem. Commun.* **1975**, 13.
- (12) Simplico, J. *Biochemistry* **1972**, *11*, 2525.
- (13) Simplico, J.; Schwenzer, K. *Biochemistry* **1973**, *12*, 1923.
- (14) Simplico, J.; Schwenzer, K.; Manepa, F. *J. Am. Chem. Soc.* **1975**, *97*, 7319.

- (15) (a) Winkleman, J. W. In *Advances in Experimental Medicine and Biology*; Kessel, D., Ed.; Plenum Press: New York, 1985; Vol. 193, pp 91-96. (b) Winkleman, J. W.; Collins, J. H. *Photochem. Photobiol.* **1987**, *46*, 801.
- (16) (a) Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901. (b) Lyon, R. C.; Faustino, P. J.; Cohen, J. S. *Magn. Reson. Med.* **1987**, *4*, 24.
- (17) The chemical shifts could be correlated to literature values of (TPPS)₂ when either DSS (4,4-dimethyl-4-silapentane-1-sulfonate) or CHCl₃/TMS was used as external standard.¹⁰
- (18) Hermann, O.; Mehdi, H.; Corsini, A. *Can. J. Chem.* **1978**, *56*, 1984.
- (19) The cmc's of SDS, CTAB, and TX-100 in neutral aqueous solutions at 20 °C are 8.1 × 10⁻³ M, 9.2 × 10⁻⁴ M, and 0.54 vol %, respectively.²⁰
- (20) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

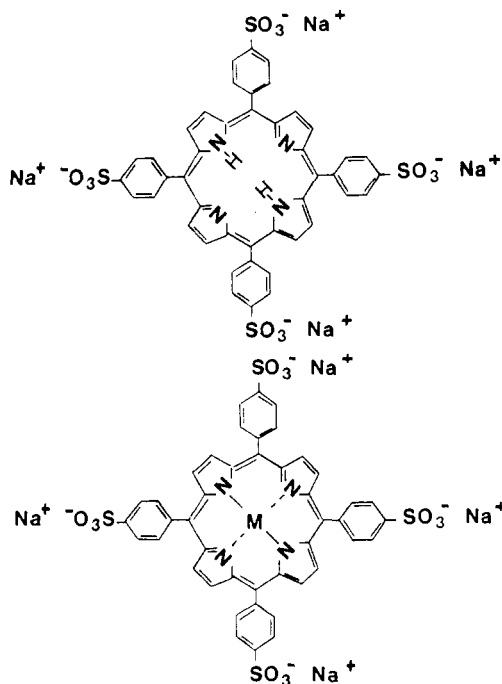


Figure 1. Structures of (TPPS) H_2 and (TPPS) M ($M = Zn(II), Cu(II), VO_2^+$).

20–30 min before spectral measurements were made. Spectral data obtained for solutions under these conditions were identical with data obtained after 12–24 h. All experiments were carried out at $23 \pm 1^\circ C$, unless otherwise specified.

Results and Discussion

UV-Visible Spectroscopy. The UV-visible absorption spectrum of 5×10^{-7} M (TPPS) H_2 in water has bands at 418 (Soret), 515, 554, 590 and 642 nm (Q-bands). As the concentration of the porphyrin is increased above 5×10^{-7} M, the apparent molar absorptivities of all bands decrease in magnitude, while the Soret band shifts to shorter wavelengths and the Q-bands shift to longer wavelengths. These types of concentration-dependent spectral changes have been reported in the literature^{6,10,11} and are attributed to an aggregation of (TPPS) H_2 in aqueous media.

The UV-visible spectra of 3×10^{-4} M (TPPS) H_2 between 350 and 450 nm in aqueous media and in three different micellar solutions are shown in Figure 2. The spectra of (TPPS) H_2 in solutions containing 0.1 M CTAB or 5% TX-100 have higher intensity Soret-band maxima, which are located at longer wavelengths than in water. As will be shown later, this effect is due to a monomerization of the porphyrin in these micellar media.

The spectrum of 3×10^{-4} M (TPPS) H_2 in 0.1 M SDS (dotted line, Figure 2) has a Soret-band maximum at 414 nm and is similar to the spectrum obtained for the aggregated complex in water (solid line). This indicates that the porphyrin remains aggregated in 0.1 M SDS. In contrast, solutions of ca. 10^{-6} M (TPPS) H_2 are monomeric in water and have a Soret-band maximum at 418 nm, which can be compared to a value of 414 nm for the aggregated compound at 10^{-6} M in 0.1 M SDS. There is also a 15% reduction in the apparent molar absorptivity of (TPPS) H_2 in SDS with respect to the value in pure water. Similar spectra are observed for dilute neutral aqueous solutions of monomeric tetracationic⁹ or tetraanionic^{4,6} porphyrins in water containing univalent salts such as KCl or NaCl, and this has been explained by the fact that the presence of salt enhances aggregation.² Thus, the spectroscopic data in this study are consistent with the fact that 10^{-6} M (TPPS) H_2 aggregates more in solutions of 0.1 M SDS than in pure water.

Spectral properties of (TPPS) M ($M = Zn(II), Cu(II), VO_2^+$) are also affected by the presence of surfactants. A summary of the maximum absorbance and apparent molar absorptivity of the Soret and Q-bands of each metalloporphyrin along with that of free-base (TPPS) H_2 in aqueous and micellar solutions in a con-

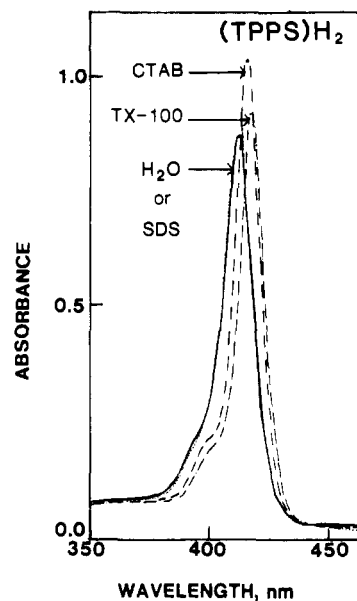


Figure 2. Electronic absorption spectra of 3.0×10^{-4} M (TPPS) H_2 in aqueous and micellar media. The spectra in H_2O (—) and SDS (⋯) are virtually overlapped.

