display an initial heat of adsorption toward nitrogen[17] comparable to that of the reinforcing channel blacks. Such materials, however, usually do not approach the large extent of surface displayed by carbon black. On the basis of these data one must conclude that high surface activity involving van der Waals forces, together with a high degree of sub-division, are the most significant factors in the reinforcement of rubber by pigments.

Acknowledgment.—We are greatly indebted to Dr. Ralph A. Beebe of Amherst College for helpful discussions of this work, and to Dr. Leslie Joyner of Mellon Institute for suggesting the use of ion exchanged or neutralized Spheron 6.

BOSTON 11, MASS. RECEIVED AUGUST 2, 1950

[17] G. L. Kington, R. A. Beebe, M. H. Polley and W. R. Smith, THIS JOURNAL, **72**, 1775 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY AND THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Polarographic Characteristics of +2 and +3 Vanadium. II. Polarography in Complexing Solutions[1]

BY JAMES J. LINGANE AND LOUIS MEITES

Data are presented on the half-wave potentials and diffusion current constants of the waves of +2 and +3 vanadium in benzoate, carbonate, citrate, cyanide, fluoride, phosphate, phthalate, pyridine, pyrophosphate, salicylate, tartrate, tetraborate, thiocyanate and thiosulfate solutions.

Introduction

This paper is an extension of previous work[2–4] on the polarography of +2 and +3 vanadium. The first paper in the present series discussed the polarographic characteristics of vanadous and vanadic ions in dilute solutions of acids and alkalies, acetate buffers and the halides: this paper discusses the ionic states and polarographic behaviors of the complexes formed by these ions in a wide variety of media.

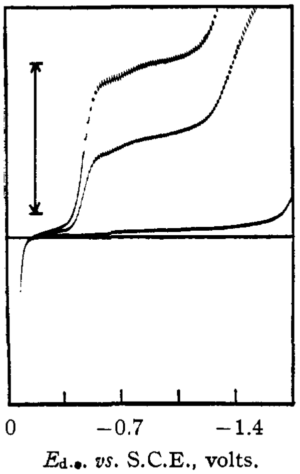

Fig. 1.—Polarograms of (a) 0, (b) 1.83 and (c) 3.44 mM +3 vanadium in 1 F ammonium thiocyanate. The height of the arrow corresponds to ten microamperes.

Data and Discussion

Of the fourteen complexing agents used in this study, only three were found to give vanadium(II–III) couples which approach thermodynamic reversibility at the dropping electrode. These three systems will be discussed in some detail, together with a few others with unusual polarographic characteristics. Data on the others are summarized in Table I.

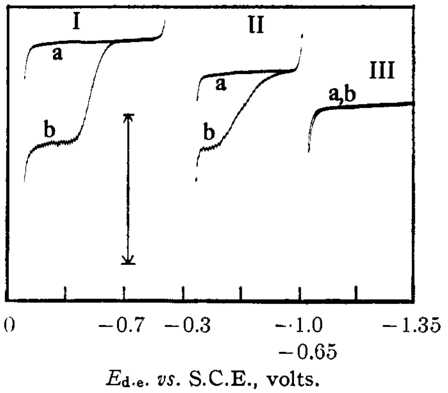

Fig. 2.—(I) Polarograms of (a) 0 and (b) 2.05 mM +2 vanadium in 1 F ammonium thiocyanate. (II) Polarograms of (a) 0 and (b) 1.85 mM +2 vanadium in 1 F sodium thiosulfate. (III) Polarograms of (a) 0 and (b) 1.40 mM +2 vanadium in 1 F potassium cyanide. The height of the arrow corresponds to six microamperes.

Figure 1 and curves I of Fig. 2 are polarograms of +3 and +2 vanadium in 1 F ammonium thiocyanate. The solutions of +3 vanadium are initially very deep green, but change to yellow-green suspensions within a few minutes, while an initially intense lavender vanadium(II) solution soon develops a turbidity and becomes decolorized. In this medium +3 vanadium gives a single cathodic wave (Fig. 1), for which $E_{1/2} = -0.461$ v. (all potentials are referred to the saturated calomel electrode unless otherwise indicated), $I = 1.78 \pm 0.01$, and $\Delta(-E_{d.e.})/\Delta \log [i/(i_d - i] = 65$ mv., in good agreement with the value expected for a reversible one-electron reduction.[5] The corresponding data for the vanadium(II) complex are −0.465 v., −2.04 ± 0.02, and −69 mv. The two half-wave potentials are so close together that the irreversibility of the V^{+2}–V^{+3} couple must be very small, and their mean, −0.217 v. *vs.* the normal hydrogen electrode, must be within a few millivolts of the true standard potential. From this value we calculate the figure 2.4 for the ratio of the dissociation constants of the complexes $K_{V(SCN)_m^{3-m}}/K_{V(SCN)_n^{2-n}}$. As neither of the half-wave potentials is altered by changing the thio-

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[1] This paper is based in part on a thesis submitted by Louis Meites to the Graduate Faculty of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in February, 1947.

