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Two Methods to Study Aggregation of Complexing Agents Used to Alter Solute Partitioning between Phases

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Abstract

For solute partition experiments involving a complexing agent in one phase, the equilibrium partitioning is a function of physical solubility and binding with the complexing agent. This equilibrium can be further complicated by one or more solute molecules binding to the complexing agent and the complexing agent existing as monomer or aggregate in solution. Two methods are presented to investigate these issues. First, an analysis procedure is presented which can determine the reaction equilibrium constants and monomer or dimer formation based on the results of total solute partitioning experiments. This is especially useful when the dimer is formed by aggregation and cannot be readily differentiated from the monomer by spectroscopic means. In addition, the shape of the total partitioning coefficient vs solute concentration curve can give an indication of the relative values

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of the reaction equilibrium constant. Second, an optically transparent thin-layer electrochemical cell (OTTLE) can be used to measure aggregation using techniques such as UV-visible spectroscopy. Since aggregation of the complexing agent tends to occur at high concentrations, the OTTLE cell must be able to accommodate solutions with high optical absorbances. Herein is reported the design of an OTTLE that requires minimal assembly, gives highly reproducible dimensions (35.5 ± 0.5 μm path and 9.2 ± 0.2 μL volume), and also effectively excludes oxygen.

INTRODUCTION

Various chemical separation processes employ the use of a chemical complexing agent in a liquid phase to selectively enhance the separating capability of the process. These processes include reactive distillation, solvent extraction, and liquid membranes. This brief lists points out that both equilibrium stage and rate processes can benefit from this enhancement. After the extraction step, various methods can then be used to strip the solute. These methods include a pressure swing, a temperature swing, or a pH change.

In order to separate and concentrate a solute, some energy input is necessary. One method used to do this separation and concentration is the reduction and oxidation of a complexing agent (electrochemically modulated complexation, EMC) to change the binding affinity of the complexing agent. The use of EMC for chemical separations was first reported by Ward (*1*) who electrochemically cycled Fe(II) and Fe(III) in formamide solution to transport NO. He showed that NO could be transported across a liquid membrane when no NO gradient existed. This same system was further studied by Athayde and Ivory (*2*). They predicted that NO could be transported against a concentration gradient as high as 1:10. Winnick and coworkers (*3*, *4*) investigated the use of an electrochemical cell to concentrate SO_2 and CO_2. Recently O_2 concentrate from water has been reported using the electrochemical cycling of cobalt coordination compounds (*5*).

An example of EMC applied to liquid solutes involves the use of iron tetrakis(4-sulfonato-phenyl)porphyrin ($FeTPPS_4$) as an electroactive chemical complexing agent for a carrier mediated equilibrium stage separation process (*6*, *7*). The process is shown in Fig. 1. Various organosulfur and organonitrogen compounds can be extracted from an organic feed (contaminated) phase (Phase 1) and concentrated in an organic receiving (waste) phase (Phase 2). The details of the process are described elsewhere (*6*). It has been shown (*7*) that the ability to separate and concentrate varius solutes depends on the overall solute partition coefficients in the reduced and oxidized state of the complexing agent. These partition coefficients depend on the physical solubility of the solute in the aqueous phase as well as the extent of solute binding to the complexing agent.

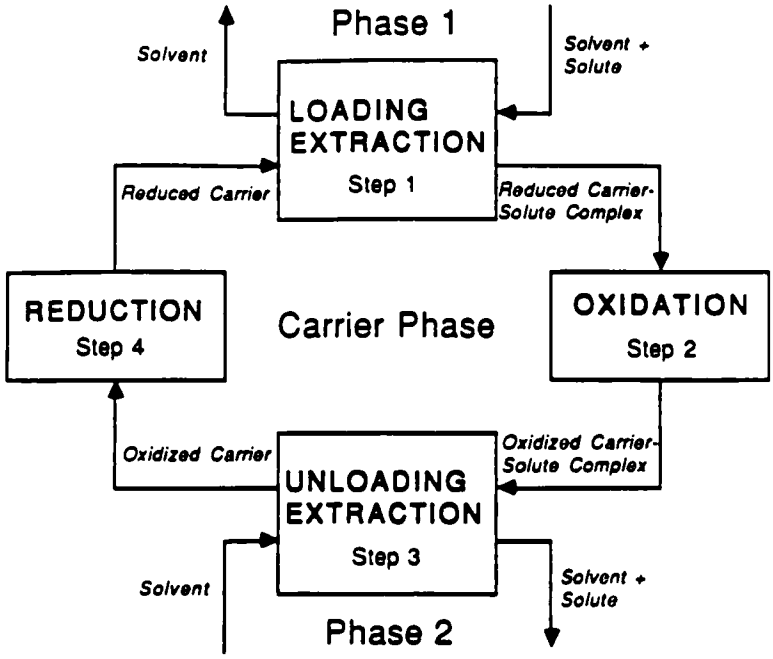

FIG. 1. Schematic for an equilibrium staged EMC process involving solutes initially contained in a hydrocarbon phase.

