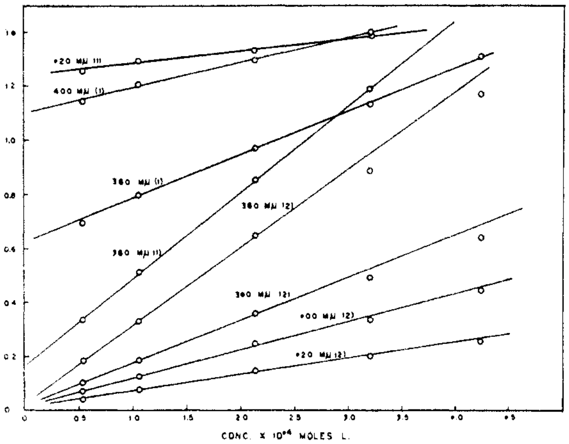

Fig. 3.—Slope-ratio method: 1, solutions with excess bromine; 2, solutions with excess tetrabutylammonium bromide.

complex is $(C_4H_9)_4NBr_3$. These results are in essential agreement with those of the method of continuous variation.

Equilibrium Constant.—The equilibrium constant for the reaction in bromotrichloromethane was calculated by the method

$$(C_4H_9)_4NBr_3 \rightleftharpoons (C_4H_9)_4NBr + Br_2$$

outlined in a previous article.[13] The mean value obtained was 6.0×10^{-5} at 25°. This result indicates that the tetra-*n*-butylammonium tribromide does not dissociate to any great extent in relatively non-polar solvents. It is a brominating agent, however, and reacts readily with solvents capable of being brominated. Consequently, measurements of properties made in such solvents must be regarded as semi-quantitative at best. The present measurements made in bromotrichloromethane are less likely to be subject to this deficiency since this solvent is not susceptible to bromination.

(13) A. I. Popov, K. Brinker, L. Campanaro and R. Rinehart, THIS JOURNAL, **73**, 514 (1951).

IOWA CITY, IOWA RECEIVED FEBRUARY 22, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Spectrophotometric Investigation of the Ionic Association of Thiocyanate Ion with Vanadium(III) and Vanadium(IV) in Aqueous Solution[1]

BY SYDNEY C. FURMAN[2] AND CLIFFORD S. GARNER

Application of Job's continuous variations method to a spectrophotometric study has shown that the complexes $VSCN^{++}$ and $VOSCN^{+}$ exist in aqueous solution. Their stability constants and heats of formation have been estimated in solutions having an ionic strength of 2.6. Evidence is presented that suggests that higher complexes of both vanadium(III) and vanadium(IV) are formed with thiocyanate ion. The spectra of the various complexes have been calculated and are presented. No evidence was found for an "interaction absorption spectrum" between vanadium(III) and vanadium(IV) in 3.9 *f* ammonium thiocyanate.

It has long been known that complex ions involving thiocyanate ions are formed with vanadium(III) and vanadium(IV). Meites[3] has found direct evidence for thiocyanate complexes of vanadium(II), vanadium(III) and vanadium(IV) in aqueous solution from polarographic studies. In some early exploratory work Locke and Edwards[4] observed that vanadium(III) is much more slowly oxidized by air in the presence of potassium thiocyanate than in solutions of other anions. Other indirect evidence for thiocyanate complexes includes the extractability of vanadium(III) thiocyanate compounds into organic solvents[5] and the preparation of solid salts of the types $M^I_2VO(SCN)_4$ and $M^I_3V(SCN)_6$.[4,6,7,8]

The absorption spectra of solutions containing these complexes have been determined[9] but no interpretation of the spectra was possible because of the lack of information regarding the species present in solution.

Investigations in progress in this Laboratory[10] have shown that the exchange of radiovanadium between vanadium(III) and vanadium(IV) perchlorates proceeds at a measurable rate in perchloric acid solutions and that this rate is enhanced in the presence of thiocyanate ion. These results suggest that thiocyanate complexes are formed under these conditions.

Accordingly, this research was undertaken to obtain information about the composition and stability constants of some of the thiocyanate complexes of vanadium(III) and vanadium(IV). The complexes of vanadium(III) were expected to be of particular interest because of the similarity of the (hydrated) tripositive ion V^{+++} to (hydrated) Fe^{+++} ion. It has been adequately shown that the $FeSCN^{++}$ ion is formed under certain conditions.[11,12,13] In addition higher complexes are known.[14,15]

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(1) Presented at a symposium on "Equilibrium and Rate Behavior of Complex Ions," University of Chicago, February 21–23, 1951.

(2) General Electric Charles A. Coffin Predoctoral Fellow, 1950–1951. Present address: Knolls Atomic Power Laboratory, Schenectady, New York.

