

TABLE IV  
 RESULTS OF SPECTROPHOTOMETRIC STUDIES IN THE IRON(III)-THIOCYANATE SYSTEM

T, °C.	$\mu$	$\beta_1$	$K_1^a$	$\Delta F^b$	$\Delta H^b$	$\Delta S^c$	Ref.
A. Observed							
16.0	0.52	4781	146.5				
26.7	.52	4621	142.5				
35.0	.52	4535	138.5				
44.8	.52	4456	135.0				
B. Comparison							
18.0	0.52	4756	145.5				This work
18.0	0.56	4946 <sup>d</sup>	145				10
25.0	0.52	4640	142.6	-4.2 <sup>e</sup>	-0.52	12	This work
25	0.50	4680	146	1070g	-4.1 <sup>e</sup>	-0.8	11

<sup>a</sup> Corrected for the hydrolysis of iron(III); uncorrected for the formation of iron(III) perchlorate complexes. <sup>b</sup> In kcal./mole. <sup>c</sup> In e.u. <sup>d</sup> This value was selected from ref. 12. <sup>e</sup> Computed at  $\mu = 0$  using the method of Rabinowitch and Stockmayer.<sup>1</sup>

In the temperature range 16–45° the plot of  $\log K_1$  vs.  $1/T$  is a straight line and the values of the thermodynamic functions at 25° and  $\mu = 0$  compare favorably with those of Lister and Rivington.<sup>2</sup> Betts and Dainton<sup>13</sup> obtained a value of  $H = -1.6$  kcal./mole. However these authors assumed  $\beta_1$  to be constant and, in effect plotted  $\log \beta_1 K_1$  vs.  $1/T$ .

Both Perrin<sup>10</sup> and this author obtained lower values of  $K_1$  from the potentiometric experiments than from the spectrophotometric experiments. Both techniques measure the sum of  $K_1$  values for the formation of outer sphere complexes as well as that for  $\text{FeSCN}^{++}$ . However the value of  $K_1$  from the spectrophotometric experiments is calculated from the observed value of  $\beta_1$  which is the weighted average of the molar absorption coefficients of all of the 1-1 complexes.<sup>14</sup> From a comparison of the  $\text{Fe}^{3+}$ - $\text{SCN}^-$  system<sup>15</sup> the error in

(13) R. H. Betts and F. S. Dainton, *THIS JOURNAL*, **75**, 572 (1953).

(14) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

(15) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

calculating  $K_1$  from potentiometric data would be less than 1% while a somewhat larger error would be anticipated from the spectrophotometric experiments.

The absorption spectra of  $\text{FeSCN}^{++}$  and  $\text{Fe}(\text{SCN})_2^+$  were found to be substantially the same as that reported by Frank and Oswalt<sup>11</sup> and Perrin,<sup>10</sup> respectively. The absorption spectrum of  $\text{FeSCNF}^+$  was obtained from optical density measurements of 0.5 M perchloric acid solutions containing iron(III), thiocyanate and hydrofluoric acid. The molar extinction coefficient  $\beta_m$  of  $\text{FeSCNF}^+$  was calculated over the range of 300–600 m $\mu$  using equation 10. This mixed complex has a single narrow band in the optical region with a maximum at 380 m $\mu$  ( $\beta_m = 6240$  moles<sup>-1</sup> cm.<sup>-1</sup>).

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[CONTRIBUTION FROM DEPARTAMENTO DE QUÍMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO, SÃO PAULO, BRAZIL]

## Polarographic Studies of Aqueous Solutions of Metal and Azide Ions. I. The Cadmium Azide Reaction

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Polarographic studies of solutions of cadmium and azide ions were carried out in perchlorate medium in the range of 0.05 to 2.00 M azide concentration at an ionic strength of 2.0 at  $25 \pm 0.1^\circ$ . The application of the method of De Ford and Hume<sup>3</sup> revealed the existence of five reaction products:  $\text{CdN}_3^+$ ,  $\text{Cd}(\text{N}_3)_2$ ,  $\text{Cd}(\text{N}_3)_3^-$ ,  $\text{Cd}(\text{N}_3)_4^{2-}$ ,  $\text{Cd}(\text{N}_3)_5^{3-}$  with formation constants 25, 400, 800, 1000 and 1800, respectively. These values were confirmed by applying Leden's<sup>4</sup> method of calculation. The formation constants of the four species known to be formed in solution of cadmium and thiocyanate ions also were determined in the same range of concentration in perchlorate medium and were compared with those determined in nitrate solution.

