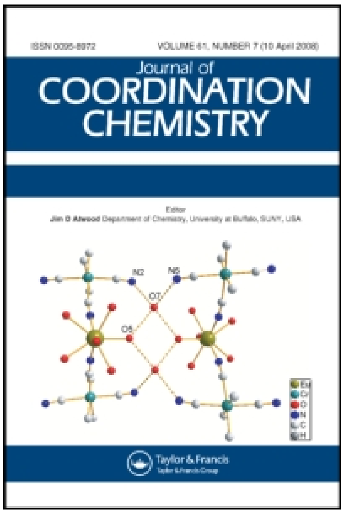

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THE VANADIUM(II) COMPLEX WITH ACRYLONITRILE

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Solutions of V(II) and acrylonitrile give a deep orange complex which was studied spectrophotometrically and polarographically. The complex is weak, $K_f \sim 1$ to 5 for a 1 : 1 V(II)-ACN. An earlier report of a strong complex was in error due to the irreversible nature of the V(II)/V(III) reduction couple in the presence of acrylonitrile.

INTRODUCTION

In 1958 Dainton and James[2] reported the existence of a strong complex between vanadium(II) and acrylonitrile (AcN) based upon a spectral displacement of the vanadium(II) sulfate charge transfer band at 5000 Å to shorter wavelengths (the pale lavender vanadium(II) solution turns bright orange on addition of AcN) and upon a potentiometric displacement of +780 mv. for the V(II)/V(III) couple when AcN was added. The ΔE corresponds to a decrease in the vanadium(II) activity by a factor of 10^{13}. The calculated stability constant, $K_f = 1.67 \times 10^{13}$, indicated a very stable complex and predicted that vanadium(III) becomes a very good oxidizing agent in the presence of AcN rather than maintaining its reducing character.

While attempting to arrive at the stoichiometry of the complex, we examined the system polarographically to determine the shift in $E_{1/2}$ of the V(II)/V(III) couple on addition of AcN. Surprisingly, no shift greater than about 15 mv could be obtained even in solutions saturated with AcN (~ 1 *M*). Consequently we have examined the vanadium(II)-acrylonitrile system by electrochemical and spectrophotometric techniques to determine the stoichiometry, stability constant and possible reasons for the reported erroneous ΔE value.

EXPERIMENTAL

Acrylonitrile (Aldrich Chemical Company, Inc.) was distilled and the fraction boiling at 77.4° C collected. All other chemicals were reagent grade and used directly. Ceric ammonium sulfate solutions were standardized against ferrous ethylenediammonium sulfate (G. F. Smith Chemical Co., Primary Standard Grade). Solutions of vanadium(II) sulfate were made by zinc amalgam reduction of V_2O_5 in deaerated 1.3 *M* H_2SO_4 and were standardized by adding aliquots to an excess of standard cerate solution and back titrating with a 0.1000 M solution of ferrous ethylene-diammonium sulfate.[3] Solutions of AcN in 1 : 1 (V/V) ethanol/H_2O were made from deaerated AcN and solvent. All solution transfers were carried out under a nitrogen atmosphere.

Polarographic and potentiometric experiments were carried out with a Beckman Electroscan 30. The electrochemical cell was equipped with a dropping-Hg indicating electrode, a platinum flag counter electrode and a saturated calomel reference electrode. Spectrophotometric data were taken on a Cary 14 spectrophotometer using an air tight 200 ml bottle equipped with two spectrophotometric cells as side arms: one a 1.00 cm cell, the other a 0.100 cm cell. Solutions of vanadium(II) showed no noticeable change in absorbance over a period of at least two days in this cell. Calculations of the vanadium(II) molar absorptivity at 560 nm using the concentrations as determined above gave $\epsilon = 3.0$ for V(II)/1 *M* H_2SO_4.[4]

RESULTS

Spectroscopy

The addition of AcN to a vanadium(II) solution gives a deep orange complex (Figure 1): charge transfer band, 375 nm.; $\epsilon_m = 625\ M^{-1}\ cm^{-1}$ [1000 fold excess of AcN to V(II)]. All the other vanadi-

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um species shown have $\epsilon_m < 20\ M^{-1}\ cm^{-1}$ and so were not used in correcting values of $\epsilon_{complex}$.

Attempts to obtain the stoichiometry of vanadium(II) to AcN in the complex by standard spectrophotometric titration techniques gave the results of Figure 2: titrations of vanadium(II) with AcN and of AcN with vanadium(II) were made. When the metal is in excess at the start (Figure 2A), a rapid change to green, indicative of vanadium(III), occurs. This decomposition limits the applicability of titrations of vanadium(II) with AcN. On the other hand, titrations of AcN with vanadium(II) (Figure 2B) are reliable at the start since the vanadium(II)-AcN complex is stable for long periods when excess AcN is present. Near the end of the titration, the solution composition approaches that of graph 2A, where metal concentrations are large, increasing the possibility of side reactions. In both titrations a stoichiometry of less than 4 : 1 (L : M) is indicated. The beginning portion of the titration of AcN with vanadium(II) indicates a ratio of 2 : 1 or 1 : 1.