(3) L. Meites, Jr., Ph.D. Thesis, Harvard University, 1947.

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(5) A. Rosenheim, E. Hilzheimer and J. Wolff, *Z. anorg. Chem.*, **201**, 162 (1931).

(6) J. Koppel and R. Goldman, *ibid.*, **36**, 281 (1903).

(7) A. Cioci, *ibid.*, **19**, 308 (1899).

(8) G. Scagliarini and G. Tartarini, *Gazz. chim. ital.*, **53**, 876 (1923), through *C. A.*, **18**, 1251[8] (1924).

(9) Y. Uzumasa, H. Okuno and K. Doi, *J. Chem. Soc., Japan*, **59**, 655 (1938), through *C. A.*, **32**, 6152[3] (1938).

(10) S. C. Furman and C. S. Garner, unpublished research.

(11) H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

(12) S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

(13) H. S. Frank and R. L. Oswalt, *ibid.*, **69**, 1321 (1947).

(14) M. Møller, Doctoral Thesis, Copenhagen, 1937, through ref. 28, p. 60.

(15) S. E. Polchlopek and J. H. Smith, THIS JOURNAL, **71**, 3280 (1949).

Experimental

The experimental procedures and preparation of materials described by Furman and Garner[16] were followed in the present work with the following exceptions.

Absorption Measurements.—Silica cells of 1.00-cm. optical length were used in the wave length region below 400 mμ. In order to study solutions having an optical density greater than 1.00, silica spacers were used to decrease the optical path length to 0.100 cm. It was also necessary to utilize Corex cells of 10.00-cm. length for some work in the region above 400 mμ. It was found that equilibrium was rapidly attained upon mixing of reactants as evidenced by the optical density remaining constant within 0.002 for a period of two hours; all measurements were performed in this interval.

The results are expressed in terms of optical density, D, or extinction coefficient, ϵ, defined by the relationship

$$\epsilon = \frac{1}{Cd}\log_{10}\frac{I_0}{I} = \frac{D}{Cd} \qquad (1)$$

where d is the optical length of the cell, C is the molar concentration of the absorbing species, and I_0 and I are the incident and transmitted light intensities, respectively.

Materials.—When sodium perchlorate was prepared from "Reagent Grade" solid sodium hydroxide and redistilled perchloric acid an impurity (presumably iron) was present in sufficient concentration to give rise in acidified thiocyanate solution to an optical absorption in the region of 300 mμ. Recrystallization of the sodium perchlorate twice from dilute perchloric acid solution decreased this absorption sufficiently for our purpose.

C.P. ammonium thiocyanate was recrystallized three times from dilute perchloric acid solution. It was found that the optical absorption of an acidified thiocyanate solution above 270 mμ was entirely negligible in the concentration region used for the major part of the work. When the spectra of the complexes were studied in solutions 4 f in SCN^- ion, reference solutions were used consisting of ammonium thiocyanate and perchloric acid at the same concentrations as in the solutions containing vanadium. The ammonium thiocyanate solutions were standardized with recrystallized silver nitrate by the method of Kolthoff and Lingane.[17]

Discussion

Composition of Complexes.—A very rapid and excellent method for the determination of the composition of the main complex formed in a given concentration range of the reactants is Job's[18] method of continuous variations as extended by Vosburgh and Cooper.[19] This method has been used to determine the existence of a 1:1 mole ratio of vanadium to thiocyanate for both the vanadium(III) and vanadium(IV) complexes.

In Fig. 1 are shown, for three wave lengths, the optical densities, Y, that exceed the optical densities expected for no reaction in various mixtures of equiformal solutions of vanadium(IV) perchlorate and ammonium thiocyanate. The perchloric acid concentration was held constant at 0.50 f and the total formal concentration of vanadium(IV) and thiocyanate was 0.0500 throughout. The results are typical of those found at eleven wave lengths in the region 540–850 mμ.

The mole fraction, x, of vanadium(IV) at which the optical density Y is a maximum can be related to the number n of thiocyanate ions per vanadium atom in the complex by the equation[18]

$$n = x/(1 - x) \qquad (2)$$

Although the results clearly indicate that the $VOSCN^+$ complex is formed, the data are not precise enough, owing to the large corrections for the absorption of VO^{++}, to permit an interpretation of the shapes of the curves in Fig. 1. It appears, from the broadness of the maxima, that the complex is not especially stable.[20,21]