Table I. UV-Visible Spectral Data for the Tetraanionic Porphyrins in Aqueous and Micellar Media^a

compd	λ , nm ($10^{-3}\epsilon$, $M^{-1} cm^{-1}$) ^b			
	H_2O	0.1 M SDS	0.1 M CTAB	5% TX-100
(TPPS) H_2	413 (214)	414 (214)	417 (280.0)	419 (269)
	515 (10.8)	516 (9.3)	514 (16.5)	514 (13.8)
	553 (5.5)	552 (5.0)	551 (8.1)	549 (6.8)
	580 (6.6)	590 (4.5)	589 (6.4)	596 (4.5)
	632 (2.6)	634 (3.0)	642 (3.1)	644 (3.0)
(TPPS)Zn	422 (348)	422 (340)	427 (426)	428 (356)
	556 (15.5)	556 (20.5)	558 (20.5)	561 (19.5)
	595 (6.5)	596 (9.8)	600 (9.8)	601 (10.7)
(TPPS)Cu	412 (186)	412 (151)	415 (213)	416 (222)
	551 (11.4)	549 (11.4)	546 (14.7)	539 (23.4)
(TPPS)VO	438 (168)	437 (174)	427 (275)	426 (358)
	565 (11.3)	566 (13.9)	548 (16.6)	549 (18.7)
	605 (2.7)	605 (5.1)	585 (2.0)	585 (2.4)

^a Porphyrin concentrations varied from 5×10^{-4} to 6.5×10^{-4} M.
^b Error limits are ± 1 nm for λ_{max} and $\pm 10\%$ for ϵ values.

centration range of 5×10^{-4} to 6.5×10^{-4} M is listed in Table I.²¹ In the presence of either CTAB or TX-100, the Soret bands of (TPPS) H_2 , (TPPS)Zn, and (TPPS)Cu undergo a red shift and an increase in apparent molar absorptivity with respect to the spectrum in H_2O . In contrast, the absorbance maxima and apparent molar absorptivities of the above porphyrins in this concentration range are almost identical in aqueous media and in 0.1 M SDS. Thus, the UV-visible data in Table I suggest that (TPPS) H_2 , (TPPS)Cu, and (TPPS)Zn are monomerized in both cationic CTAB and neutral TX-100 micelles but not in anionic SDS, where the compounds remain aggregated.

A confirmation of the above results comes from Beer's law plots in different media. An example is given in Figure 3 for the case of (TPPS) H_2 . The compound does not follow Beer's law behavior in water, and this is consistent with a reported aggregation of the free-base porphyrin under similar experimental conditions.^{6,10,11} The plot also does not follow Beer's law behavior in 0.1 M SDS

(21) At concentrations less than 10^{-5} M, the equilibrium concentrations of the aggregates were insufficient to produce detectable spectral changes with respect to CTAB or TX-100 additions, and at concentrations larger than 10^{-3} M, the absorbances of the Soret band were too high to be accurately measured by using a cell with a path length of 0.01 cm. Thus, concentrations of $\sim 5 \times 10^{-4}$ M were chosen to investigate the effects of added surfactants on the UV-visible region of the porphyrin absorption spectra.

Table II. ^1H NMR Data for Surfactants in D_2O in the Absence and Presence of (TPPS)Zn or (TPPS) H_2

surfactant/substrate	chem shifts, ppm ^a			
	$-(\text{CH}_3)$	$-(\text{CH}_2)_9$	$\beta\text{-CH}_2$	$\alpha\text{-CH}_2$
0.1 M SDS	0.91	1.32	1.70	4.04
0.1 M SDS/ 1×10^{-3} M (TPPS) H_2	0.92	1.32	1.71	4.05
0.1 M SDS/ 6×10^{-3} M (TPPS)Zn	0.89	1.30	1.69	4.04

surfactant/substrate	chem shifts, ppm ^a				
	$-(\text{CH}_3)$	$-(\text{CH}_2)_{13}$	$\beta\text{-CH}_2$	$\text{N}^+(\text{CH}_3)_3$	$\alpha\text{-CH}_2$
0.05 M CTAB	0.98	1.36	1.85	3.25	3.56
0.05 M CTAB/ 1×10^{-3} M (TPPS) H_2	0.88	1.27/1.51 ^b	1.91	3.31	3.91
0.05 M CTAB/ 6×10^{-3} M (TPPS)Zn	0.87	1.25/1.64 ^b	2.40	3.44	3.71

surfactant/substrate	chem shifts, ppm ^a					
	$-(\text{CH}_3)_3$	$-(\text{CH}_3)_2$	$-\text{CH}_2-$	$-(\text{OCH}_2\text{CH}_2)_n$	$-\text{OH}$	2,6-H/3,5-H
0.1 M TX-100	0.68	1.25	1.63	3.63	4.00	6.80/7.18
0.1 M TX-100/ 1×10^{-3} M (TPPS) H_2	0.59	1.17	1.54	3.61	3.99	6.75/7.09
0.1 M TX-100/ 6×10^{-3} M (TPPS)Zn	0.56	1.13	1.50	3.60	3.95	6.72/7.04

^aError limits for the chemical shifts are ± 0.01 ppm. ^bRange of the methylene peak splitting in ppm.