[2] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

[3] J. J. Lingane and L. Meites, *ibid.*, **69**, 1021 (1947).

[4] J. J. Lingane and L. Meites, *ibid.*, **70**, 2525 (1948).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 167–170.

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF +2 AND +3 VANADIUM COMPLEXES

Supporting electrolyte	Oxidation state of V	$E_{1/2}$ vs. S.C.E., v.	I	$(-E_{d.e.})/\log i/(i_d - i)$ mv.	Oxidation state of product	Remarks
Benzoic acid–Na benzoate (1 *F* total benzoate), *p*H 5.3	+2	(−0.80)	−1.7 ± 0.1		+3	Very irreversible
		(−0.12)			+4	
	+3	(+0.15)			+4	$(BzO)_2VOH$, $K_{s.p.}$ = *ca.* $10^{-4.6}$; solns. turbid yellowish-green
		−1.0			+2	
		−1.3			+2	
0.1 *F* $KHCO_3$, satd. CO_2, *p*H 6.7	+2	(−0.70)		−122	+3	
		(−0.03)		−123	+5	
	+3	(−0.06)			+5	
1.0 *F* $KHCO_3$, satd. CO_2, *p*H 7.6	+2	(−0.792)	−1.15 ± 0.01		+3	
		(−0.07)	−4.75 ± 0.05		+5	
	+3	(−0.20)	−2.99 ± 0.02		+5	
0.5 *F* $KHCO_3$–0.5 *F* Na_2CO_3, *p*H 9.4	+2	(−0.75)	−1.19 ± 0.01	−131	+3	
		(−0.18)	−4.16 ± 0.03	− 70	+5	
	+3	(−0.337)	−2.80 ± 0.01	− 60	+5	
1.0 *F* Na citrate, *p*H 6.8			See text			
1.0 *F* KCN	+2	No wave before anodic dissolution of Hg				Solns. clear, colorless
	+3	−1.17	0.71 ± 0.01			V(OH)$^{++}$
		−1.77	1.33 ± 0.02	55	+2	Reducible species unknown, solns. faint rose, turbid
1.0 *F* KF	+2	(-0.70_1)	−1.96 ± 0.01	−166	+3	
		(-0.1_5)			+4	Ill-defined
		$(+0.2_1)$			+5	Ill-defined
	+3	No wave; K_2VF_6 apparently quant. pptd.				
1.0 *F* Na_3PO_4, *p*H 5.0	+2	(−0.70)	−1.329 ± 0.005		+3	
		(+0.2)			(+5)	Ill-defined
	+3	$(+0.2_0)$			+5	
		(−0.06)	−1.00 ± 0.01	− 64	+4	
		−1.36	1.15 ± 0.05	220	+2	VO$^+$ (?)
1.0 *F* Na_3PO_4, *p*H 6.5	+2	(-0.77_4)	−1.159 ± 0.008	−155	+3	
		(+0.03)	−3.46 ± 0.05	− 24	+5	Reversible
	+3	(+0.02)		− 64	+5	Reversible
		(−0.04)		−141	+4	
		-1.39_5		145	+2	
1.0 *F* Na_3PO_4, *p*H 7.8	+2	(−0.81)			+3	Cryst. white ppt., V(HPO_4) (?)
		(+0.04)			+5	
	+3	(-0.16_5)	−1.43 ± 0.03 (up to 1.1 m*M*, i_d const. at higher concns.)	−127, −61	+4	Gelatinous green ppt., sol. 2 *N* but not 0.1 *N* H_2SO_4: V(OH)(HPO_4) (?)
		−1.54		122	+2	
Satd. KH phthalate, *p*H 5.2			See text			
1 *F* pyridine–pyridinium sulfate, *p*H 5.5–6.5			See text			
Satd. $Na_4P_2O_7$, *p*H 5.5	+2	(−0.96)	−1.48 ± 0.01	−170	+3	Solns. colorless
	+3	$-1._5$			+2	Small turbidity
Salicylic acid–Na salicylate (1 *F* total salicylate), *p*H 4.7	+2	(−0.764)	−1.16 ± 0.02		+3	
		(−0.15)	−3.52 ± 0.03		+5	
	+3	(−0.06)	−1.17 ± 0.02	− 97	+4	Solns. turbid yellowish-green
		−0.97)	0.257 ± 0.005	66	+2	V(OH)$^{++}$
		−1.21	1.26 ± 0.02	66	+2	VO$^+$
1.0 *F* Na tartrate, *p*H 6.2			See text			
Satd. $Na_2B_4O_7$, *p*H 5.1	+2	(−0.55)	−1.92 ± 0.02	−105	+3	Solns. clear, colorless
		(−0.03)			+4	
		(+0.13)			+5	
	+3	(+0.1)			(+5)	Light green ppt., soly. *ca* 0.8 m*M*
		−1.1			+2	
1.0 *F* NH_4SCN			See text			
1.0 *F* $Na_2S_2O_4$	+2	(−0.63)	−2.16 ± 0.03		+3	Very irreversible
	+3	−0.60				Reducible species unknown
		−1.0			+2	V(OH)$^{++}$. Some pptn.