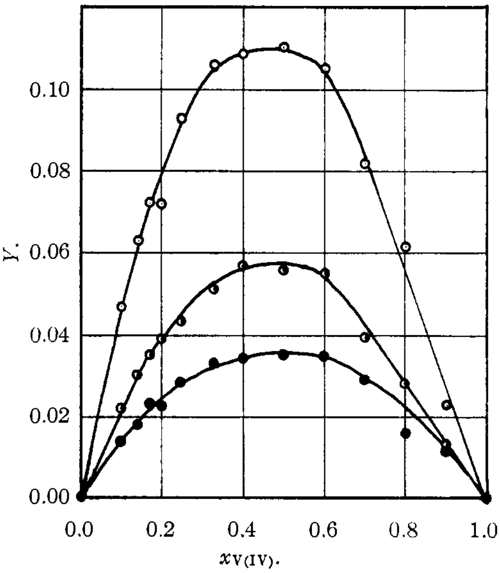

Fig. 1.—Optical density difference, Y, for mixtures of equiformal (0.0500 f) solutions of $VO(ClO_4)_2$ and NH_4SCN; $HClO_4$ = 0.50 f. Data taken at 25°: ○, 750 mμ; ◑, 580 mμ; ●, 850 mμ.

Similar results were obtained for the vanadium(III) thiocyanate complex with mixtures of equiformal (0.00500 f) solutions of vanadium(III) perchlorate and ammonium thiocyanate. For these experiments the perchloric acid concentration was held constant at 1.00 f. Figure 2 shows representative results at three wave lengths. In the region of absorption studied, 270–400 mμ, there is a negligible absorption due to V^{+++} or VOH^{++} and therefore the curves in Fig. 2 are considered

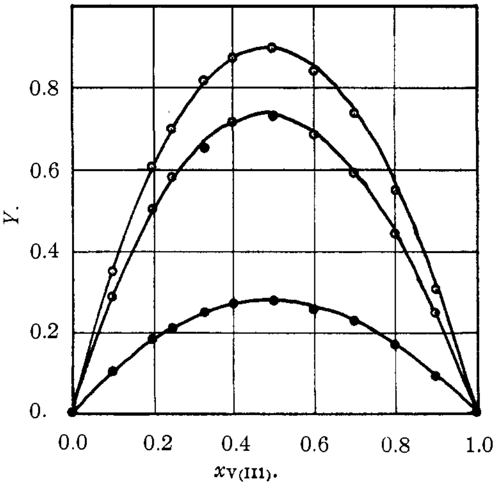

Fig. 2.—Optical density difference, Y, for mixtures of equiformal (0.00500 f) solutions of $V(ClO_4)_3$ and NH_4SCN; $HClO_4$ = 1.00 f. Data taken at 25°: ○, 290 mμ; ◑, 300 mμ; ●, 350 mμ.

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[16] S. C. Furman and C. S. Garner, THIS JOURNAL, **72**, 1785 (1950).

[17] I. M. Kolthoff and J. J. Lingane, *ibid.*, **57**, 2126 (1935).

[18] P. Job, *Ann. chim.*, [10] **9**, 113 (1928); [11] **6**, 97 (1936).

[19] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[20] R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942).

[21] R. T. Foley and R. C. Anderson, *ibid.*, **71**, 909 (1949).

fairly reliable. Although the data clearly show the existence of the species $VSCN^{++}$, the fact that the curves in Fig. 2 are not exactly symmetrical about their maxima indicates that there may be a contribution of higher complexes to the absorption, especially at the lower wave lengths.

Association Constant and Heat of Formation of $VOSCN^+$.—In an attempt to determine the concentration equilibrium constant for the formation of $VOSCN^+$ we have studied solutions having a constant formal concentration of vanadium(IV) perchlorate and constant ionic strength, but varying ammonium thiocyanate concentrations. The treatment of the data was similar to that used by Frank and Oswalt[13] in their determination of the association constant of $FeSCN^{++}$.

If small contributions from higher complexes are ignored, the observed optical densities may be taken as the sum of the absorption due to the two main species, VO^{++} and $VOSCN^+$, and may be written as

$$D = (a - c)\epsilon_{VO^{++}} + c\epsilon_{VOSCN^+} \qquad (3)$$

where a represents the total formal concentration of vanadium(IV) and c the molar concentration of $VOSCN^+$. If $VOSCN^+$ arises from the reaction

$$VO^{++} + SCN^- \longrightarrow VOSCN^+ \qquad (4)$$

and the total formal concentration of SCN^- is given as b, then the concentration association constant K can be represented as