SOLUTE PARTITIONING STUDIES

An important issue in solute partitioning in these systems is whether one or two solute molecules will bind with the complexing agent and whether the complexing agent exists as a monomer, dimer, or higher aggregate. This paper will first describe a procedure to determine the equilibrium constants for the solute binding and determine whether the complexing agent exists as a monomer or dimer.

The solute partition coefficient is defined as

$$K_{r\,(o)} = \frac{\text{solute concentration in aqueous phase } (C_a)}{\text{solute concentration in organic phase } (C_o)} \tag{1}$$

where the subscript r or o refers to the reduced or oxidized state of the complexing agent. The description in this paper is related to K_r since the complexing agent described in the experimental portion, Fe(II)TTPS$_4$, has the highest affinity for complexation in the reduced state. The procedure can be used in principle for K_r or K_o.

Experimental Procedure for Solute Partitioning Experiments

The procedure for synthesizing the complexing agent Fe(II)TPPS$_4$ is reported elsewhere (*6*). For K_r measurements, the extraction was conducted in a glove box under N_2 atmosphere. A given amount of Fe(II)TPPS$_4$ in an aqueous phase and the organic phase (isooctane) containing the solute were placed into a separatory funnel or a centrifuge tube, and then shaken for 2 minutes. After approximately 5 minutes, a sample was taken from the organic phase. K_r was determined using

$$K_r = \frac{(C_{o,i} - C_{o,e})V_o}{C_{o,e}V_a} \tag{2}$$

where $C_{o,i}$ is the initial concentration of solute in the organic phase. $C_{o,e}$ is the equilibrium solute concentration in the organic phase as determined by UV-vis spectroscopy. V_a is the volume of aqueous phase (Fe(II)TPPS$_4$ – buffer solution). V_o is the volume of organic phase.

The measurement of m (physical solubility coefficient) was conducted outside the glove box. For m measurements, the aqueous phase was buffer solution (pH = 9.2, μ = 1.0). The experimental determination of m is carried out in the same manner as K_r. The concentration of solute in isooctane was determined by using an HP8452 A Diode Array Spectrophotometer with a 1-cm cell.

The experimental results used in this study are for 2-amino-naphthalene as the solute and isooctane as the organic phase solvent. The value of m previously reported is 0.087 (*6*). The monomer concentration of Fe(II)TPPS$_4$ was 10 mM. Table 1 lists the experimental results.

Analysis of Solute Partitioning Experiments

Consider the following reactions in the aqueous phase

$$C + R \overset{K_1}{\rightleftharpoons} CR \tag{3}$$

$$CR + R \overset{K_2}{\rightleftharpoons} CR_2 \tag{4}$$

where C = complexing agent
R = solute
K_i = equilibrium constant for reaction step i

The solute aqueous phase concentration C_a is given by

$$C_a = mC_o + 2[CR_2] + [CR] \tag{5}$$

where m = the physical solubility coefficient
C_o = solute concentration in the organic phase

TABLE 1
Experimental Results for Solute Partitioning Experiments[a]

Concentration of pollutant in the organic phase (mM)		
Initially	At equilibrium	K_r
0.0642	0.0386	2.65
0.0917	0.0535	2.86
0.1180	0.0678	2.96
0.1830	0.1060	2.91
0.2230	0.1260	3.08
0.3600	0.1920	3.50
0.4330	0.2280	3.60
0.8400	0.4350	3.72
1.6280	0.8350	3.80
2.9130	1.5810	3.37
3.0330	1.6480	3.26
4.4190	2.6680	2.63

[a]Pollutant: 2-amino-napthalene. Aqueous phase contains 0.1 M boric acid buffer, pH 9.2, 0.95 M $NaClO_4$, ionic strength I = 1.0 M, and 10 mM $FeTPPS_4$. Organic phase: isooctane. (aqueous phase volume)/(organic phase volume) = 0.25.