The reactions between a number of metal ions and azide ions in aqueous solutions are being studied systematically in this Laboratory by the polarographic method.

This first paper reports results obtained in the study of solutions containing cadmium and azide ions.

### Experimental

Measurements were made with a Sargent Model III Polarograph, the voltage being checked with a Leeds and

Northrup student potentiometer. A small H cell similar to that described by Pecsok and Juvet<sup>1</sup> was employed. Both compartments of the cell were separated by a medium porosity sintered glass disc from the cross arm which had two small openings allowing the use of small rubber stoppers. In all experiments carried out in perchlorate medium the cross arm was filled with 2.0 M sodium perchlorate solution (about 2.5 ml.). The reference electrode was a saturated calomel electrode prepared with saturated sodium chloride solution instead of potassium chloride in order to avoid

(1) R. L. Pecsok and R. S. Juvet, *Anal. Chem.*, **27**, 165 (1955).

precipitation of potassium perchlorate at the interface. A plug of 4% agar-saturated sodium chloride gel was also used on the side of the reference anode. The volume of the solution under study in the polarographic cell was of approximately 8 ml. Solutions containing azide ions were deaerated with purified nitrogen which was bubbled through a thermostatted solution of sodium azide of the same concentration and  $pH$  of the sample solution. All measurements were taken at  $25 \pm 0.1^\circ$ . The capillary electrode used in the study of solutions containing azide ions had a value of 1.78 for  $m^{2/3} t^{1/3}$ , measured at  $-0.900$  volt vs. reference electrode in a solution  $2 \times 10^{-3} M$  in cadmium ions and  $2.0 M$  in sodium perchlorate. The capillary employed in the study of thiocyanate containing solutions under the same experimental conditions had a value of 1.74 for  $m^{2/3} t^{1/3}$ .

The potential corresponding to half the diffusion current was always taken as the half-wave potential, and it was determined by interpolation of values obtained at 5 mv. intervals. As the cell resistance was found to be 460 ohms, half-wave potential values were corrected accordingly. No correction for residual current of current values reported in Tables II and III was found to be necessary.

Half-wave potentials were evaluated to 0.1 mv. in all determinations, and reproducibility was always well within 1 mv.

No maximum suppressor was found to be necessary in the study of cadmium azide solutions in perchlorate medium.

In the study of the cadmium thiocyanate reactions in perchlorate solutions sodium lauryl sulfonate was employed as maximum suppressor at a concentration of  $4 \times 10^{-5} M$ .

Cadmium perchlorate stock solution was prepared from C.P. cadmium carbonate and C.P. 20% perchloric acid, a slight excess of the former being employed. Standardization was carried out gravimetrically with anthranilic acid.<sup>2</sup>

Sodium azide was purified by dissolving in water, filtering and precipitating with ethyl alcohol and finally dried at  $110^\circ$ .

C.P. sodium thiocyanate was freed from traces of iron by repeated batch extractions of concentrated aqueous solutions with ethyl ether. Anhydrous sodium perchlorate used to adjust ionic strength was prepared from C.P. sodium carbonate and C.P. perchloric acid. Acidity was adjusted by means of standardized solutions of perchloric acid.

### Results and Discussion

Preliminary experiments were carried out at different  $pH$  in order to observe the effect of addition of acid. In Table I results of two series of experiments are reported. In each series the concentration of free azide ion was kept constant and the concentration of hydrazoic acid varied by adding varying amounts of standardized perchloric acid. Results show that the diffusion current decreases by increasing the concentration of hydrazoic acid in the solution whereas the half-wave potential is not affected.

It should be noted that data reported in the fourth column of Table I were carefully corrected for residual current since it was found that the magnitude of this current increased considerably in acidic medium.

As a result of the observations reported above, the polarographic study of solutions of cadmium ions containing increasing amounts of sodium azide was conducted with a constant concentration of hydrazoic acid. This was easily achieved by using a standard solution of cadmium ions containing a small amount of perchloric acid which was sufficient to avoid any possible hydrolysis of solutions containing low concentration of complexing anion.

It may be mentioned that variation of cadmium ion concentration, from  $5 \times 10^{-3}$  to  $5 \times 10^{-4} M$ , in solutions having a constant amount of azide

(2) F. Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand Co., New York, N. Y., 1949, p. 197.