$$K = c/(a - c)(b - c) \qquad (5)$$

and

$$c^2 - (a + b + 1/K)c + ab = 0 \qquad (6)$$

By expanding equation (6) by means of an infinite series we find

$$c = ab/(a + b + 1/K) + (ab)^2/(a + b + 1/K)^3 + \cdots \qquad (7)$$

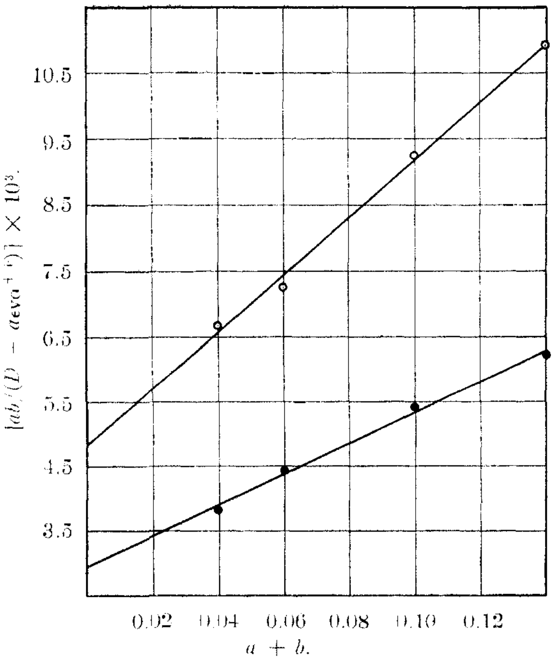

Fig. 3.—Determination of stability constant of $VOSCN^+$ at 25° (see equation 7); a = $(VO(ClO_4)_2)$ = 0.0200 f, b = (NH_4SCN) = 0.0200–0.120 f. $(HClO_4)$ = 1.01 f, μ = 2.6, maintained with $NaClO_4$: ○, 625 mμ; ●, 725 mμ.

The rate of convergence of this series is very dependent on the values of a, b and K, and when the second and higher terms are neglected it is important that the approximation be justified. In the present study involving vanadium(IV) an error of 3% is introduced by neglecting the second term at the highest concentration of ammonium thiocyanate. By substituting c from equation (7) in equation (3) and rearranging, the equation is obtained

$$ab/(D - a\epsilon_{VO^{++}}) = (a + b)/(\epsilon_{VOSCN^+} - \epsilon_{VO^{++}}) + 1/K(\epsilon_{VOSCN^+} - \epsilon_{VO^{++}}) \qquad (8)$$

In Fig. 3 $ab/(D - a\epsilon_{VO^{++}})$ has been plotted against $(a + b)$ for three different wave lengths. In these solutions a = 0.0200 f and b varied from 0.0200 to 0.120 f; the perchloric acid concentration was constant at 1.01 f and sodium perchlorate was added to provide a constant ionic strength of 2.60. The slopes of the curves permit us to calculate $(\epsilon_{VOSCN^+} - \epsilon_{VO^{++}})$ and in turn to calculate K from the measured intercepts. The results, calculated by means of a least-squares treatment, are given in Table I, the values of the extinction coefficient of VO^{++} having been taken from the work of Furman and Garner.[16]

TABLE I

ASSOCIATION CONSTANT AND EXTINCTION COEFFICIENTS OF $VOSCN^+$ AT 25.0°

λ, mμ	K	$\epsilon_{VO^{++}}$	ϵ_{VOSCN^+}
580	7.5	4.30	26.4
600	9.3	6.13	25.3
625	9.0	7.90	30.8
650	9.2	9.46	35.4
675	8.3	11.1	47.2
700	7.8	13.4	56.4
725	8.1	15.8	57.9
750	8.5	17.0	53.4
775	7.8	16.6	47.1
800	7.6	14.7	37.0
Av.	8.3 ± 0.6		

The agreement of K calculated at various wave lengths is considered satisfactory in view of the approximations involved; together with the linearity of the curves in Fig. 3, this constancy of K supports the assumptions inherent in equation (3). The spectral data of Table I are presented graphically in Fig. 4. The spectrum of $VOSCN^+$ thus shown exhibits a new maximum at 580 mμ in addition to the maximum at 725 mμ, which is also a characteristic maximum in the spectrum of VO^{++}.

It was observed that a 25° increase in temperature decreased the optical densities by approximately 4%. Of this small decrease approximately one-half of it can be attributed to temperature dilution effects. The small net temperature effect corresponds to an approximate value of 0.4 ± 0.4 kcal./mole for the ΔH of formation of $VOSCN^+$.

Association Constant and Heat of Formation of $VSCN^{++}$.—The method of calculation of the association constant of $VSCN^{++}$ is the same as that used in the studies with vanadium(IV) with the exception that equation (8) takes the form[22]

$$ab/D = (a + b)/\epsilon_{VSCN^{++}} + 1/K\epsilon_{VSCN^{++}} \qquad (9)$$

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(22) In this work the second term of equation (7) constituted less than 1% of the first and was therefore neglected.