Substituting for $[CR]$ and $[CR_2]$ in terms of the equilibrium relations for Eqs. (3) and (4),

$$C_a = mC_o + 2K_1K_2[C](mC_o)^2 + K_1[C](mC_o) \tag{6}$$

Equation (6) can be rearranged to form the total partition coefficient K_r:

$$K_r = \frac{C_a}{C_o} = m + 2m^2K_1K_2[C]C_o + mK_1[C] \tag{7}$$

A material balance on the complexing agent concentration $[C]$ yields

$$[C] = C_T - [CR] - [CR_2] \tag{8}$$

where C_T = total concentration of complexing agent present (as monomer in this case).

Substitution of the equilibrium relations for Eqs. (3) and (4) in Eq. (8) and rearrangement yields

$$[C] = \frac{C_T}{1 + K_1 m C_o + K_1 K_2 m^2 C_o^2} \tag{9}$$

Combining Eq. (7) and Eq. (9):

$$\frac{K_r}{m} - 1 = \frac{K_1 C_o + 2mK_1K_2C_o^2}{1 + K_1 m C_o + K_1 K_2 m^2 C_o^2} \left(\frac{C_T}{C_o}\right) \tag{10}$$

Equation (10) is based on the assumption that the complexing agent is present as a monomer.

It is also possible that the complexing agent is present as a dimer. In that case the dimer concentration C_T^d is one-half of the monomer concentration C_T. For the dimer (C_T^d), exactly the same procedure is followed and a similar equation is obtained.

$$\frac{K_r}{m} - 1 = \frac{K_1 C_o + 2mK_1K_2C_o^2}{1 + K_1 m C_o + K_1 K_2 m^2 C_o^2} \left(\frac{C_T^d}{C_o}\right) \tag{11}$$

To analyze the experimental data to determine if the complexing agent is present as a monomer or dimer, at low pollutant concentration (C_o) we assume that the total complexing agent concentration is constant (since the latter is much greater than the former by one order of magnitude at least). Equations (10) and (11) assume the form

$$\frac{\frac{K_r}{m} - 1}{[C]} = K_1 + 2mK_1K_2C_o \tag{12}$$

Here $[C]$ can refer to either the monomer (C_T) or dimer (C_T^d) concentration of the complexing agent. This analysis assumes that the complex exists as either monomer or dimer but not both. Comparison with experimental data will confirm the validity of this assumption.

Analysis Results

The analysis developed above can be used with experimental results of m and K_r vs C_o to determine two principal aspects of the chemistry associated with the extraction. First, the values of K_1 and K_2 are determined

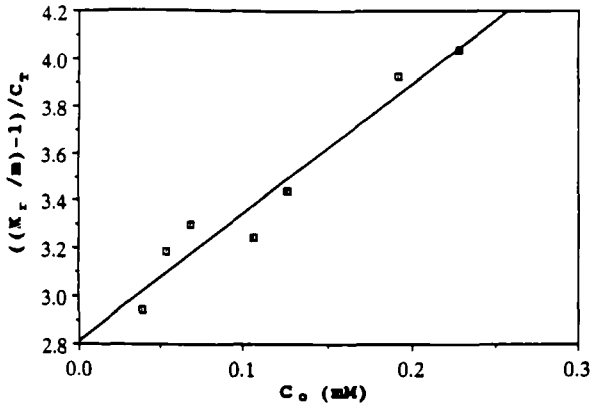

FIG. 2. Comparison of experimental data and Eq. (12) assuming that the complexing agent is present as monomer.

from a plot of the experimental data at low values of C_o. Referring to Eq. (12), a plot of the experimental data can be made based on the assumption of the complexing agent being present as monomer ($[C] = C_T$) (Fig. 2) or dimer ($[C] = C_T^d = C_T/2$) (Fig. 3). For each figure, the values of K_1 and K_2 are determined from the slope and intercept of the line. The values are shown below.

Monomer (Fig. 2)	Dimer (Fig. 3)
$K_1 = 2.8 \times 10^3\ M^{-1}$	$K_1^d = 5.6 \times 10^3\ M^{-1}$
$K_2 = 1.1 \times 10^4\ M^{-1}$	$K_2^d = 1.1 \times 10^4\ M^{-1}$

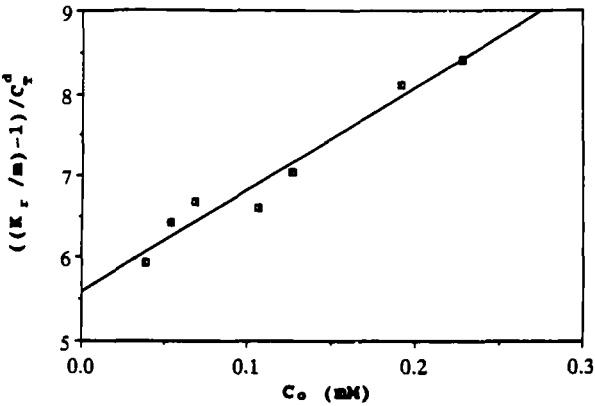

FIG. 3. Comparison of experimental data and Eq. (12) assuming that the complexing agent is present as dimer.