cyanate concentration to 0.33 *F* or 0.1 *F*, *n* must equal *m* in these formulas.

One of us has recently described the volumetric and amperometric titrations of chromate and ferric iron in thiocyanate media with standard vanadium(II) solutions.[6]

Typical polarograms of the jade-green complex of +3 vanadium in a solution of *p*H 5.2 saturated with potassium biphthalate are shown as curves II in Fig. 3. The half-wave potentials of the anodic and cathodic waves are −0.10 and −0.877 v., and the corresponding diffusion current constants are −1.132 ± 0.007 and 1.221 ± 0.003. Plots of $-E_{\rm d.e.}$ *vs.* $[i/(i_{\rm d} - i)]$ for the cathodic wave consist of two intersecting straight lines whose slopes are 130 and 270 mv., showing that this wave actually corresponds to the reduction of two ionic species in sluggish equilibrium.

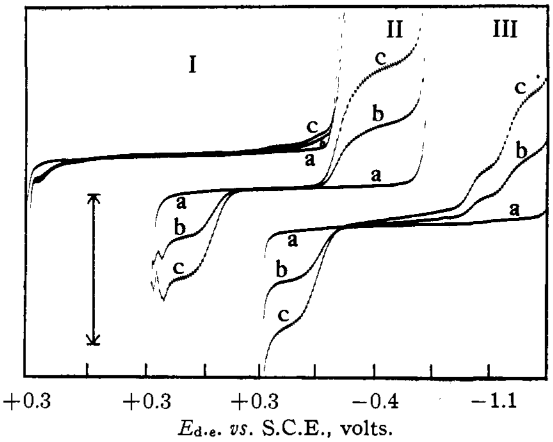

Fig. 3.—Polarograms of (a) 0, (b) 1.83 and (c) 3.44 m*M* +3 vanadium in (I) benzoic acid–sodium benzoate buffer (1 *F* total benzoate), *p*H 5.3, (II) potassium phthalate–potassium biphthalate buffer of *p*H 5.2, and (III) salicylic acid–sodium salicylate buffer (1 *F* total salicylate), *p*H 4.7. The height of the arrow corresponds to ten microamperes.

Solutions of +2 vanadium in this phthalate–biphthalate buffer are bright yellow in color, and give two anodic waves of equal height (see Fig. 4), corresponding to oxidation to the +3 and +4 states. The half-wave potentials of these waves are −0.840 and −0.153 v., and their diffusion current constants are −1.78 ± 0.01 and −3.53 ± 0.01 (all diffusion currents are referred to the residual current and not, as is frequently done, to the plateau of a preceding wave). Both of these waves are nearly reversible: $\Delta(-E_{\rm d.e.})/\Delta \log [i/(i_{\rm d} - i)]$ is −77 mv. for the wave representing oxidation to the +3 state, and −69 mv. for the second wave. Although the complexity of the cathodic V^{+3} wave makes the calculation somewhat uncertain, the half-wave potentials of the anodic and cathodic waves of the vanadium(II–III) couple are so nearly equal that the reversible half-wave potential must be very nearly equal to their mean, −0.86 v. Therefore, the formal potential in this medium is close to −0.61 v. *vs.* N.H.E.