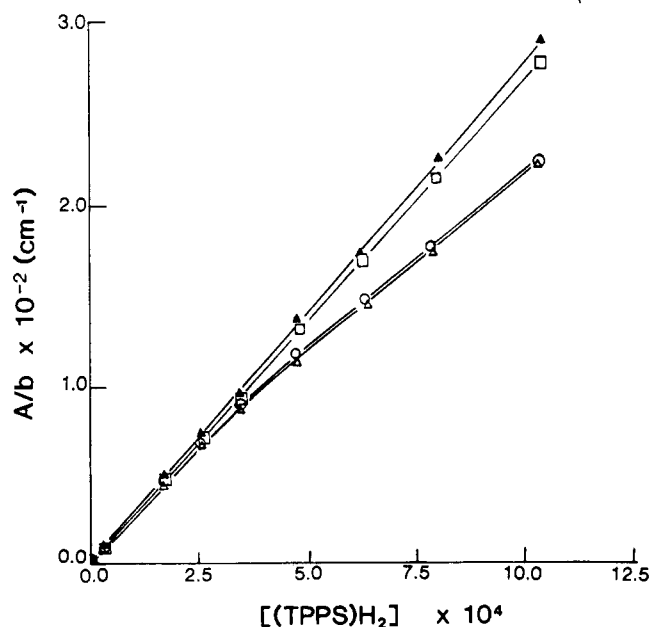


Figure 3. Beer's law plots for (TPPS) H_2 in water (O), 0.1 M SDS (Δ), 0.05 M CTAB (\blacktriangle), and 0.1 M TX-100 (\square). A/b corresponds to the absorbance (Soret band) path length ratio, where b varies from 0.01 to 1.0 cm.

solutions, which is consistent with an aggregation of (TPPS) H_2 in this media. However, higher apparent molar absorptivities of the Soret-band maxima are obtained at all concentrations of (TPPS) H_2 in the presence of either 0.1 M CTAB or 5% TX-100, and under these solution conditions, the plots are linear up to porphyrin concentrations of 10^{-3} M. Similar absorbance vs concentration plots were obtained for (TPPS)Zn and (TPPS)Cu in aqueous and micellar environments, thus suggesting an aggregation of the porphyrin in 0.1 M SDS or water and a monomerization of the porphyrin in 0.1 M CTAB and 5% TX-100.

The situation is complex for the case of (TPPS)VO. A comparison of the (TPPS)VO spectrum in H_2O ($\lambda = 438, 565,$ and 605 nm; see Table I) and in CH_2Cl_2 ($\lambda = 425, 549,$ and 604 nm) suggests that (TPPS)VO(H_2O) is the predominant form in aqueous media. This is consistent with other vanadyl porphyrin complexes that are known to axially bind solvent molecules and form a six-coordinate (P)VO(L) complex.²²

For example, (TPP)VO (TPP is the dianion of *meso*-tetraphenylporphyrin) has absorption bands at 423 and 547 nm in CH_2Cl_2 . These bands are red-shifted to 436 and 562 nm upon

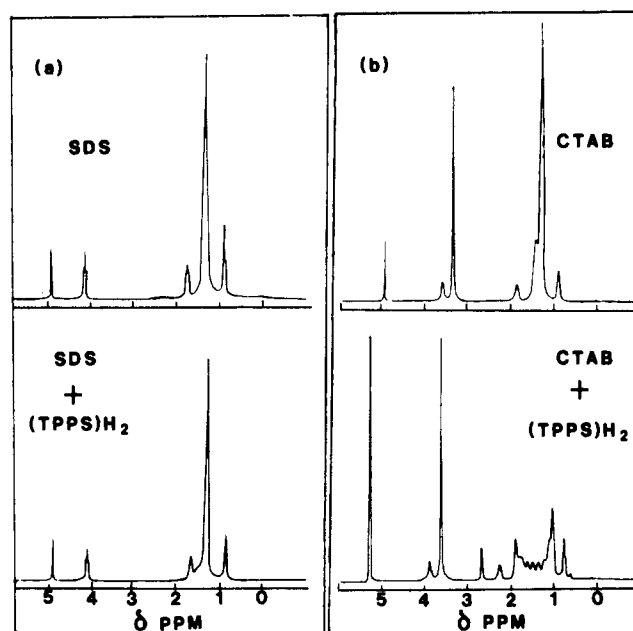


Figure 4. ^1H NMR spectra of (a) 0.1 M SDS in D_2O with and without 1.1×10^{-2} M (TPPS) H_2 and (b) 0.05 M CTAB in D_2O with and without 1.1×10^{-2} M (TPPS) H_2 .

formation of (TPP)VO(L) (L = dimethyl sulfoxide).^{22a} Similarly, a red shift in the UV-visible bands of (TPPS)VO and (TPyP)VO (TPyP is the dianion of *meso*-tetrapyrrolylporphyrin) was noted upon addition of increasing amounts of the coordinating dimethylformamide solvent to CH_2Cl_2 solutions containing these porphyrins.^{22b}

The spectra of (TPPS)VO in $\text{CH}_2\text{Cl}_2/0.1$ M CTAB or 5% TX-100 are similar. However, differences of up to 12 nm in the Soret band and up to 20 nm in the Q-bands are observed between the UV-visible spectra of (TPPS)VO in H_2O and in solutions containing 5% TX-100 or 0.1 M CTAB (see Table I). This cannot be attributed to a simple interaction between the solvated (TPPS)VO and the hydrophobic region of the micelle as in the case of (TPPS)Zn or (TPPS)Cu, and a loss of the ligated water molecule from (TPPS)VO(H_2O) is postulated to occur upon intercalation of the porphyrin in the cationic and neutral micelles. A similar loss of solvent ligand has been observed upon interaction of [(TPyP)Ni(H_2O)₂]⁴⁺ with DNA.²³

In contrast to what is observed in solutions of CTAB or TX-100, the UV-visible spectrum of (TPPS)VO(H_2O) in water does not change significantly upon the addition of 0.1 M SDS to solution,

(22) (a) Bencosme, S.; Romero, C.; Simoni, S. *Inorg. Chem.* **1985**, *24*, 1603. (b) Kadish, K. M.; Sazou, D.; Araullo, C.; Liu, Y. M.; Saijoubi, A.; Ferhat, M.; Guillard, R. *Inorg. Chem.* **1988**, *27*, 2313.