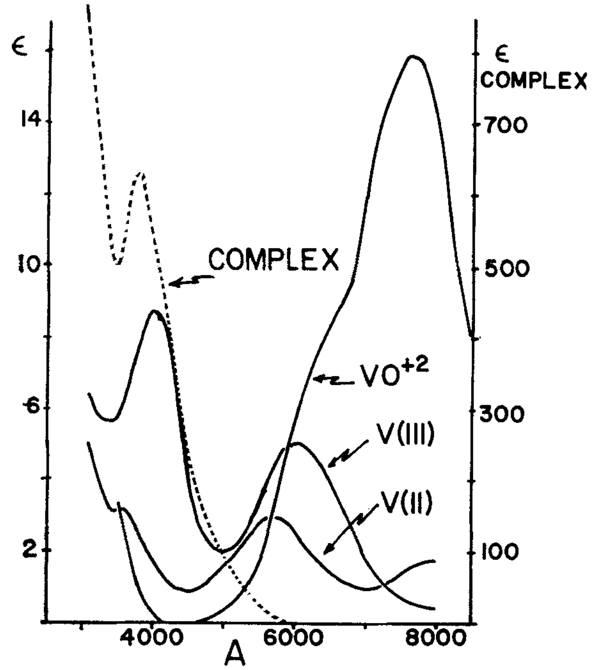

FIGURE 1 Visible absorption spectra of vanadium species: vanadium(II)-AcN complex (right scale) vanadyl sulfate, vanadium(III) sulfate and vanadium(II) sulfate (left scale).

A dilution study was carried out to avoid complications arising from the side reactions at low molar ratios of AcN to vanadium(II). Solutions of vanadium(II)/excess AcN were diluted with deaerated water while the peak at 375 nm was monitored. By disturbing the equilibrium between aquated vanadium(II) and AcN complexed vanadium(II) in this way, one can determine K_f. This method seems applicable to many weak complexes; however it assumes that there is only a single complex in the solution.

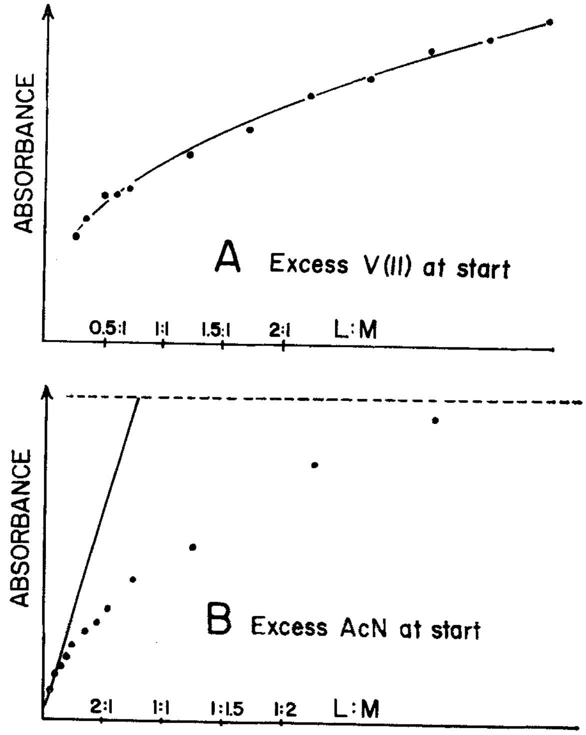

FIGURE 2 Spectrophotometric titrations of (A) vanadium(II) sulfate with AcN and (B) AcN with vanadium(II) sulfate.

For the equilibrium:

$$V^{2+} + xL \rightleftarrows VL_x^{2+} \tag{1}$$

with formation constant

$$K_f = [VL_x^{2+}]/[V^{2+}][L]^x \tag{2}$$

the analytical concentration of V(II) is

$$C_{V(II)} = [V^{2+}] + [VL_x^{2+}]. \tag{3}$$

Rearrangement of equation 3 gives

$$\frac{[V^{2+}]}{[VL^{2+}]} + 1 = \frac{C_{V(II)}}{[VL_x^{2+}]} = \beta \tag{4}$$

where $\frac{C_{V(II)}}{[VL_x^{2+}]}$ can be obtained by using the molar absorptivity of vanadium (II)AcN complex. Combining equations 2 and 4 gives

$$\beta = 1/K_f[L]^x + 1$$

Plots of β vs $1/[L]$ and $1/[L]^2$, corresponding to stoichiometries ML and ML_2 respectively, are given in Figure 3. The plots should give straight lines with an intercept of 1.0 and a slope of $1/K_f$. Plots of β vs $1/[L]$ give a more nearly linear correlation than those of $1/[L]^2$ (Figure 3). The stoichiometry of 1 : 1 and a K_f of 1.55 are very close to the electrochemical data: $K_f = 1.8$ for a 1 : 1 complex (see below).