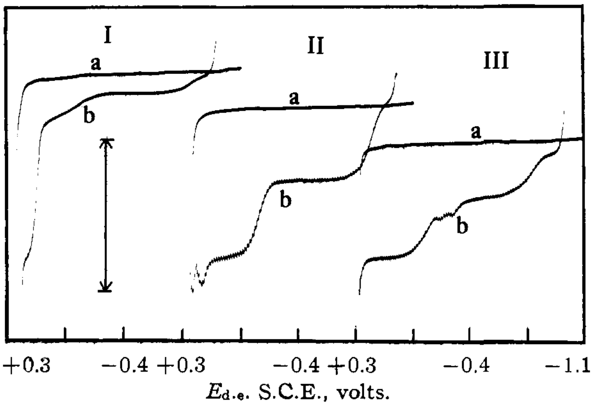

Fig. 4.—Polarograms of (I) (a) 0 and (b) 0.91 m*M* +2 vanadium in benzoic acid–sodium benzoate buffer (1 *F* total benzoate), *p*H 5.3; (II) (a) 0 and (b) 1.10 m*M* +2 vanadium in potassium phthalate–saturated potassium biphthalate buffer, *p*H 5.2; and (III) (a) 0 and (b) 0.79 m*M* +2 vanadium in salicylic acid–sodium salicylic buffer (1 *F* total salicylate), *p*H 4.7. The height of the arrow corresponds to ten microamperes.

In 1 *F* sodium citrate at *p*H 6.2 + 3 vanadium gives three waves, two anodic at $E_{1/2}$ = +0.08 and −0.10 v., and a single cathodic wave, $E_{1/2}$ = −1.60 v. While none of these waves has a plateau sufficiently well defined to permit accurate measurement of its height, it is evident from inspection of the polarograms (curves II, Fig. 5) that all three are approximately equal, and hence that each must represent a one-electron change.

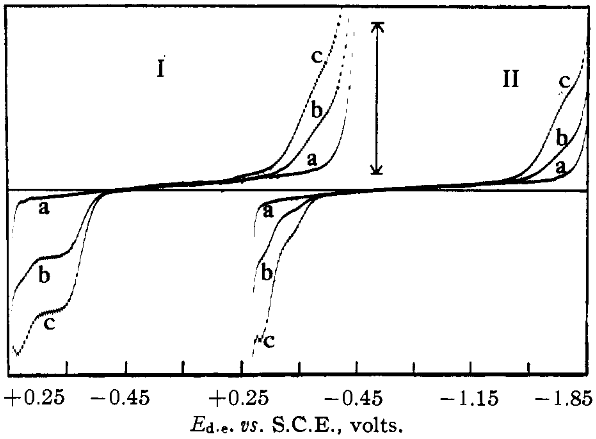

Fig. 5.—Polarograms of (a) 0, (b) 0.94 and (c) 1.83 m*M* +3 vanadium in (I) 1 *F* sodium tartrate, *p*H 6.2, and (II) 1 *F* sodium citrate, *p*H 6.8. The height of the arrow corresponds to four microamperes.

In this citrate medium +2 vanadium (curves II, Fig. 6) gives two ill-defined anodic waves, $E_{1/2}$ = +0.10 and −0.04 v. (substantially identical with the corresponding waves in +3 vanadium solutions), representing oxidation to the +4 and +5 states. These are preceded by another anodic wave for which *I* = −0.871 ± 0.008. The half-wave potential of this wave is too negative to be measured in the presence of excess citrato–zinc complex. With zinc-free solutions, prepared from vanadous sulfate kindly furnished by the late Professor Grinnell Jones, $E_{1/2}$ is found to be −1.166 ± 0.002 v. (Fig. 7) and $E_{3/4} - E_{1/4}$ to be 57 mv., in agreement with the expected value for a reversible one-electron oxidation.

These data show the vanadium(II) citrate complex to be an extremely powerful reducing

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[6] L. Meites, *J. Chem. Ed.*, **27**, 458 (1950).