(23) Blom, N.; Odo, J.; Nakamoto, K.; Strommern, D. P. *J. Phys. Chem.* **1986**, *90*, 2847.

and this suggests that (TPPS)VO(H₂O) remains solvated and does not reside at the hydrophobic region of the SDS micelle.

¹H NMR Spectra of Surfactants. Figure 4a illustrates ¹H NMR spectra of 0.1 M SDS in D₂O with and without added (TPPS)H₂. The porphyrin does not exhibit resonances between 0 and 5 ppm, but SDS shows separate peaks for the terminal methyl (0.91 ppm), α-methylene (4.04 ppm), and β-methylene (1.70 ppm) groups and a single large composite peak for the nine interior methylene groups (1.32 ppm). The addition of 1.1×10^{-2} M (TPPS)H₂ to this solution does not produce significant changes in the SDS spectrum (see Figure 4a). Similarly, the chemical shifts of SDS are virtually unchanged when 6×10^{-3} M (TPPS)Zn is added to a D₂O solution of the surfactant (see Table II).

The above results contrast with ¹H NMR results for CTAB in the presence of (TPPS)H₂ or (TPPS)Zn (see Table II). The ¹H NMR spectrum of CTAB in the absence of (TPPS)H₂ or (TPPS)Zn contains distinct resonances for the *N*-methyl groups (3.25 ppm), the α-methylene (3.56 ppm) and β-methylene protons (1.85 ppm), 13 internal methylene groups (1.36 ppm), and a terminal methyl group (0.96 ppm). These peaks are shown in Figure 4b, which illustrates the ¹H NMR spectrum of 0.05 M CTAB in D₂O with and without added (TPPS)H₂. The addition of either (TPPS)H₂ (see Figure 4b) or (TPPS)Zn (see Table II) to this solution results in a splitting of the methylene peak, which indicates an interaction of the porphyrin with the hydrophobic core protons of the micelle.²⁰ There is an upfield shift of the terminal methyl group resonances of CTAB in solutions containing these anionic porphyrins, and under these conditions a significant downfield shift also occurs for resonances due to protons near the polar head group of the surfactant.

Resonances due to the TX-100 protons in D₂O with and without (TPPS)H₂ or (TPPS)Zn are also listed in Table II. The peak assignments for TX-100 are based on the chemical shifts as well as upon data from integrated intensities. As seen in this table, the addition of (TPPS)H₂ or (TPPS)Zn to the TX-100 solution shifts the proton resonances of TX-100 in an upfield direction, thus suggesting an interaction of the above porphyrins with the micelle.

In summary, the ¹H NMR data indicate that (TPPS)H₂ and (TPPS)Zn influence the micellar protons (particularly the hydrophobic methylene) of cationic CTAB and neutral TX-100 but not anionic SDS. Similar ¹H NMR results have been reported for SDS and CTAB solutions containing Co(II) macrocycles.²⁴

¹H NMR Spectra of Porphyrins. Changes in the concentration of (TPPS)H₂ from 8×10^{-4} to 1×10^{-2} M in D₂O induce upfield shifts in the β pyrrole and ortho and meta phenyl proton resonances. (TPPS)H₂ is aggregated with the molecules vertically stacked and the planes parallel, and this orientation induces ring currents that result in an upfield shift of the β pyrrole and ortho and meta phenyl protons.¹⁰ The ¹H NMR spectrum of a 1.1×10^{-2} M (TPPS)H₂ in D₂O at room temperature shows two broad resonances at 8.84 and 7.21 ppm due to the β pyrrole protons and two doublets at 7.69 and 8.26 ppm due to the meta and ortho phenyl protons. Two broad peaks are attributed to the β pyrrole protons and are largely due to a slow rate of tautomerism of the porphyrin central imine (-NH) protons.^{10,25}

The addition of surfactants to solutions of (TPPS)H₂ or (TPPS)Zn at concentrations below their cmc's does not produce any changes in the ¹H NMR spectra. However, the addition of surfactants above the cmc has a deshielding effect on the proton resonances at all concentrations of (TPPS)H₂. This is illustrated in Figure 5 for an aqueous solution of 1.1×10^{-2} M (TPPS)H₂ with and without CTAB.

The addition of 0.05 M CTAB to (TPPS)H₂ results in a shift of the β pyrrole proton resonances from 8.84 ppm to 9.39 ppm, consistent with a monomerization of the (TPPS)H₂ aggregates in the presence of CTAB. The resonances of the ortho and meta

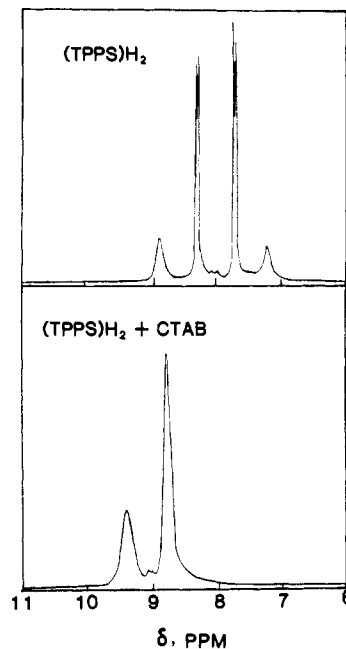


Figure 5. ¹H NMR spectra of 1.1×10^{-2} M (TPPS)H₂ in D₂O and in D₂O containing 0.05 M CTAB.

phenyl protons, which appear as an A₂B₂ multiplet at 7.69 and 8.26 ppm in D₂O, collapse into a broad singlet at 8.75 ppm in D₂O solutions containing CTAB. A coalescence of the A₂B₂ patterns was also reported for para-disubstituted phenyl compounds that were solubilized in aqueous SDS solutions.²⁶ These effects are less pronounced than in CTAB but have been noted for (TPPS)H₂ in TX-100 solutions. The ¹H NMR spectrum of 1.1×10^{-2} M (TPPS)H₂ in 0.05 M CTAB and 5% TX-100 is similar to the ¹H NMR spectrum obtained for a 5×10^{-3} M solution of this porphyrin at 100 °C.¹⁰ Under these latter conditions, (TPPS)H₂ exists exclusively as a monomer, and this suggests that (TPPS)H₂ is also present as a monomer in CTAB and TX-100 micelles.