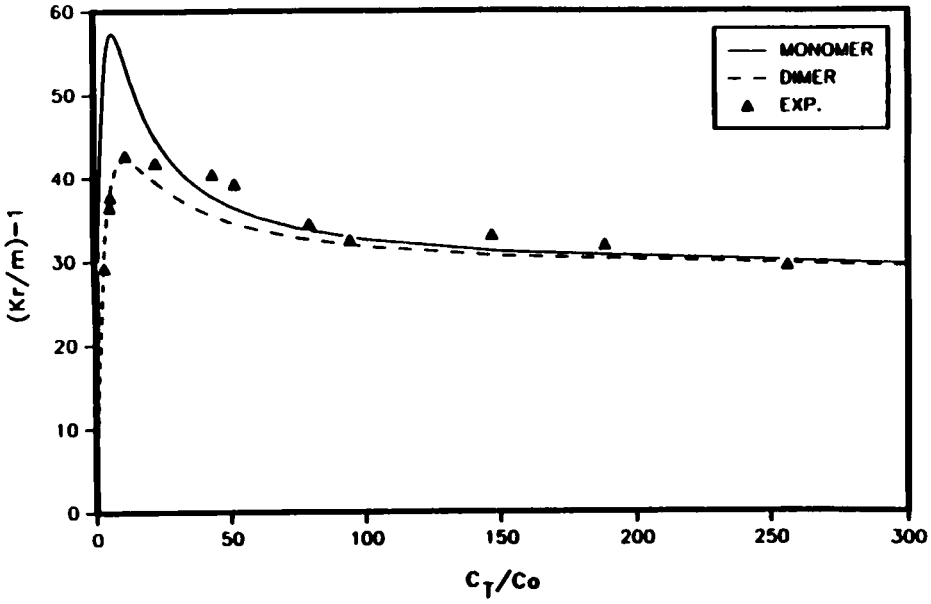

FIG. 4. Plot of Eqs.(10) and (11) and experimental results (▲).

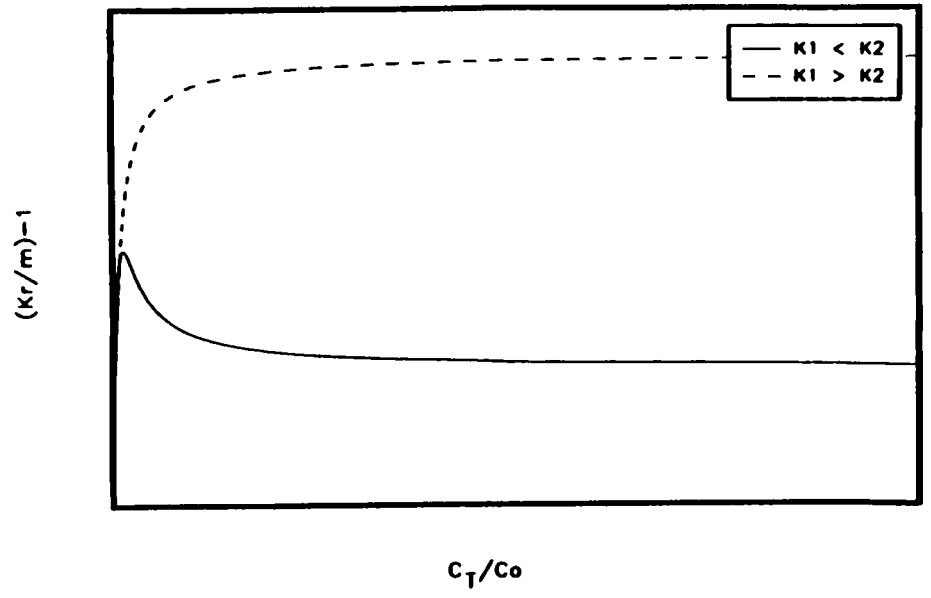

FIG. 5. Typical plot of K_r vs C_o for $K_1 > K_2$ and $K_2 > K_1$.

The value of K_1 for the monomer is twice the value of K_1 for the dimer (K_1^d). K_2 equals K_2^d. This is a direct result of Eq. (12). The values of the vertical axis for the dimer are twice those for the monomer since C_T^d equals Cr/2. Therefore, the slope of Fig. 3 is twice that of Fig. 2. K_1 is directly related to the intercept value (vertical axis), so $K_1^d = 2K_1$. Since the slope in Fig. 3 is twice that in Fig. 2 and $K_1^d = 2K_1$, K_2 is equal in each case.