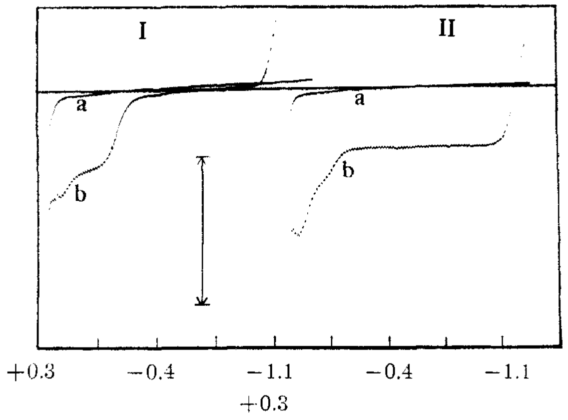

Fig. 6.—(I) Polarograms of (a) 0 and (b) 2.34 mM +2 vanadium in 1 F sodium tartrate, pH 6.2. (II) Polarograms of (a) 0 and (b) 2.44 mM +2 vanadium in 1 F sodium citrate, pH 6.8. The height of the arrow corresponds to ten microamperes.

agent. Accordingly, we have made many attempts to develop its obvious possibilities for potentiometric and amperometric titrations. At a platinum electrode, the +2 vanadium complex is nearly quantitatively oxidized by water or hydrogen ion regardless of the composition of the solution as would be expected from free energy considerations. At a stationary or dropping mercury electrode a solution of this complex, with or without added +3 vanadium, is stable for some hours if air is rigorously excluded. When, however, there is also present any ion capable of being reduced to a metal (*e. g.*, silver, copper, lead or cadmium), the colloidal metal particles initially formed appear to induce the reduction of water or hydrogen ion. This "side reaction" is fairly small with silver, but it is so great with lead or cadmium that these metals are only secondary products of the over-all reaction. Only in homogeneous reactions, such as the reduction of iron(III), chromium(VI) or titanium(IV) can even a moderate degree of accuracy be secured on titration with vanadium(II) in neutral or alkaline citrate media, and even in these favorable cases the attainable accuracy is rather poor. These observations confirm earlier experience[6] with titrations in thiocyanate media.

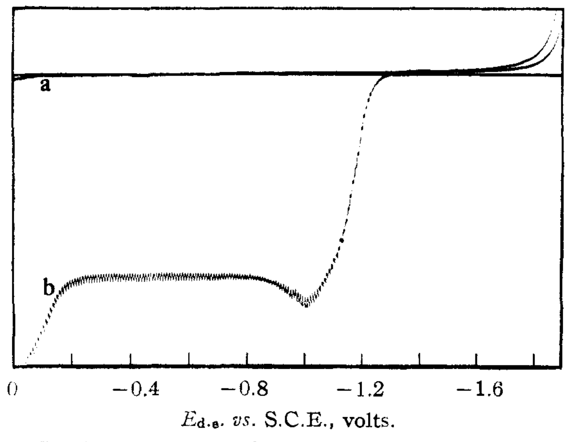

Fig. 7.—(a) Polarogram of 1 F sodium citrate, pH 6.8; (b) after addition of a sample of pure vanadous sulfate.

Addition of +3 vanadium to a pyridine–pyridinium sulfate buffer of pH 5.4 (1 F total pyridine) gives a yellowish-brown solution which soon changes into a dirty green suspension. A polarogram of such a mixture is shown in Fig. 8. It consists of two anodic and two cathodic waves, whose half-wave potentials are, *seriatim*, +0.13, −0.16, −0.65 and −0.97 v. In very dilute (<1 mM vanadium) solutions, the total cathodic diffusion current constant is 1.21 ± 0.02, and the total anodic diffusion current constant is −1.3 ± 0.1; from these figures we conclude that the reduction and oxidation proceed only to the +2 and +4 states. The first anodic and first cathodic waves, whose diffusion current constants are nearly equal (−0.67 ± 0.01 and 0.657 ± 0.006) must, therefore, be due to some subsidiary species.

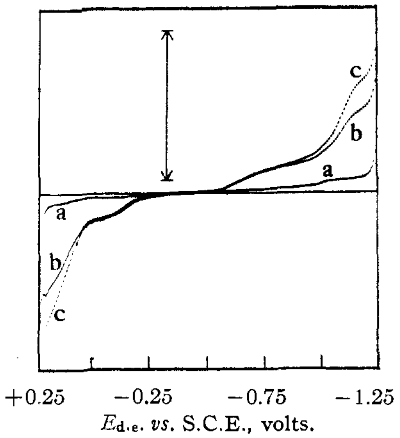

Fig. 8.—Polarograms of (a) 0, (b) 2.65 and (c) 4.45 mM +3 vanadium in 1 F pyridine–pyridinium sulfate buffer of pH 5.45. The height of the arrow corresponds to ten microamperes.