Interestingly, a single β pyrrole proton resonance is observed for (TPPS)H₂ in D₂O containing 0.05 M CTAB. This contrasts with the two broad signals observed for the same protons in the absence of CTAB (see Figure 5). A similar single β pyrrole proton resonance is also observed for 4.4×10^{-3} M (TPPS)H₂ in deuterated DMSO.¹⁰ This indicates that the rate of -NH tautomerism of (TPPS)H₂ is faster in 0.05 M CTAB than in pure D₂O and also that the porphyrin is intercalated in these micelles and resides in a more hydrophobic environment, such as is observed in DMSO. Finally, the addition of SDS does not have an appreciable effect on the proton resonances of 1.1×10^{-2} M (TPPS)H₂, and this suggests that (TPPS)H₂ remains aggregated in SDS.

¹H NMR spectra of (TPPS)Zn at different concentrations in D₂O are shown in Figure 6. There is an upfield shift of the β pyrrole and ortho and meta phenyl protons with increased concentration of the porphyrin, which supports an aggregation of (TPPS)Zn.¹⁰ The addition of surfactants to a 6.0×10^{-3} M solution of (TPPS)Zn changes the NMR spectrum, as shown in Figure 7. In D₂O solutions containing 0.1 M SDS, the porphyrin β pyrrole proton resonances shift upfield by 0.13 ppm, while the ortho and meta phenyl protons coalesce into a broad singlet. This same spectrum is obtained upon increasing the concentration of (TPPS)Zn from 6×10^{-7} to 1.0×10^{-2} M (see Figure 6) or by adding 0.05 M NaCl to 10^{-3} M (TPPS)Zn in D₂O. These data all indicate that aggregation of (TPPS)Zn is enhanced in the presence of SDS.

The addition of 0.1 M CTAB to (TPPS)Zn has a deshielding effect on all of the proton resonances, as shown in Figure 7. It is interesting to note that the ¹H NMR spectrum of 6×10^{-3} M

(24) Kamau, G. N.; Leipert, T.; Shukla, S. S.; Rusling, J. F. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *233*, 173.

(25) Koehorst, R. B. M.; Hofstra, J.; Schaafsma, T. J. *Magn. Reson. Chem.* **1988**, *26*, 167.

(26) Tokiwa, F.; Aigami, K. *Kolloid Z. Z. Polym.* **1971**, *246*, 688.

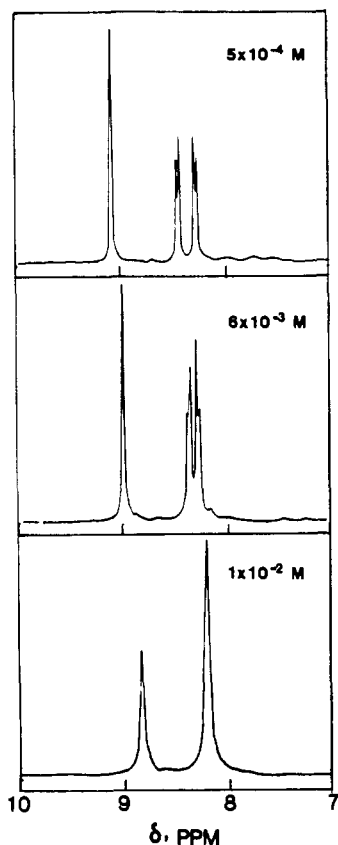


Figure 6. Concentration dependence of the (TPPS)Zn ^1H NMR spectra in D_2O .

(TPPS)Zn in D_2O containing 0.05 M CTAB is similar to the spectrum of 5×10^{-4} M (TPPS)Zn in D_2O without CTAB (see Figure 6). The deshielding effect of CTAB on the proton resonances of (TPPS)Zn is therefore consistent with a monomerization of the porphyrin.

The β pyrrole proton resonance of 6×10^{-3} M (TPPS)Zn in 0.1 M TX-100 is broader than that for the same compound in pure D_2O (see Figure 7). Also, the ortho and meta phenyl protons in TX-100 coalesce into a broad singlet at 8.10 ppm. These spectral changes may or may not indicate a disaggregation of (TPPS)Zn in TX-100, but the UV-visible spectral data clearly indicate a disaggregation of this porphyrin in TX-100. The coalescence of the ortho and meta phenyl proton resonances of (TPPS)Zn in TX-100 solutions is similar to what is observed for the A_2B_2 patterns of para-disubstituted phenyl compounds that are solubilized in SDS medium.²⁶ Hence, it is possible that the ^1H NMR spectrum merely depicts a micellized (TPPS)Zn monomer in TX-100 solutions. In any case, it is certain that (TPPS)Zn must be micellized to give the observed spectral changes. This is because the addition of TX-100 to 10^{-2} – 10^{-4} M solutions of (TPPS)Zn at concentrations less than its cmc produces no appreciable changes in either the (TPPS)Zn or the surfactant spectra.