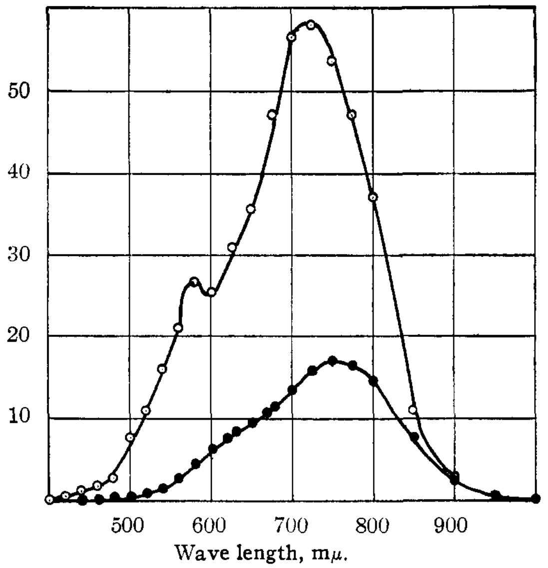

Fig. 4.—Absorption spectra of $VOSCN^+$ (○) and VO^{++} (●) at 25°.

ignoring contributions from higher complexes, for in the wave length region investigated the extinction coefficients of V^{+++} are entirely negligible compared to the extinction coefficients of $VSCN^{++}$. The results at three wave lengths are given in Fig. 5. Table II includes the least-squares values of the association constant and extinction coefficient of $VSCN^{++}$ at a number of wave lengths.

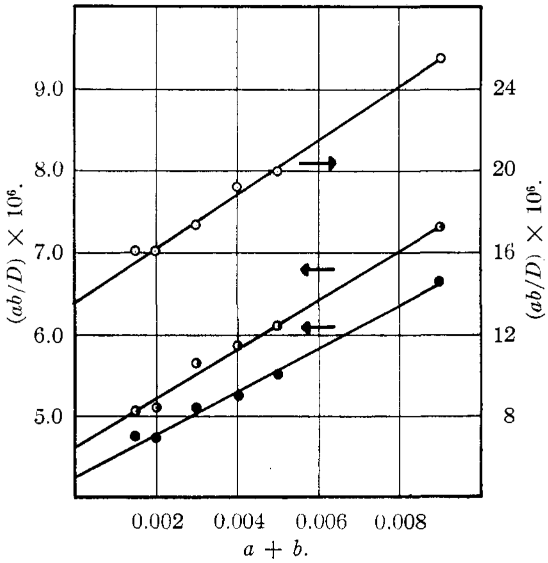

Fig. 5.—Determination of stability constant of $VSCN^{++}$ at 25° (see equation 8); $a = (V(ClO_4)_3) = 0.00100\,f$, $b = (NH_4SCN) = 0.000500\text{-}0.0120\,f$, $(HClO_4) = 2.50\,f$, $\mu = 2.5$: ●, 360 mμ; ◑, 280 mμ; ●, 290 mμ.

TABLE II

ASSOCIATION CONSTANT AND EXTINCTION COEFFICIENTS OF $VSCN^{++}$ AT 25.0°

λ, mμ	K	$\epsilon_{VSCN^{++}}$
260	81	1410
270	78	2050
280	66	3310
290	63	3760
300	48	3730
310	46	2060
320	72	910
330	99	725
340	106	765
350	99	810
360	99	752

It is apparent by inspection of Table II that there is a systematic trend of K with wave length and that the average deviation from the mean of 20% is much greater than would be expected from the instrumental errors, showing that equation (9) is only an approximation. In attempting to explain this, we assumed that the spectra of $VSCN^{++}$ and of a higher complex overlapped and that this was the cause of the asymmetry of the continuous variation curves in Fig. 2. Assuming that the higher complex is $V(SCN)_2^+$ and recognizing that any contribution of higher complexes to the absorption tends to give a low value of the stability constant of $VSCN^{++}$, we took approximately the highest value of K found, namely, 100, to obtain an estimate of the absorption of the assumed $V(SCN)_2^+$ from the data of Fig. 2. Correction for this apparent contribution of $V(SCN)_2^+$ increases K, decreases the average deviation of K from its mean value to 10%, and decreases $\epsilon_{VSCN^{++}}$ at all wave lengths. Inasmuch as the validity of these assumptions regarding a higher complex is uncertain these calculations are not reported here. Therefore, the spectrum of $VSCN^{++}$, as shown in Fig. 6, is only approximate, and the association constant is good only to an order of magnitude.