The diffusion currents of these inner waves increase linearly with the +3 vanadium concentration up to about 1.1 mM, and then remain approximately constant. Simultaneously the diffusion current constants of the outer waves begin to decrease slowly, so that at 2.00 mM vanadium the total diffusion currents are only 1.8 times those found with 1.00 mM vanadium.

These observations indicate that the outer waves are due to the colloidal species or, perhaps, to $V(OH)^{++}$ ions in moderately rapid equilibrium with the colloid at the drop surface. The limiting heights of the inner waves would then correspond to the concentration of unhydrolyzed vanadium(III) ions in (presumably very slow) equilibrium with the solid. After the solution becomes saturated, the heights of these waves would be expected to increase only as dilution of the solutions decreases the pyridine concentration and thus increases the equilibrium concentration of +3 vanadium, and this predicted very slow increase is actually found. Since a colloidal particle would be expected to have a smaller diffusion coefficient than an ion in true solution, the slow decrease in the total diffusion current constant is also in agreement with this interpretation.

Solutions of +2 vanadium in pyridine–pyridinium sulfate buffers are deep orange in color even with extremely low concentrations of vanadium (0.1 mg./l.): this reaction is much more sensitive than the classical hydrogen peroxide–vanadium(V) test and might be useful for the detection of traces of vanadium. At vanadium concentrations above about 1 m*M* a dirty brown precipitate is formed. Polarograms of clear solutions are shown in Fig. 9: they consist of three anodic waves which are approximately equal in height and therefore represent successive oxidation to the +3, +4 and +5 states. The half-wave potentials of these waves at *p*H 6.5, 6.0 and 5.5 with 1 *F* total pyridine are, in order, −0.47, −0.46 and −0.50 v. for the wave corresponding to oxidation to the +3 state, −0.04, -0.1_0 and -0.1_5 v. for the second wave, and +0.1, +0.1 and $+0.0_7$ v. for the third wave. Although the shape of the first wave shows that it is irreversible, the agreement between its half-wave potentials in these media and that found[2,4] for the oxidation of simple vanadous ion, together with the observations on the behavior of +3 vanadium in pyridine solutions, shows that the pyridine complexes of +2 and +3 vanadium cannot be very stable.

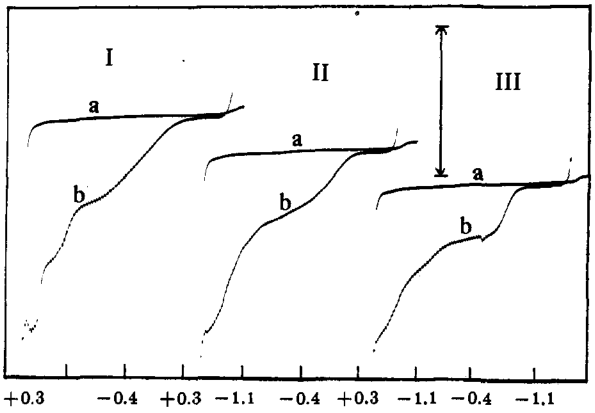

Fig. 9.—Polarograms of +2 vanadium in 1 *F* pyridine–pyridinium sulfate buffers. (I) (a) 0 and (b) 1.87 m*M* vanadium, *p*H 5.45. (II) (a) 0 and (b) 1.66 m*M* vanadium, *p*H 6.0. (III) (a) 0 and (b) 1.28 m*M* vanadium, *p*H 6.55. The height of the arrow corresponds to ten microamperes.

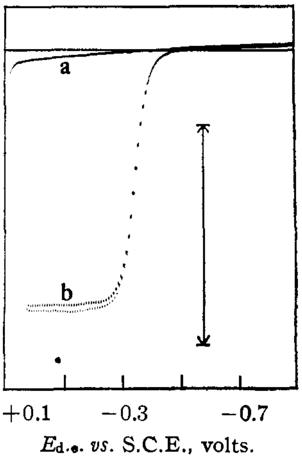

Fig. 10.—Polarograms of (a) 0 and (b) 1.39 m*M* +3 vanadium in 0.5 *F* potassium bicarbonate–0.5 *F* sodium carbonate, *p*H 9.4. The height of the arrow corresponds to six microamperes.