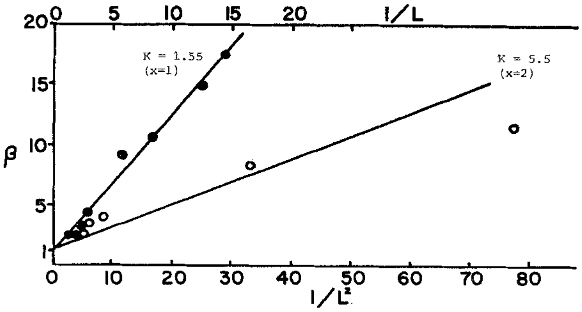

FIGURE 3 Plots of β vs $1/[L]$ (solid circles, top scale) and $1/[L]^2$ (open circles, bottom scale).

Electrochemistry

For reversible couples, the stoichiometry of the complex can be determined by a plot of $E_{1/2}$ vs log [ligand]. Plots of $E_{1/2}$ for V(II)/V(III) vs log [AcN] cannot give valid determinations of stoichiometry since electron exchange between V(III) and V(II) in the presence of AcN is irreversible (Figure 4). It can also be seen from Figure 4 that only a small shift in the potential at zero current ($E_{i=0}$) occurs even with a large excess of AcN. The $\Delta E_{i=0}$ is no greater than 15 mv. with concentrations of 1 *M* AcN. This value can be only approximate since AcN is not completely soluble in water, leading to errors in determining the molarity of AcN (and more importantly its activity). A K_f of less than 10 for the vanadium(II) complex falls in line with other weak vanadium(II) complexes such as vanadium(II) thiocyanate:[5] $K_f = 11$. Experiments were done in $SO_4^{=}$, ClO_4^- and BF_4^- media to observe effects of the anion on the V(II)/V(III)-AcN system. No significant change ($\Delta E_{i=0} < 1$ mv.) could be detected.

Since both vanadium(II) and vanadium(III) waves were lowered on addition of AcN, it was thought that perhaps the waves split into two parts, one 780 mv. anodic to the ones being observed. However, polarograms using a rotating platinum electrode from +1 v to −1 v showed only the V(III)/V(II) waves, about −0·55 v.

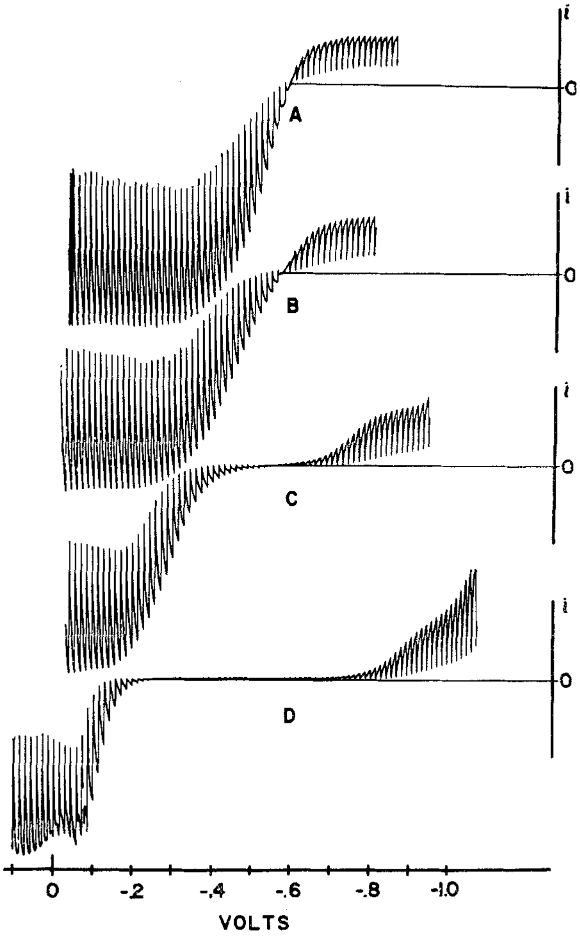

FIGURE 4 Polarograms of V(II) 8×10^{-3} *M*, 40 ml, with varying molar amounts of AcN.