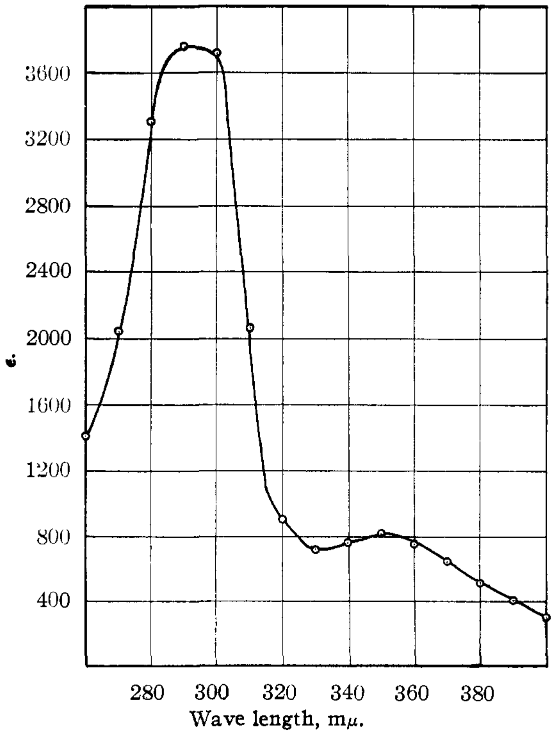

Fig. 6.—Absorption spectrum of $VSCN^{++}$ at 25°.

For convenience in making comparisons the following association constants for the monothiocyanate complexes of some other trivalent elements are collected

$FeSCN^{++}$, $K^0 = 890$, $\mu = 0$ (extrapolated)[13]
$CrSCN^{++}$, $K^0 = 1260$, $\mu = 0$ (extrapolated)[23]
$BiSCN^{++}$, $K = 10.7$, $\mu = 0.40$[24]

Because of the location and the large extinction coefficient (log ϵ 3.6) it is inviting to associate the maximum at 290 mμ with an electron-transfer band[25] of $VSCN^{++}$. The complex VOH^{++}, for which log $\epsilon = 3.7$,[16,26] may similarly exhibit an electron-transfer spectrum having a maximum near 250 mμ.

The effect of temperature on this equilibrium was much more pronounced than in the previously discussed study involving vanadium(IV). ΔH has been calculated at two wave lengths by the use of the relationship

$$d \log K/d(1/T) = -\Delta H/2.3R \qquad (10)$$

The calculated value of −3.6 kcal./mole for ΔH was obtained by employing the extinction coefficients given in Table II and is expected to be affected to a lesser extent by any higher complex than is the value of the association constant at a given temperature. This value may be compared to the value of $\Delta H = -3.5$ kcal./mole for the formation of VOH^{++}, calculated from the heat of hydrolysis determined by Furman and Garner[16] and the heat of ionization of water as reported by Pitzer.[27]

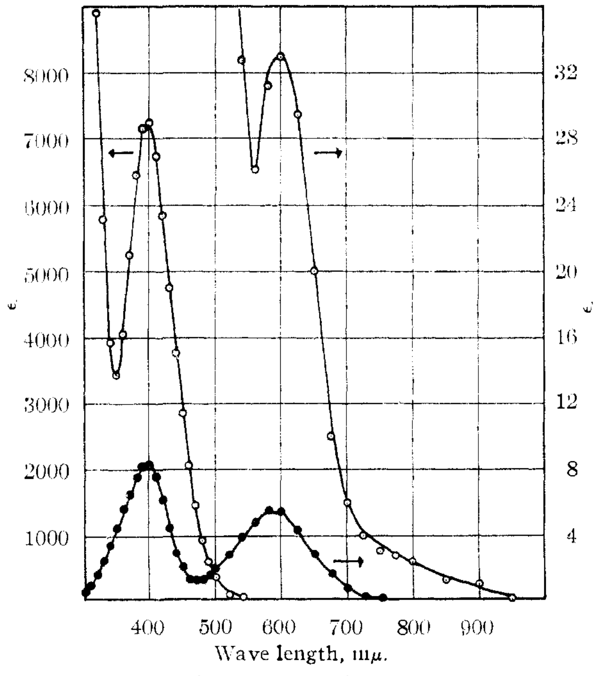

Fig. 7.—Absorption spectra of hydrated V^{+++} (●), and complex (O) of 0.00100 *f* $V(ClO_4)_3$ in 3.89 *f* NH_4SCN, $HClO_4$ = 0.200 *f*, 25°.