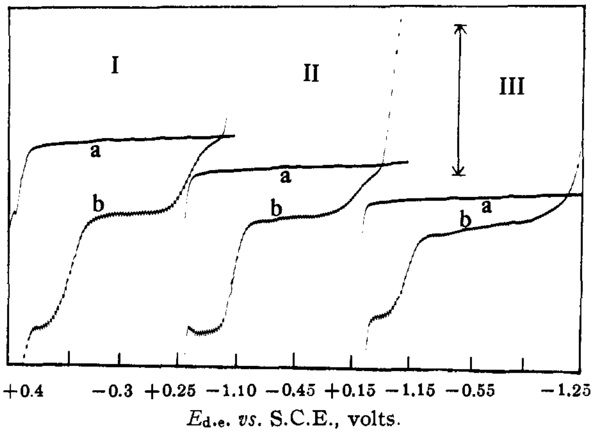

Fig. 11.—Polarograms of (I) (a) 0 and (b) 1.39 m*M* +2 vanadium in 0.1 *F* potassium bicarbonate saturated with carbon dioxide, *p*H 6.7; (II) (a) 0 and (b) 1.32 m*M* +2 vanadium in 1.0 *F* potassium bicarbonate saturated with carbon dioxide, *p*H 7.6; (III) (a) 0 and (b) 1.05 m*M* +2 vanadium in 0.5 *F* potassium bicarbonate–0.5 *F* sodium carbonate, *p*H 9.4. The height of the arrow corresponds to ten microamperes.

In 1 *F* sodium tartrate at *p*H 6, +3 vanadium gives a faintly green solution of which typical polarograms are shown in curves I of Fig. 5. There are two anodic waves, the first at $E_{1/2}$ = -0.20_3 v., for which I = −1.071 ± 0.005, representing oxidation to the +4 state. The half-wave potential of this wave is more negative than that observed with any other complex of +3 vanadium we have studied: this is in accord with other evidence of the stability of the vanadium(IV) tartrate complex.[7] The second wave, for which $E_{1/2}$ = $+0.1_4$ v., is due to further oxidation to the +5

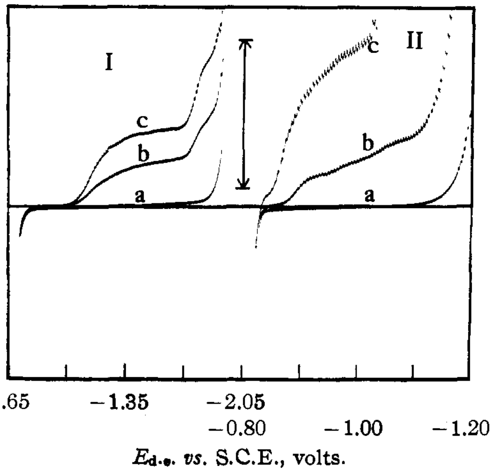

Fig. 12.—Polarograms of (a) 0, (b) 1.83 and (c) 3.44 m*M* +3 vanadium in (I) in 1 *F* potassium cyanide and (II) 1 *F* sodium thiosulfate. The height of the arrow corresponds to ten microamperes.

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[7] J. J Lingane and L. Meites, THIS JOURNAL, **69**, 1882 (1947).

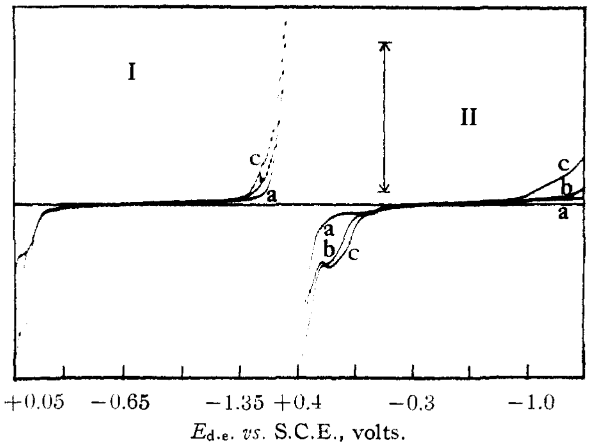

Fig. 13.—Polarograms of (a) 0, (b) 1.83 and (c) 3.44 mM +3 vanadium in (I) sodium pyrophosphate saturated at pH 5.5, and (II) sodium tetraborate saturated at pH 5.1. The height of the arrow corresponds to ten microamperes.

state, while the cathodic wave at about −1.6 v. represents reduction to the +2 state.