The broadness of the (TPPS)Zn resonances in micellar media may arise from a hindered rotational tumbling motion, as has been explained for the larger width of the ring methyl proton resonances of hexacoordinate (protoporphyrinato IX)iron(III) complexes inside SDS micelles.²⁷ Thus, ^1H NMR data for (TPPS) H_2 and (TPPS)Zn in 0.05 CTAB and 5% TX-100 solutions indicate that the porphyrins exist as monomers as a consequence of porphyrin solubilization into these micelles. In contrast, the NMR data in 0.1 M SDS solutions clearly show that the porphyrin remains aggregated in this micellar media.

ESR Spectroscopy. Figure 8 shows ESR spectra of 1.5×10^{-3} M (TPPS)Cu under various solution conditions. The ESR

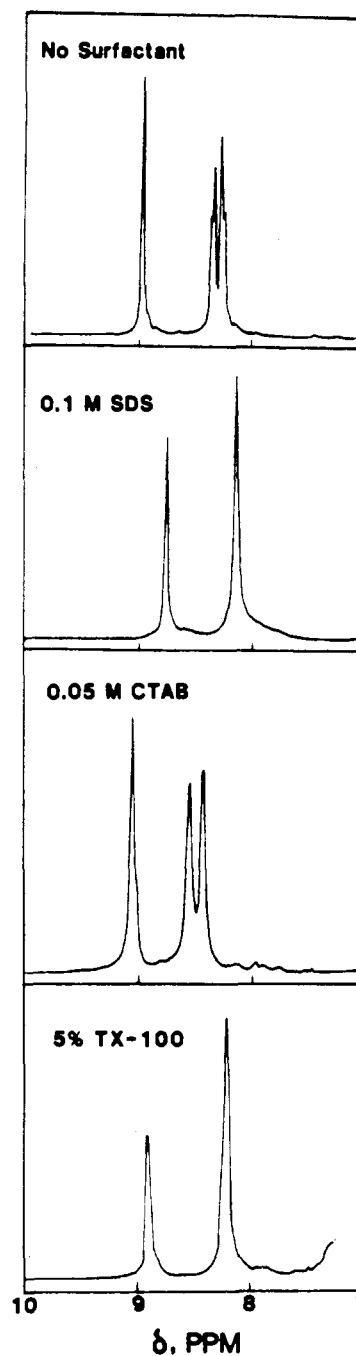


Figure 7. ^1H NMR spectra of 6×10^{-3} M (TPPS)Zn in D_2O under various solution conditions.

spectrum in H_2O at 26 $^\circ\text{C}$ is isotropic and has five resonance peaks of unequal intensity with an apparent g_{av} of 2.117. Additional hyperfine structure is not observed for either an almost monomeric (1×10^{-5} M) or an aggregated (1.5×10^{-2} M) form of the complex in H_2O . As the porphyrin concentration is increased from 1.5×10^{-5} to 1.0×10^{-2} M, the signal at the highest field with a g factor of 1.999 decreases considerably in intensity. A similar effect is observed upon addition of NaCl to the solution. An example of this decrease in signal is given by the ESR spectrum of 1.5×10^{-3} M (TPPS)Cu in water containing 0.1 M NaCl (see Figure 8).

The addition of each surfactant to (TPPS)Cu below their respective cmc's produces no perceptible effect on the ESR spectral features of this porphyrin, but the ESR spectral features of 1.5×10^{-3} M (TPPS)Cu in 5% TX-100 are different from those in aqueous media (see Figure 8). Although the spectral pattern remains almost unchanged at lower magnetic fields, there is a change of g_{av} from 2.117 to 2.114 with a concomitant appearance of well-resolved superhyperfine structure in the high-field region

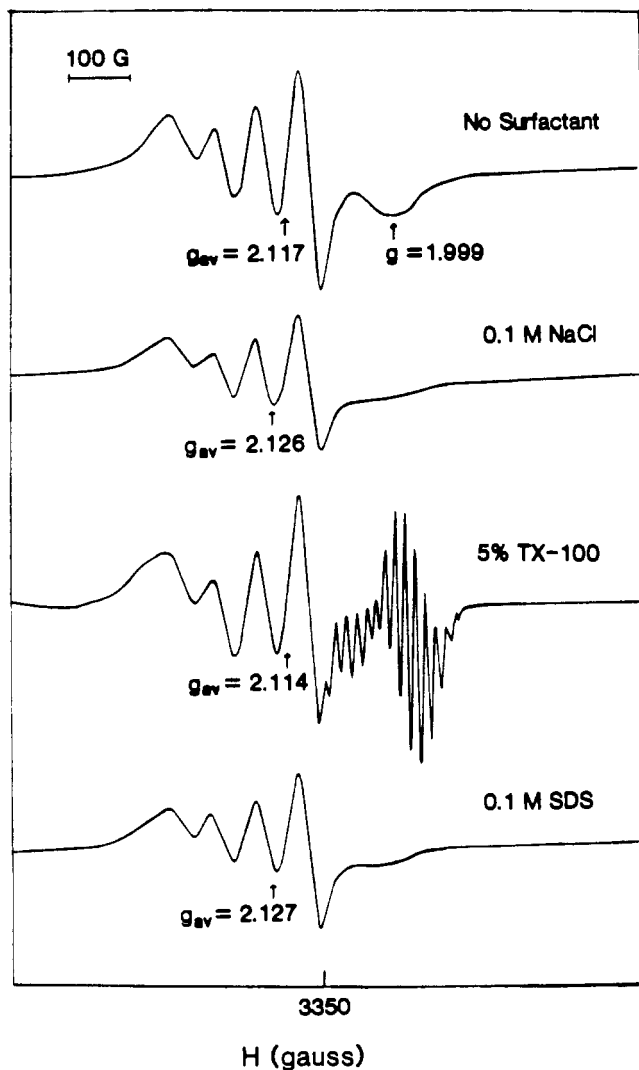


Figure 8. ESR spectra of 1.5×10^{-3} M (TPPS)Cu at 23 °C under various solution conditions.

of the spectrum upon going from aqueous solutions to solutions of TX-100.