The important issue is to determine which set of values is correct. In Fig. 4, the experimental results are plotted as well as Eq. (10) and Eq. (11). As can be clearly seen from Fig. 3, the complexing agent is present in the dimer form. This result indicates that K_1^d and K_2^d are the correct values of the equilibrium constants for this case.

The shape of the curve K_r versus C_o depends on the magnitude of K_1^d and K_2^d as illustrated in Fig. 5. If $K_1 > K_2$, the curve has the shape given by the dashed line. The solid line demonstrates the behavior for $K_1 < K_2$. Thus, the shape of the curve can indicate the relative value of the reaction equilibrium constants for solute bending. This result gives qualitative information as to whether one or two solute molecules are bound to the complexing agent molecule.

SPECTROSCOPIC STUDIES

In previous publications we described the chemistry of iron tetrakis(4-sulfonatophenyl)-porphyrin ($FeTPPS_4$) for application as an electroactive chemical complexing agent ina carrier-mediated separation scheme (*6*, *7*). For this study, spectroelectrochemical information of concentrated (>1 m*M*) aqueous solutions of Fe(II)$TPPS_4$ was needed. Since Fe(II)$TPPS_4$ is highly colored and easily oxidized by air, an anaerobic optically transparent thin-layer electrochemical cell (OTTLE) with a short path length was required. Several long and short path length OTTLE cell designs have been described for techniques such as UV-visible, IR, Raman, and ESR spectroscopy (*8–18*). Generally, these cells must be assembled and disassembled in order for them to be filled and cleaned (*8–15*, *19–23*). This can lead to errors in the path length and cell volume of the OTTLE requiring frequent recalibrations, especially among different workers. Described below is an OTTLE cell design that eliminates these difficulties.

Experimental Section for OTTLE Cell

Cell Fabrication

An illustration of the OTTLE cell is shown in Fig. 6 and is related to two previously published designs (*24*, *25*). The upper and lower cell body were blown from Pyrex glass. The ports in the upper body hold the counter

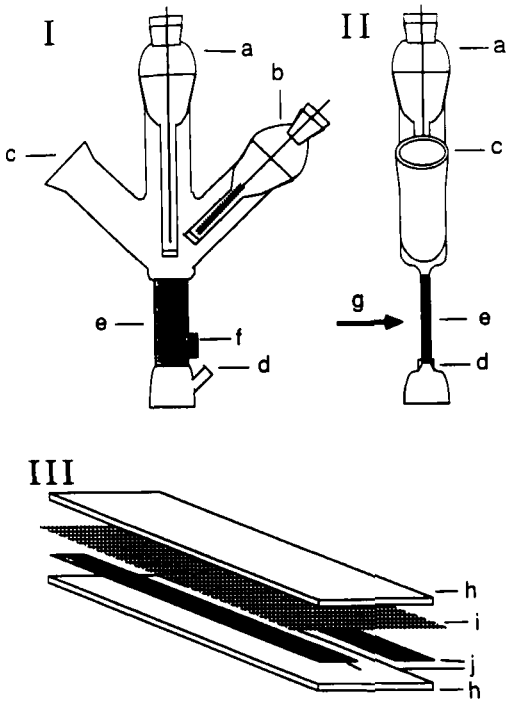

FIG. 6. OTTLE cell design: (I) front view, (II) side view, (a) reference electrode, (b) auxiliary electrode compartment, (c) solution inlet, (d) solution outlet, (e) OTTLE sandwich, (f) electrical contact, (g) light path. (III) OTTLE sandwich construction: (h) 1 × 3 cm quartz plates, (i) gold minigrid, (j) TEFZEL strips.

and reference electrodes. The reference electrode (Ag/AgCl, saturated KCl) was constructed of Pyrex glass with a ground glass joint to provide a vacuum-tight seal to the upper body. The end of the reference electrode was tipped with a Vycor frit (EG & G PAR) and a Ag/AgCl wire was sealed in the glass stopper with Torr Seal epoxy (Varian). The auxiliary compartment was also Pyrex glass with a ground glass joint tipped with a Vycor frit. The auxiliary electrode consisted of platinum gauze sealed in a glass stopper with Torr Seal. The third port was covered with a rubber septum and was used as an inlet for solution and the nitrogen/vacuum line.