The faintly bluish-green solutions of +2 vanadium in this tartrate medium give a single anodic wave at −0.175 v. (curves I, Fig. 6), which has a diffusion current constant of −1.070 ± 0.002. Since this is equal to the value found for a one-electron oxidation of +3 vanadium in this medium, +2 vanadium is oxidized only to the +3 state in tartrate solutions. In view of the easy oxidizability of +3 vanadium, this result is surprising. The alternative is that the +2 vanadium complex is actually oxidized to the +4 state but that its diffusion coefficient is only one-fourth that of the vanadic tartrate complex: this seems very improbable. Apparently the vanadic complex formed at the electrode surface is a metastable form which must rearrange before it can be easily oxidized to the +4 state, and this rearrangement is so slow as to inhibit the further oxidation at the dropping electrode. A similar example of a metastable complex formed at the dropping electrode was recently reported by Pecsok and Lingane.[8]

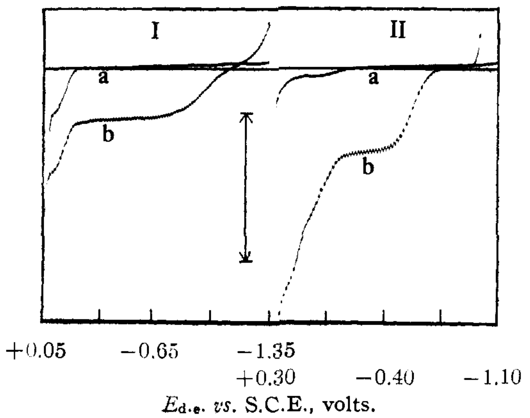

Fig. 14.—Polarograms of (I) (a) 0 and (b) 2.22 mM +2 vanadium in saturated sodium pyrophosphate at pH 5.5; (II) (a) 0 and (b) 2.24 mM +2 vanadium in saturated sodium tetraborate at pH 5.1. The height of the arrow corresponds to ten microamperes.

No indication of reduction below the +2 state was observed in any of the media used.

[8] R. L. Pecsok and J. J. Lingane, THIS JOURNAL, **72**, 189 (1950).

CAMBRIDGE, MASS.
NEW HAVEN, CONN.

RECEIVED DECEMBER 14, 1950

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLIX. Conductance of Some Salts in Water at 25°[1]

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Following up the observations of Bair and Kraus, that the equivalent resistance of long chain quaternary ammonium ions is less than that of corresponding symmetrical ions, the conductance of a series of alkyltrimethylammonium ions has been measured from ethyltrimethyl- to tetradecyltrimethylammonium inclusive, in steps of two carbon atoms. Up to, and including, the hexyltrimethylammonium ion, the equivalent resistance of the unsymmetrical ions is greater than that of corresponding symmetrical ions. For the octyltrimethylammonium ion and ions with longer chains, the resistance of the unsymmetrical ions is less than that of the symmetrical ions. The resistance of the three partially substituted methylammonium ions has been determined as has also that of the phenyltrimethylammonium ion. The conductances of potassium bromide and of tetramethylammonium picrate have also been measured.

I. Introduction

Kuhn and Kraus[3] and Bair and Kraus[4] have measured the conductance of several long chain salts at concentrations below the critical. Dodecyl- and tetradecyltrimethylammonium salts exhibit the normal behavior of 1–1 salts. Hexadecyl- and octadecyltrimethylammonium salts exhibit a behavior that diverges from that of 1–1 salts in that the limiting slopes of the $\Lambda-\sqrt{C}$ plots are much greater than the theoretical for 1–1 salts and approximate that of 2–1 salts. Bair[4] determined the limiting conductance of the long chain ions of the above measured salts and found that the equivalent resistance of these ions is much less than that of symmetrical quaternary ammonium ions[5] having the same number of carbon atoms. It seemed of interest to investigate the conductance of alkyltrimethylammonium ions as influenced by the length of the hydrocarbon chain.

We have measured the conductance of these

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[1] This paper is based on a portion of a thesis presented by Maurice J. McDowell in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1950.

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[3] D. W. Kuhn and C. A. Kraus, THIS JOURNAL, **72**, 3676 (1950).

[4] E. J. Bair and C. A. Kraus, *ibid.*, **73**, 1129 (1951).

[5] H. M. Daggett, E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).