TABLE I  
EFFECT OF HYDRAZOIC ACID ON THE DIFFUSION CURRENT  
AND HALF-WAVE POTENTIAL  
 $Cd^{2+} = 0.005 M$ ; ionic strength = 2.0

$N_3^-$ , $M$	$HN_3$ , $M$	$pH$	$i_d^a$	$E_{1/2}$
0.50	0.00	7.30	181.5	0.6320
	.25	4.65	178.5	.6316
	.50	4.35	176.0	.6313
1.00	.00	7.60	177.5	.6620
	.25	4.95	177.0	.6625
	.50	4.65	175.5	.6629
	.75	4.45	174.0	.6608
	1.00	4.35	173.0	.6634

<sup>a</sup> Galvanometer scale divisions; current multiplier = 50.

ions ( $2.0 M$ ) did not affect the half-wave potential. This observation excludes the possibility of existence of poli-nuclear complexes.

As a plot of  $E_{1/2}$  against the logarithm of the concentration of azide gave a curve, indicating the probable consecutive formation of complexes, the well known method of De Ford and Hume<sup>3</sup> was employed to interpret the polarographic results. This was possible also because a plot of  $\log i/(i_d - i)$  vs.  $E$  showed the waves to be reversible.

Data are reported in Table II. It can be seen that the values of  $F_4(X)$  give a straight line with a positive slope when plotted against azide concentration, and the values of  $F_5(X)$  give a straight horizontal line, thus indicating that five complexes can exist in the range of concentration studied. By extrapolating the  $F(X)$  curves to zero azide ion concentration the values for the successive "over-all" formation constants were obtained which were: 25, 400, 800, 1000 and 1800, respectively.

In Fig. 1 the per cent. distribution of the different species present in solutions of cadmium and azide ions at an ionic strength of 2.0 is reported as a function of azide ion concentration.

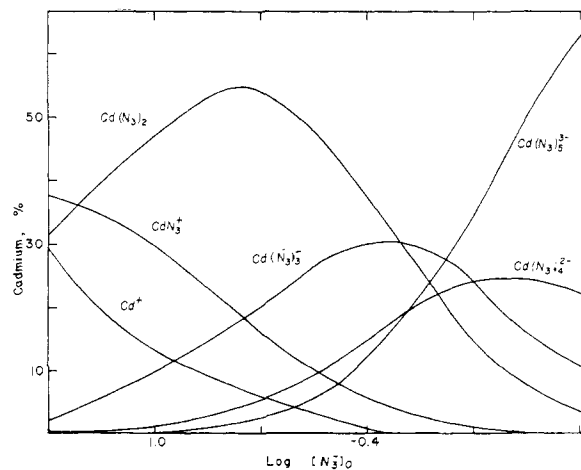


Fig. 1.—Percentage of cadmium in its various forms as a function of free azide ions concentration.

The method of Leden for the calculation of the successive constants of mononuclear complexes<sup>4</sup>

(3) D. D. De Ford and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(4) I. Leden, *Z. physik. Chem.*, **A168**, 160 (1941); J. Sullivan and J. C. Hindman, *J. Am. Chem. Soc.*, **74**, 6091 (1952).

TABLE II  
ANALYSIS OF  $E_{1/2}$  OF CADMIUM IN AZIDE-PERCHLORATE MEDIUM  
 $Cd^{2+} = 0.0020 M$ ; ionic strength = 2.0

NaNa, $M$	$E_{1/2}$ , v.	$i_d$ , $\mu amp.$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$	$F_5(X)$
0.000	0.5557	15.35	1.000	.....	...	...	..	..
.049	.5705	15.27	3.186	44.60	400	...	..	..
.074	.5774	15.25	5.462	60.29	477	1041	..	..
.100	.5827	15.25	8.257	72.57	476	760	..	..
.125	.5874	15.25	11.91	87.28	498	784	..	..
.150	.5923	15.09	17.64	110.9	572	1448	..	..
.200	.5974	14.64	27.01	130.0	525	625	..	..
.520	.6315	14.40	392.5	752.5	1400	1923	2160	..
.700	.6437	14.40	1018	1453	2040	2343	2204	1720
1.000	.6614	14.24	4062	4061	4036	3636	2836	1836
1.300	.6758	14.24	12520	9630	7390	5378	3521	1940
1.700	.6898	13.92	38080	22398	13160	7507	3945	1732
2.000	.6997	13.83	83000	41500	20740	10370	4785	1892

$$K_0 = 1; K_1 = 25; K_2 = 400; K_3 = 800; K_4 = 1000; K_5 = 1800$$

also was employed, making use of the same polarographic data reported in Table II. Five species also were evident, with the "over-all" formation constants: 25, 400, 800, 1000 and 1600.