The OTTLE was built from two 1 × 3 cm quartz plates, a gold minigrid electrode (200 lines/inch, Buckbee-Mears Industries), and 500LZ TEFZEL film (E. I. du Pont de Nemours & Co.). The OTTLE sandwich was constructed by welding two TEFZEL strips between the over-sized

minigrid and quartz plates as presented in Fig. 6. The sandwich was held together by metal clips and placed in an oven that consisted of a large beaker inverted on a hot plate. The OTTLE sandwich remained in this transparent oven at 300°C until the TEFZEL film was observed to be melting. This usually took about one to two minutes. When the sandwich cooled, the TEFZEL reconstituted, forming two parallel gaskets. It is important to note that the path length of the cell will be less than the original thickness of the TEFZEL since it is melted and then reconstituted under compression. 500LZ TEFZEL is nominally 127 μm thick; however, if other cell path lengths are desired, TEFZEL is available in several thicknesses ranging from 12.7 to 2300 μm.

A piece of copper foil was attached to the over-hanging gold minigrid with conductive epoxy to make an electrical lead to the OTTLE. The copper foil was then firmly epoxied to the OTTLE sandwich with Torr Seal so as not to risk tearing the delicate gold minigrid. The OTTLE sandwich was then mounted between the upper and lower cell body with Torr Seal. Torr Seal was also applied to the edges of the OTTLE sandwich to improve the rigidity of the cell.

Reagents

Potassium ferrocyanide (Baker) and sodium perchlorate (Fisher) were used as purchased. The sodium salt of iron(III) tetrakis(4-sulfonatophenyl)porphyrin ($Na_3Fe(III)$-$TPPS_4$) was synthesized according to a published procedure (*6*).

Instrumentation

Thin-layer cyclic voltammograms and spectra were obtained using instrumentation described previously (*6*). All potentials were reported versus the sodium chloride saturated calomel electrode (SSCE).

Filling Procedure

Two methods were used to fill the OTTLE cell. For redox couples that are not air sensitive (i.e., $Fe(CN)_6^{3-/4-}$), the solution was purged through the OTTLE sandwich by applying a positive pressure of nitrogen on the upper portion of the cell containing the solution. For air sensitive redox couples (i.e., $FeTPPS_4^{3-/4-}$), a different filling procedure was used. In this case the solution was placed in a pear-shaped flask and sealed with a rubber septum. The solution was purged with nitrogen through a nitrogen/vacuum line for 15 minutes. Next, a second nitrogen/vacuum line was placed in the lower septum on the OTTLE cell and the upper portion of the cell was connected to the solution flask via a stainless steel cannula. The entire

system was then evacuated for 30 minutes. Care must be taken to fill the reference and auxiliary electrodes completely with solution and seal well, or else the filling solution may be sucked through the frit. The solution was then transferred from the solution flask to the OTTLE cell by lowering the cannula into the solution and applying a positive pressure of nitrogen on the solution flask nitrogen/vacuum line. The solution was then forced down through the OTTLE sandwich by positive nitrogen pressure in the upper portion of the cell and vacuum in the lower section until the lower chamber of the cell was filled. The vacuum line on the lower part of the cell was then removed.

RESULTS AND DISCUSSION

OTTLE Characterization

The pertinent dimensions of optical path length and thin layer electrode volume were examined by repeated spectroscopic and electrochemical determinations. The path length of the OTTLE was measured by repeated determination of the absorbance at 394 nm ($\Sigma = 15.2 \times 10^4\ M^{-1}cm^{-1}$)(*20*) of a 2.03 mM solution of Fe(III)$TPPS_4^{-3}$ in 1.0 *M* $NaClO_4$. Ten calibration runs were made as the solution was flowed through the cell by applying a positive nitrogen pressure in the upper cell body. The average path length calculated was 35.5 ± 0.5 μm. This OTTLE provided a highly reproducible path length that seemed only to be limited by how reproducibly it was placed in the light path of the spectrophotometer. Also, the short path length makes it suitable for the study of highly concentrated solutions and analytes with large molar absorptivities, as will be shown later.

The volume of the OTTLE was determined by electrolysis of a 2.08 m*M* solution of $Fe(II)(CN)_6^{4-}$ in 1.0 *M* KCl at +0.6 and 0.0 V. Exhaustive electrolysis of the solution occurred after about 100 seconds. From eight repetitive electrolysis, an average charge of 1850 ± 30 μC was found. This indicated a highly reproducible cell volume of 9.2 ± 0.2 μL. Thin layer cyclic voltammograms (TLCV) obtained for $Fe(II)(CN)_6^{4-}$ under the same conditions exhibit the effects (ΔE_p = 75 mV at a scan rate of 1 mV/s) of uncompensated resistance, typical of most OTTLEs, although some designs have shown the problems can be eliminated (*8–15*). Nonetheless, this design gives a TLCV that shows the exhaustive electrolysis expected of OTTLEs (*26*). A value for $E^{\circ\prime}$ of +0.21 V was calculated from the difference in peak potentials and is in good agreement with the literature (*27*).