(A) O AcN (B) 2 ml (0.03 mole) AcN (C) 7 ml (0.106 mole) AcN (D) 17 ml (0.258 mole) AcN.

Addition of acetonitrile to the vanadium(II) solutions causes similar changes in the electrochemical properties of the V(II)/V(III) couple but the spectral behavior is more nearly similar to the thiocyanate complex (Table I). Apparently the olefinic group is involved in the charge-transfer process.

TABLE I

Constants for Vanadium(II) with Ligands

Ligand	λ_{max}(nm)	ϵ_{max}	$\Delta E_{(i=0)}$[a]	K_f
Acrylonitrile	380	626	15 mv.[c]	1·55–5·5
Thiocyanate	520	23	10–15 mv.[c]	3–1(11)[b]
Acetonitrile	730	16	10–15 mv.[c]	
	490	14		1·15–3[d]
EDTA	—	—	55 mv.	—

[a] $\Delta E_{(i=0)}$ per ten fold change in ligand concentration.
[b] Reference 5.
[c] Potentiometrically determined; irreversible waves.
[d] J. H. Carney private communication.

DISCUSSION

The Dainton and James report of a complex between vanadium(II) and AcN with a K_f of 10^{13} is certainly erroneous. Figure 4C and D shows the most probable reason for their results. A potentiometric determination of $E_{i=0}$ would have to be performed with extraordinary care to detect the exact zero point. The non-reversible nature of the couple separates the vanadium(II) and vanadium(III) waves such that the region of $E_{i \approx 0}$ is very large. Without considering this problem, one might choose the extreme anodic region of the wave and thus find a $\Delta E_{i=0}$ of about 600 mv. (Figure 4D). The potential $E_{i=0}$ measured polarographically and corrected for residual current is identical with the value that would be measured potentiometrically. The advantage in obtaining the value via polarography is that the ratio of anodic to cathodic wave heights allows direct correction for any change in V(II)/V(III) ratio. It was necessary to monitor this ratio since the V(II) is particularly sensitive to air oxidation.

Acrylonitrile can coordinate through the olefinic group as a π-acceptor or through the nitrile group as a σ-donor.[6] Its vanadium complexes are very few. The only isolated compounds have been the anhydrous vanadium(III) chloride complexes: $VCl_3 \cdot 3AcN$[7] and $VCl_3 \cdot 2AcN$.[8] In these the AcN is σ-bonded thru the lone pair of electrons on the nitrile. In aqueous acid solutions vanadium(III) sulfate gives no spectral nor polarographic shifts when AcN is added. Consequently one can assume that the nitrile group is a poor donor toward aquated vanadium(III). In general AcN σ-donation is formed when the electron density on the central metal is low[6], but here the nitrile cannot compete with strong basicity of water.

In the case of the more electron-rich vanadium(II), the acidity of the metal has dropped and one observes a high potential for release of electrons thru oxidation: $V(II) \rightarrow V(III) + e^-$, $E^\circ = 0.26$.[9] In the V(II)·AcN complex there should be a ready donation of electrons from the vanadium(II) to the most accessible unoccupied orbital of the ligand: the π^* orbital of the olefin. Our polarographic data shows that the AcN complexing ability increases on going from vanadium(III) to vanadium(II) although the latter is still very weak. The spectral data on the weak complex indicates that the olefinic bond must participate in the electronic transition at 375 nm. The molar absorptivity indicates a charge transfer transition, $L \leftarrow M$, whereby the vanadium(II) undergoes a lowering of its electron density.

These conclusions are strengthened by the behavior of V(II) in the presence of acetonitrile. Spectra of V(II) in aqueous acetonitrile solutions show that while the two weak V(II) absorptions at 590 and 800 nm are shifted to higher energies, no intense absorption characteristic of a charge transfer transition occurs. Polarographic data indicate a V(II): acetonitrile complex similar to that with acrylonitrile: K_f for a 1 : 1 complex about 3. Spectroscopic data indicate a weak 1 : 1 complex with K_f about 1.15. These K_f's are similar to that of the V(II)-AcN complex and indicate a somewhat similar mode of coordination of AcN and acetonitrile under these aqueous conditions. The similarities indicate that the large charge transfer band of the V(II)-AcN system must involve the olefinic bond of the AcN.

Attempts to establish structural features by EPR (vanadium(II), (II) and IV) are paramagnetic but V(III) has a large zero field splitting and is seldom observed—no change in the V(II) spectrum was observed on adding AcN), infrared (the aqueous acid solution, the reducing power of vanadium(II) and (III) and the large excess of AcN necessary to obtain concentrated solutions of V(II) AcN complex prevented studies) and laser Raman spectroscopy (absorption losses prevented studies) were not fruitful.

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