It is not possible to calculate a value of ΔS° that would retain significance because of the high ionic strengths used in this study. However, because of the negative sign of ΔH and the order of magnitude of K it appears that ΔS° for the formation of $VSCN^{++}$ is considerably lower than that observed for the analogous halide complexes of iron(III).[28]

Spectra of Vanadium(III) and Vanadium(IV) in High SCN^-.—In an attempt to find evidence for "interaction absorption"[29] between vanadium(III) and vanadium(IV) complexes under the most favorable conditions solutions were studied in which the thiocyanate ion concentrations were approximately 4000 times those of the vanadium ions. It was found that within the experimental error there was no observable interaction. In Fig. 7 the spectrum of the vanadium(III) complex formed in 3.89 *f* ammonium thiocyanate is shown. The appearance of the large maximum (log ϵ 3.9) at 400 mμ clearly proves the existence of complexes other than $VSCN^{++}$. Because of the rather large association constant of $VSCN^{++}$ and the expected trend[30] of the consecutive reactions it is probable that the complex formed in 3.89 *f* SCN^- is the "coördinatively saturated" complex $V(SCN)_6^{\equiv}$. The spectrum of the vanadium(IV) complex formed under similar conditions, as shown in Fig. 8, is different enough from that of $VOSCN^+$ to warrant the conclusion that higher complexes are formed

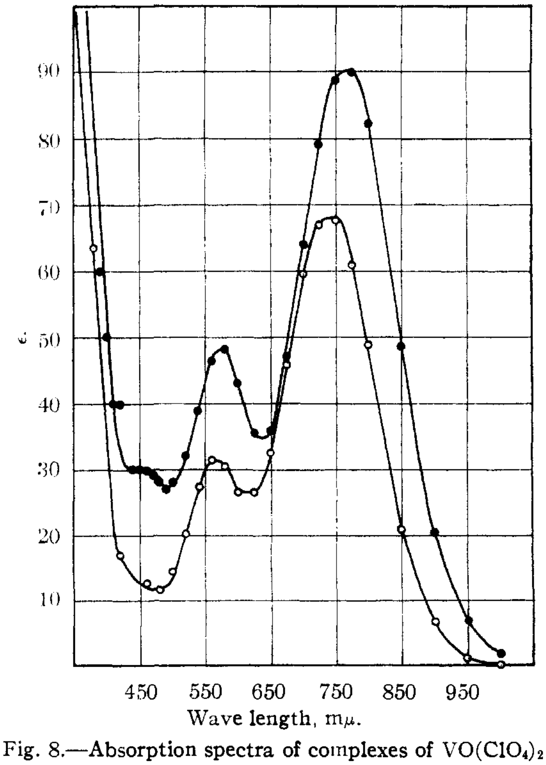

Fig. 8.—Absorption spectra of complexes of $VO(ClO_4)_2$ in NH_4SCN, 25°: O, 0.0100 *f* $VO(ClO_4)_2$, 3.79 *f* NH_4SCN, 0.400 *f* $HClO_4$; ●, 0.00100 *f* $VO(ClO_4)_2$, 3.89 *f* NH_4SCN, 0.200 *f* $HClO_4$.

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[23] N. Bjerrum, *Z. anorg. Chem.*, **119**, 189 (1921).

[24] W. D. Kingery and D. N. Hume, THIS JOURNAL, **71**, 2393 (1949).

[25] E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

[26] This difference of $\Delta\bar{\nu}$ = 5500 cm.$^{-1}$ should be compared to $\Delta\bar{\nu}$ = 8800 cm.$^{-1}$ for the uncomplexed anions OH^- and SCN^-, as reported in reference 25 (Table III, p. 119).

[27] K. S. Pitzer, THIS JOURNAL, **59**, 2365 (1937).

[28] E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

[29] J. E. Whitney and N. Davidson, *ibid.*, **69**, 2076 (1947); **71**, 3809 (1949).

[30] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 60.

under certain conditions. It appears that there is a shift of the maximum near 750 mμ toward the "red" as the ratio $(SCN^-)/(VO^{++})$ increases; this is borne out by the spectrum, also shown in Fig. 8, obtained when $(SCN^-)/(VO^{++}) = 400$. The extinction coefficients appearing in Figs. 7 and 8 are based on formal concentrations of vanadium in order to facilitate comparisons of spectra obtained in solutions of different thiocyanate ion concentrations.

LOS ANGELES 24, CALIFORNIA RECEIVED MARCH 26, 1951

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Potentiometric Titrations of a Polydicarboxylic Acid: Maleic Acid–Styrene Copolymer

BY EDWARD R. GARRETT[1] AND RALPH L. GUILE

The polydicarboxylic nature of saponified maleic anhydride–styrene copolymers is demonstrated and generalized Henderson–Hasselbalch equations presented for both carboxyls. Quantitative procedures for copolymer analyses by aqueous and anhydrous titrations are given. Certain copolymer properties are discussed.