The ability of the OTTLE to exclude oxygen was tested in two ways. First, a background scan was done on 1.0 *M* $NaClO_4$ that was introduced to the cell under anaerobic conditions. The TLCVs showed no indication of ox-

ygen reduction between +0.1 and −1.0 V. Next, a solution of Fe(III)$TPPS_4$ in 1.0 *M* $NaClO_4$ was introduced to the cell under the same conditions. Following complete reduction at −0.5 V, the cell was turned off and the absorbance for Fe(II)$TPPS_4$ at 394 nm was monitored. The absorbance was found to decrease by only 1% within 40 minutes following the electrolysis, indicating good exclusion of oxygen.

Fe(II)$TPPS_4$ Spectroelectrochemistry

Seven solutions of Fe(III)$TPPS_4$ in 1.0 *M* $NaClO_4$ with concentrations ranging from 0.4 to 8.0 m*M* were purged with nitrogen for 10 to 15 minutes and then introduced into the OTTLE cell under anaerobic conditions as described above. An electrolysis was carried out at −439 mV with the end point detected by current decay. Following complete reduction, the absorbance at 546 nm was observed and recorded. A plot of the data is given as Fig. 7. No solute was present during these experiments. The deviation of the plot from a straight line is evidence for aggregation.

This figure agrees well with Pasternak and coworkers (*28*) report on the unmetallated trisulfonated species $TPPS_3$. Unfortunately, we are unable to study the Fe(II)$TPPS_4$ system in the absence of electrolyte (it must be produced from Fe(III)$TPPS_4$ electrochemically) as Pasternak and associates demonstrated was necessary to fully determine the degree of this dimerization. It is important to note that the concentration range studied here reaches to 8.0 m*M*, very near the solubility limit of this porphyrin.

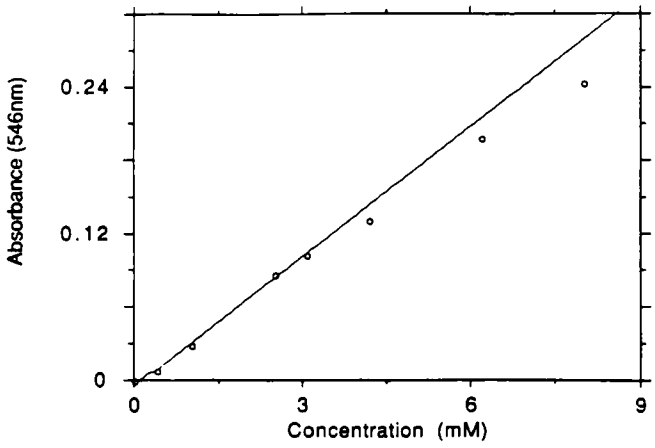

FIG. 7. Beer's law plot for 546 nm absorbance maximum of Fe(II)TPPS in 1.0 *M* $NaClO_4$ as determined in OTTLE cell. Reduction was done at −439 mV vs SSCE. The line represents linear regression for FeTPPS concentrations ≤3 m*M*.

Pasternak et al. reported data for $TPPS_3$ concentrations of less than 0.02 m*M*. The short path length of the cell described here clearly increases the concentration range available for OTTLE studies of molecules with high absorbtivities. The ability to investigate high concentrations is necessary when molecules like $FeTPPS_4$ are used to alter solute partitioning.

COMPARISON OF THE TWO METHODS

This study serves to illustrate several important features associated with the use of complexing agents to affect the partitioning of solutes between two phases. One must realize that use of molecules like $FeTPPS_4$ for these purposes is quite different from the use of surfactants or detergents which enhance the partitioning of organics into aqueous phases via the formation of micelles. Since micelles accomplish their purpose by the formation of hydrophobic domains within the aqueous phase, they are generally non-selective with respect to a variety of hydrophobic solutes. The use of molecules like $FeTPPS_4$ for solute partitioning can be quite selective because the partitioning results from a distinct chemical reaction between the complexing agent and solute. Unlike the use of micelle-forming extractants, it is undesirable for the complexing agent to aggregate in the aqueous phase because this tends to lessen the amount of complexing agent available for binding solute. Unfortunately, due to the structure of molecules like $FeTPPS_4$, aggregation tends to occur when the complexing agent is at high concentrations, which is undesirable in terms of having the greatest effect on the parition coefficient.