A shift of the g_{av} for (TPPS)Cu suggests a change of environment from an aqueous phase to a micellar subphase, and the appearance of superhyperfine structure, which is due to macrocyclic nitrogen interactions with the unpaired electron on the Cu(II) center, gives direct evidence for a reduction in the tumbling rate of these solute molecules.^{28,29} The average superhyperfine coupling constant (A_{av}) of (TPPS)Cu in 5% TX-100 solutions is calculated as 16 G from the spectrum shown in Figure 8. The magnitude of A_{av} is similar to the values for (TPP)Cu in nonpolar solvents like benzene or CHCl_3 at the same temperature.³¹ This similarity in A_{av} indicates that (TPPS)Cu resides in a relatively nonpolar environment in 5% TX-100 solutions compared to a polar environment, as in aqueous media. The ESR spectra of 1.5×10^{-3} M (TPPS)Cu in 0.1 M CTAB are indistinguishable from the ESR spectra in solutions of TX-100 and can be interpreted similarly.

The addition of 0.02–0.2 M NaCl to (TPPS)Cu solutions containing 0.1 M CTAB or 5% TX-100 has no effect on the ESR spectral parameters, and the spectra still exhibit superhyperfine

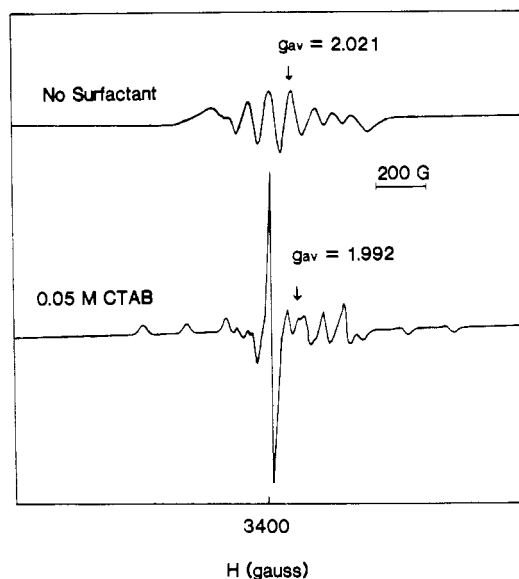


Figure 9. ESR spectra of 2×10^{-3} M (TPPS)VO at 23 °C in H_2O and in 0.05 M CTAB.

coupling. This indicates that (TPPS)Cu remains monomerized in both CTAB and TX-100 despite the presence of Na^+ ions, which are known to induce aggregation.² On the other hand, the ESR spectrum of 1.5×10^{-3} M (TPPS)Cu in 0.1 M SDS is similar to the one obtained in a solution containing 0.1 M NaCl (see Figure 8), which further suggests that SDS enhances aggregation.

The ESR spectra of 2.0×10^{-3} M (TPPS)VO in aqueous solutions and in 0.1 M CTAB solutions at 26 °C are given in Figure 9. The spectrum in water exhibits eight lines and is similar to the isotropic spectrum observed for other vanadyl porphyrins.^{30,31} The addition of either 5% TX-100 or 0.05 M CTAB (see Figure 9) to solutions of (TPPS)VO induces an anisotropy in the spectrum. A similar change from an isotropic to an anisotropic spectrum is observed for the VO^{2+} ion in VOSO_4 upon going from a pure aqueous solution to an acid Nafion membrane phase containing a fractional water content less than 0.1 by weight at room temperature.³²

The ESR spectrum of (TPPS)VO in 0.1 M CTAB is typical for vanadyl porphyrins in nonaqueous solvents at liquid-nitrogen temperatures.³¹ This indicates that (TPPS)VO resides in a relatively nonaqueous environment of the micellar subphase in either 0.1 M CTAB or 5% TX-100 solutions and that the molecular tumbling rate of (TPPS)VO is altered under these conditions.^{30,32} Finally, the spectrum of (TPPS)VO in 0.1 M SDS solutions is indistinguishable from the one in water, which suggests that the tetraanionic porphyrin is present in an aqueous environment in this anionic micelle.

Summary. We have shown that the four investigated tetraanionic porphyrins can be solubilized into micellar solutions containing positively charged or neutral surfactants but not into solutions containing anionic surfactants. We have also shown that there is an interaction of the tetraanionic porphyrins with CTAB or TX-100 and this micellar effect brings about a disaggregation of the negatively charged porphyrin molecules. This occurs even in the presence of Na^+ ions, as suggested by the ESR spectrum of (TPPS)Cu solubilized in cationic or nonionic media containing NaCl. Finally, our data indicate that SDS does not disrupt the aggregation of tetraanionic porphyrins but rather promotes their aggregation. This parallels effects observed upon the addition of salt solutions to these same porphyrins in aqueous media.

The micellar effects on (TPPS) H_2 and its metal(II) derivatives in CTAB are a consequence of Coulombic factors, but the effects of the neutral surfactant TX-100 can be dominantly hydrophobic in origin. It is possible that a large area of these charged rigid porphyrin structures are hydrophobic and hence are unavailable

(28) MacCragh, A.; Storm, C. B.; Koski, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 1470.

(29) McIntire, G. L.; Fendler, E. J., Eds. *Solution Chemistry of Surfactants*; Plenum Press: New York, 1980; Vol. 2, pp 1101–1119.

(30) Subramanian, J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 13.

(31) Lin, W. C. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 4, Part C, Chapter 7.

(32) Barklie, R. C.; Girard, O.; Braddell, O. *J. Phys. Chem.* **1988**, *92*, 1371.

for solvation in an aqueous environment. This hydrophobic property of the water-soluble porphyrins, in turn, can facilitate a solubilization through hydrophobic interactions.

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Registry No. (TPPS)₂, 39050-26-5; (TPPS)Cu, 67204-03-9; (TPPS)Zn, 42712-11-8; TPPS(VO), 93410-57-2.