Katchalsky and Spitnik[2] have mentioned that dibasic group copolymers such as polyallyl acetate–maleic acid may be assigned two different dissociation constants and these copolymers may be considered as polydibasic acids but have presented no data pertaining thereto. They have applied potentiometric titration techniques to polymonobasic acids such as polyacrylic and polymethacrylic acids and have found that their resultant curves can be described by a generalized form of the Henderson–Hasselbalch equation

$$p\mathrm{H} = pK - n \log \frac{1-\alpha}{\alpha} \qquad (1)$$

Alfrey and Lavin[3] as well as Wilde and Smets[4] have stated that they have used potentiometric methods for maleic anhydride composition of such or similar copolymers but they have not asserted its polydicarboxylic nature or provided sufficient data for its use as an analytical technique.

In view of the fact that no conclusive evidence has been heretofore provided as to the polydicarboxylic nature of such copolymers, it is our belief that such evidence is worthy of presentation.

Aqueous potentiometric titrations have been applied to three copolymers of maleic anhydride–styrene, the dibasic character of such polymers have been substantiated and the distal parts of the resulting potentiometric curves analyzed in relation to equation (1) to provide the constants for this copolymer. The potentiometric curve provides a valid method of analysis of the maleic anhydride composition of the copolymer.

Anhydrous potentiometric titrations of the polymeric mono-ester in acetone media have also been shown to be practical. The rate constant of copolymerizations has been evaluated.

Experimental

A. Copolymerizations of Maleic Anhydride and Styrene.—Dow styrene was vacuum distilled and the fraction distilling at 41–43°, 14–16 mm., $n^{20}\mathrm{D}$ 1.5446 was used immediately after distillation.

Eastman Kodak Co. maleic anhydride was redistilled at 135° at 80 mm. The polymerizations[5] were carried out in thiophene-free benzene, while nitrogen gas, washed by alkaline pyrogallol, was bubbled under the surface of the solvent. The mixture was agitated.

A 1:1 molar ratio of reactants of 0.233 mole of anhydride to 0.233 mole of styrene, a 1:3 ratio of 0.116 mole of anhydride to 0.349 mole of styrene and a 3:1 ratio of 0.349 mole of anhydride to 0.116 mole of styrene were copolymerized in 615.2 g. of benzene in the presence of 0.2333 g. of benzoyl peroxide.

The rate of appearance of copolymer in refluxing benzene is first order with $k = 5.3 \times 10^{-4}$ sec.$^{-1}$. This was determined by filtering weighed aliquots of the reaction mixture through tared gooch crucibles and washing several times with hot benzene; the crucibles were vacuum dried at 3 mm. pressure at 140° for three weeks and then cooled and reweighed. The copolymerizations can be duplicated.

B. Preparation of Copolymer for Titration.—The reaction mixture was filtered after practical stoichiometric completion of the reaction as based on the evaluated rate constant and the concentration of the lesser reactant. The solid polymer was washed several times with hot benzene. The polymer was then extracted by benzene in Soxhlet extractors for three weeks and vacuum dried at 140° at 3 mm. for three weeks.

For the aqueous titrations, 1 g. of copolymer was dissolved in acetone and standard excess of 0.1 *N* NaOH added very slowly with constant stirring. The acetone was boiled off on a hot-plate until the solutions became water clear and no odor of acetone remained. The total volume of the solution was measured. This solution was titrated with 0.1 *N* HCl followed by alternate titrations with standard alkali and acid.

For the anhydrous titrations 1 g. of the anhydride copolymer dissolved in acetone was titrated with 0.1 *N* methanolic NaOH.

A Beckman *p*H meter equipped with out-side glass electrodes was used at the usual room temperature of 25°.

C. Properties of the Copolymer.—The copolymer as prepared is soluble in alkali and acetone. It is also soluble in small chain primary alcohols. The acid copolymer is soluble in acetone and water mixtures while the anhydride copolymer is insoluble in water. The anhydride and acid copolymer are insoluble in benzene. The monosodium salt of the acid copolymer is insoluble in acetone. The acid copolymer provides good buffering action in the acid range 3.5–4.5 *p*H, lathers well and possesses dispersive properties which are unusual properties for an acidic soap. In alkaline regions where the disodium salt is partially present, the dispersive properties are considerably decreased, probably due to a decrease in the non-polar length of molecule which is available for contact with the oil phase.

The acid copolymer will start precipitating at an approximate *p*H of 2.2 but will not be completely precipitated until the *p*H has been considerably lowered. This property may possibly be correlated with chain length and the number of free anionic groups still on the molecule.

I. Determination of Maleic Anhydride Content of Copolymers. A. Aqueous Titrations.—The copolymers prepared from three differing molar ratios of the reactants, maleic anhydride and styrene, were potentiometrically titrated. Curves that are typical of many titrations are shown in Fig. 1. The stoichiometric titer for one-half the total car-

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