The results presented here for the partitioning of 2-amino-napthalene between an organic and aqueous phase, and how this partitioning can be altered with a molecular complexing agent, demonstrate the effects described above. The analysis, which requires only total solute partitioning data in the presence and absence of the complexing agent, provides information about both the stoichiometry of the complexation reaction and about aggregation of the complexing agent. In the case investigated experimentally, the analysis was more consistent with the existence of $FeTPPS_4$ as a dimer (Fig. 4). This is an important result because capacity of the aqueous phase to extract organonitrogen compounds like 2-amino-napthalene is lower for the dimer as compared to the monomer. The spectroscopic studies, which involved the design and testing of a previously unreported type of OTTLE cell, completely support the results of the analysis. Notice that the highest concentration of $FeTPPS_4$ investigated in Fig. 7 is 8 m*M*, which is lower than the concentrations used in the solute partitioning experiments, 10 m*M*. The spectroscopic studies support dimer formation which would be expected for these types of molecules in aqueous

solutions containing added salt. It should be added that the cell design has uses other than observing deviations from Beer's law. Complete spectra can be obtained for air-sensitive solutions with extremely high absorbances, and these spectra can be useful for understanding the chemistry that occurs in such solutions.

Acknowledgments

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REFERENCES

1. W. J. Ward, III, *Nature, 227,* 162 (1970).
2. A. L. Athayde and C.F. Ivory, *J. Membr. Sci., 24,* 309 (1985).
3. D. Townley and J. Winnick, *Ind. Eng. Chem., Process Des. Dev., 20,* 435 (1981).
4. D. Townley and J. Winnick, *Electrochim. Acta, 28,* 389 (1983).
5. J. Ciccone, L. Deardurff, E. Decastro, J. Kerr, and B. Zenner, Paper 897 presented at the 172nd Meeting of the Electrochemical Society, Honolulu, 1987.
6. C. A. Koval, S. M. Drew, R. D. Noble, and J. Yu, *Inorg. Chem., 29,* 4708 (1990).
7. N. Jemaa, R. D. Noble, C. A. Koval, and J. Yu, *Chem. Eng. Sci., 46*(4), 1017 (1991).
8. T. P. Degelis and R. Heineman, *J. Chem. Educ., 53,* 594 (1976).
9. M. D. Porter, D. Shaojung, Y. P. Gui, and T. Kuwana, *Anal. Chem., 56,* 2263 (1984).
10. D. A. Scherson, S. Sarangapani, and F. L. Urbach, *Ibid., 57,* 1501 (1985).
11. X. Q. Lin and K. M. Kadish, *Ibid., 57,* 1498 (1985).
12. X. Q. Lin and K. M. Kadish, *Ibid., 58,* 1493 (1986).
13. J. P. Bullock, D. C. Boyd, and K. R. Mann, *Inorg. Chem., 26,* 3084 (1987).
14. Y. Gui, S. A. Soper, and Y. Kuwana, *Anal. Chem., 60,* 1645 (1988).
15. W. A. Nevin and A. B. P. Lever, *Ibid., 60,* 727 (1988).
16. T. Kuwana and W. R. Heineman, *Acc. Chem. Res., 9,* 241 (1976)
17. W. R. Heineman, *J. Chem. Educ., 60,* 305 (1983).
18. D. Dewold, J. W. Watkins, R. C. Elder, and W. R. Heineman, *Anal. Chem., 58,* 2968 (1986).
19. P. Hambright and E. B. Fleischer, *Inorg. Chem., 9,* 1757 (1970).
20. E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Am. Chem. Soc., 93,* 3162 (1971).
21. P. A. Forshey and T. Kuwana, *Inorg. Chem., 22,* 699 (1983).
22. M. A. Kline, M. H. Barley, and T. J. Meyer, *Ibid., 26,* 2197 (1987).
23. M. H. Barley, M. R. Rhodes, and T. J. Meyer, *Ibid., 26,* 1746 (1987).
24. D. Lexa, J. M. Saveant, and J. Zickeler, *J. Am. Chem. Soc., 99,* 2786 (1977).
25. W. P. G. Pilkington, B. A. Coles, and R. G. Compton, *Anal. Chem., 61,* 1787 (1989).
26. A. J. Bard and L. R. Faulkner, Wiley, New York, 1980.
27. I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem., 39,* 945 (1935).
28. R. F. Pasternak, P. R. Huber, P. Boyd, G. Engasser, L. Franesconi, E. Gibbs, P. Fasella, G. C. Venturo, and L. dC. Hinds, *J. Am. Chem. Soc., 94,* 4511 (1972).

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