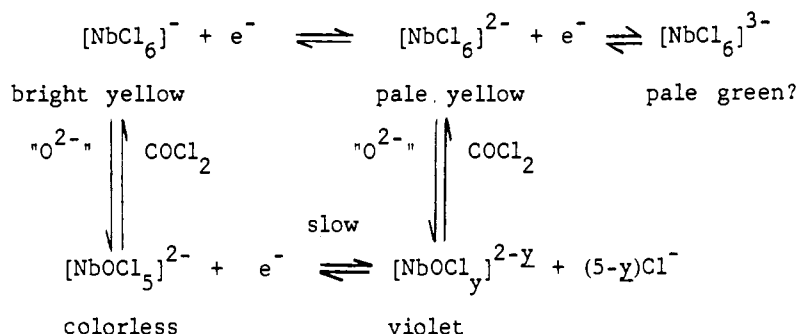
Contribution from the Department of Chemistry,
University of Mississippi, University, Mississippi 38677

Electrochemistry of Niobium Chloride and Oxide Chloride Complexes in the Basic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Room-Temperature Ionic Liquid

I-Wen Sun and Charles L. Hussey*

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Niobium(V) is complexed as $[\text{NbCl}_6]^-$ in the basic aluminum chloride-1-methyl-3-ethylimidazolium chloride ionic liquid, and it can be reduced to $[\text{NbCl}_6]^{2-}$ and $[\text{NbCl}_6]^{3-}$ in successive, one-electron, reversible redox reactions at a glassy-carbon electrode with voltammetric half-wave potentials of 0.17 and -0.93 V, respectively, in the 44.4/55.6 mol % melt at 40 °C, referenced to aluminum in the 66.7/33.3 mol % melt. The average Stokes-Einstein products for $[\text{NbCl}_6]^-$ and $[\text{NbCl}_6]^{2-}$ in the ionic liquid are 3.5×10^{-10} and 2.1×10^{-10} cm² s⁻¹ K⁻¹, respectively. The addition of oxide ion to solutions of $[\text{NbCl}_6]^-$ in basic melt produces $[\text{NbOCl}_5]^{2-}$. This species can be electrochemically reduced to a strongly paramagnetic monomeric niobium(IV) species, which is associated with a single oxide ion, possibly $[\text{NbOCl}_4]^{2-}$ or $[\text{NbOCl}_3]^{2-}$. The niobium(V)/niobium(IV) oxide chloride electrode reaction exhibits quasireversible behavior with a standard heterogeneous rate constant of 9.0×10^{-7} cm s⁻¹ and a cathodic transfer coefficient of ca. 0.8. The formal electrode potential of the niobium(V)/niobium(IV) oxide chloride redox couple is -0.521 V in the 44.4/55.6 mol % melt. The Stokes-Einstein products of $[\text{NbOCl}_5]^{2-}$ and the related niobium(IV) oxide chloride complex are 1.9×10^{-10} and 1.4×10^{-10} cm² s⁻¹ K⁻¹, respectively. The overall electrochemical scheme for niobium complexes in the AlCl_3 -MeEtimCl ionic liquid is summarized as follows:



Introduction

Room-temperature chloroaluminate ionic liquids are obtained when anhydrous aluminum chloride is combined with certain organic chloride salts, which are normally solids at room temperature. Two examples of these organic salts are 1-(1-butyl)pyridinium chloride (BupyCl) and 1-methyl-3-ethylimidazolium chloride (MeEtimCl).¹ The latter salt is more resistant to reduction than the former, and basic melts² containing this salt are superior for dynamic electrochemical measurements at very negative potentials.³

Basic room-temperature chloroaluminate melts have been shown to be excellent solvents for stabilizing anionic transition-metal chloride complexes. Some of the factors that are believed to contribute to the unusual stability of these species in these ionic liquids relative to other solvents have been discussed;⁴ they include the absence of both the solvation and solvolysis reactions encountered in molecular solvents and the thermally promoted

dissociation and disproportionation reactions associated with high-temperature molten salts. A comprehensive list of the various transition-metal complexes that have been investigated in room-temperature chloroaluminate melts has been published.⁵

There is a paucity of information about the electrochemistry and solution chemistry of niobium chloride complexes. These elusive species are very difficult to study in solution because they react with the trace quantities of moisture that are often present in rigorously purified molecular solvents and with the unavoidable, difficult to remove, oxide-containing contaminants that are found in some molten salts. Recently, we reported an effective procedure for removing oxide impurities from AlCl_3 -MeEtimCl ionic liquids.⁶ This procedure, which employs phosgene, can also be used to convert some oxide-containing transition-metal complexes, including niobium oxide chloride complexes, to their respective chloride complexes in situ. By employing this procedure, it should be possible to study transition-metal solutes that are very reactive toward oxide, e.g., high-oxidation-state niobium and tantalum complexes, in these ionic liquids.

The electrochemistry of niobium complexes has not been studied previously in room-temperature chloroaluminate ionic liquids with the exception of an initial investigation that was conducted in this laboratory to test the efficacy of phosgene as an agent for eliminating oxide. However, some limited electrochemical studies involving niobium have been conducted in alkali metal chloride

- (1) For reviews see: (a) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407-423. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185-230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55-78.
- (2) Basic room-temperature chloroaluminate ionic liquids contain a molar excess of the organic salt component relative to AlCl_3 , while the acidic ionic liquids contain a molar excess of AlCl_3 relative to the organic salt; the excess chloride ion in the former can act as a Lewis base (cf. ref 1).
- (3) Lipsztajn, M.; Osteryoung, R. A. *Electrochim. Acta* **1984**, *29*, 1349.
- (4) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature* **1986**, *323*, 614.

(5) Hussey, C. L. *Pure Appl. Chem.* **1988**, *60*, 1763.

(6) Sun, I-W.; Ward, E. H.; Hussey, C. L. *Inorg. Chem.* **1987**, *26*, 4309.