As the reaction of several metal ions with azide ions is very similar to that with thiocyanate,<sup>5</sup> it was of interest to compare the results obtained in this study with those concerning the solutions of cadmium and thiocyanate inasmuch as this reaction was chosen by De Ford and Hume as the first example to apply their method of mathematical analysis.<sup>6</sup> These authors found that four reaction products can be formed between cadmium ions and thiocyanate in the range of 0.1–2.0  $M$  of thiocyanate and calculated the corresponding formation constants. Since these data were obtained at 30° and in nitrate medium, the measurements were repeated at 25° using perchlorate instead of nitrate to adjust ionic strength. Results are summarized in Table III.

TABLE III  
ANALYSIS OF  $E_{1/2}$  OF CADMIUM IN THIOCYANATE-PERCHLORATE MEDIUM  
 $Cd^{2+} = 0.0024 M$ ; ionic strength = 2.0

NaSCN, $M$	$E_{1/2}$	$i_d$ , $\mu amp.$	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.00000	0.5554	17.31	.....	.....	.....	...	..
.03915	.5641	17.16	1.986	25.19	.....	...	..
.07829	.5710	17.05	3.485	31.74	86.1	...	..
.1005	.5807	16.89	7.360	39.63	91.7	104	..
.3210	.5947	16.74	22.10	65.73	126.9	161.7	244
.4976	.6069	16.70	57.34	113.2	177.3	205.5	242
.7342	.6210	16.42	174.9	265.7	272.6	262.0	235
.9992	.6334	16.41	463.3	462.8	438.2	363.5	279
1.249	.6421	16.31	911.2	728.8	563.7	391.4	245
1.498	.6503	16.20	1740	1160	757.4	455.4	259
1.998	.6633	16.01	4850	2426	1202	563.8	240

$$K_0 = 1; K_1 = 25; K_2 = 75; K_3 = 85; K_4 = 240$$

The values of the formation constants in perchlorate medium being considerably different from those obtained by Hume, De Ford and Cave,<sup>6</sup> we have repeated the determination in nitrate medium both at 25 and 30°, but our results were in perfect agreement with those of the mentioned authors. One should thus infer that interaction

between cadmium and nitrate ions affects the reaction between cadmium and thiocyanate ions in the range of concentration studied.

The importance of this type of interaction in the evaluation of chloro complexes of cadmium has been pointed out by Vanderzee and Dawson<sup>7</sup> who obtained higher values for the formation constants of these complexes in perchlorate than in nitrate medium as previously determined. These authors have shown by calculation that if the formation constant of  $CdNO_3^+$ , as determined by Leden,<sup>8</sup> is taken into consideration, this discrepancy can be explained. The same kind of calculation with the data discussed above for the thiocyanate complexes showed that the reduction of the constants observed in nitrate medium is really dependent on the magnitude of the constant of the cadmium nitrate complex.

The values of the formation constants reported for the azide complexes reveal a more pronounced tendency of cadmium ion to complex with azide than with thiocyanate. It must be noted, however, that results also show that cadmium and azide ions are able to form five different species instead of four as in the case of thiocyanate.

The existence of the fifth species—although not common in cadmium complexes—is not only shown by plotting the data of Table II, as already mentioned, but also can be evidenced by calculating the number of ligands corresponding to the last increment of azide concentration (1.700 to 2.000  $M$ ) in the conventional manner from the plot of  $E_{1/2}$  against  $\log C$ . In fact, in this way, a value corresponding to 4.7 ligands was obtained. Furthermore, this value was confirmed in experiments run at an ionic strength of 3.0 which made possible the calculation for the increment of 2.0–3.0  $M$  of sodium azide.

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(5) P. Senise, *J. Am. Chem. Soc.*, **81**, 4196 (1959).

(6) D. N. Hume, D. De Ford and G. C. B. Cave, *J. Am. Chem. Soc.*, **73**, 5323 (1951).

(7) C. E. Vanderzee and H. J. Dawson, Jr., *ibid.*, **75**, 5659 (1953).

(8) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941); *C. A.*, **36**, 4044 (1942).