We also wish to acknowledge an illuminating discussion with Dr. O. R. Quayle.

Summary

The ultrasonic velocity has been measured in twenty-five organic halides at 20°. It is found that the molecular sound velocity is essentially the same for two compounds structurally alike but for the substitution of a bromine for a chlorine atom. The property is highly constitutive in nature and the summation of atomic or bond increments to obtain the molecular sound velocity of organic halides must be done with care.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Polarographic Investigation of Hexamminecobaltic Chloride in Various Supporting Electrolytes[1]

BY H. A. LAITINEN, JOHN C. BAILAR, JR., HENRY F. HOLTZCLAW, JR.,[2] AND J. V. QUAGLIANO[3]

Preliminary work on the polarographic reduction of cobaltic coördination compounds was undertaken in this laboratory by Herda.[4] Using tenth molar potassium nitrate as the supporting electrolyte, 0.02% gelatin to suppress maxima and a minute droplet of octyl alcohol to prevent foaming of the gelatin solution, he measured half-wave potentials and diffusion currents for over thirty coördination compounds of cobalt.

Willis, Friend and Mellor[5] studied the polarographic behavior of a number of cobaltic compounds in N and 0.1 N potassium sulfate and 0.1 N sodium acetate without the use of maximum suppressing agents. The series of compounds formed by the progressive substitution of nitro groups for ammonia molecules in the hexamminecobaltic ion were studied both by Herda and by Willis, *et al.* While the general trend of the half-wave potentials was in agreement, the absolute values differed considerably.

It was therefore of interest to determine the effects of various capillary active substances and supporting electrolytes upon the half-wave potential and the diffusion current for the reduction of the hexamminecobaltic ion. It was found that both gelatin and octyl alcohol have a pronounced effect upon the half-wave potential. Supporting electrolytes of good coördinating ability, including sulfate as used by Willis, Friend and Mellor, have a significant effect both on the half-wave potential and the diffusion current.

Experimental

Polarograms were obtained in the early parts of the investigation with a manual apparatus essentially like that described by Lingane and Kolthoff,[6] but using a Fisher Elecdropode to measure the current instead of the shunted galvanometer and resistance box. A Sargent Model XX Polarograph was used in the more recent stages of the investigation. The potentials of the dropping electrode, during electrolysis, were measured against an external saturated calomel electrode. A cell of the type described by Lingane and Kolthoff[6] was used. Purified nitrogen or hydrogen was passed through the cell before each run. Values of m and t for the dropping mercury electrodes used were checked from time to time. The temperature in the cell was maintained at 25.0 ± 0.1° by means of a water thermostat. The hexamminecobaltic chloride was prepared and recrystallized according to the methods of Bjerrum and McReynolds.[7,8]

Results and Discussion

The effects of gelatin, octyl alcohol and methyl red upon the half wave potential, the slope of the current–voltage curve, and the diffusion current for the first reduction wave, Co(III) to Co(II), in 0.1 N potassium chloride are shown in Table I.

TABLE I

EFFECT OF CAPILLARY ACTIVE SUBSTANCES ON FIRST REDUCTION WAVE

0.001 M Hexamminecobaltic chloride: m equals 2.1 mg./sec.; t equals 3.4 sec./drop in 0.1 M KCl, open circuit

Supporting electrolyte	Half-wave potential $-E_{1/2}$ (*vs.* S. C. E.)	Slope	Diffusion current, microamperes (−0.8 v.)
0.1 M KCl	0.215 v	0.120	4.04
0.1 M KCl; 0.02% gelatin	0.320	0.100	3.81
0.1 M KCl; 0.02% gelatin; droplet octyl alcohol	.530	.080	3.91
0.1 M KCl; 0.0008% sodium methyl red	.240	.129	4.07
0.1 M KCl; 0.002% sodium methyl red	.271	.075	3.84

In each case, the half wave potential was shifted to a more negative value, the slope of the curve approached more nearly the reversible value, and the apparent diffusion current decreased in the presence of maximum suppressing agents. The smallest effects on the half-wave potential were

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[1] Abstracted from the doctoral theses of James V. Quagliano, 1946, and Henry F. Holtzclaw, Jr., 1947.

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[4] M. G. Herda, M.S. Thesis, University of Illinois, 1943.

[5] J. B. Willis, J. A. Friend and D. P. Mellor, THIS JOURNAL, **67**, 1680 (1945).

[6] J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).

[7] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 241.

[8] J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses." Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 216.

noted with methyl red, which did not completely suppress the maximum until a concentration of 0.002% was used.

The decreasing wave heights observed in the presence of capillary active substances must be attributed to the elimination of stirring effects which persist even after the visible maximum has been eliminated. Buckley and Taylor[9,10] have observed similar effects of maximum suppressing agents on wave heights, and have shown that the apparent diffusion current constant, $i_d/Cm^{2/3}t^{1/6}$ varies with drop time when stirring effects are present. Only at slow drop rates, or in the presence of sufficient concentrations of maximum suppressors, would the Ilkovic equation be valid.[11,12]

To establish the conditions under which reliable diffusion current data could be obtained, the drop rate was varied by changing the height of mercury column, and the apparent diffusion current constant was calculated for the various drop rates (Table II).

TABLE II

EFFECT OF DROP RATE ON DIFFUSION CURRENT CONSTANT OF 0.001 M HEXAMMINECOBALTIC CHLORIDE

Mercury, cm.	i_d, μa	t, sec./drop	m, mg./sec.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
		First Reduction Wave		
65.0	5.15	2.27	3.68	1.89
55.0	4.70	2.70	3.10	1.87
45.0	4.06	3.31	2.53	1.79
35.0	3.40	4.29	1.95	1.71
30.0	3.16	5.01	1.67	1.72
25.0	2.85	6.01	1.39	1.70
20.0	2.49	7.53	1.11	1.66
		Second Reduction Wave		
65.0	14.50	1.82	3.68	5.51
55.0	13.44	2.16	3.10	5.56
45.0	11.47	2.65	2.53	5.25
35.0	10.03	3.44	1.95	5.23
30.0	9.22	4.01	1.67	5.20
25.0	8.44	4.82	1.39	5.21
20.0	7.65	6.03	1.11	5.21

A pronounced variation was observed for drop time values below four seconds for the first reduction wave and below two and five-tenths seconds for the combined heights of the two waves. Accordingly a mercury column height of 30 cm. was used for all subsequent work, giving a drop time of about five seconds for the first diffusion current region and four seconds for the second region.

The half-wave potentials, diffusion current constants and slopes for both waves, using supporting electrolytes of various coördination abilities in various concentrations, are listed in Tables III and IV. Sulfate, tartrate and citrate shifted the first half-wave potential markedly to more negative values. In tenth molar potassium acetate, a similar shift was observed, with a half-wave potential of −0.362 volt (*vs.* S.C.E.). Accompanying the shift of half-wave potential was a distinct trend to lower diffusion current constants. In Table IV, relative values of the diffusion coefficient of the cobaltic complex are calculated from the Ilkovic equation, using the base value of 1.00 for 0.1 molar potassium nitrate solution containing 0.002 per cent. methyl red.

TABLE III

EFFECT OF SUPPORTING ELECTROLYTE ON FIRST REDUCTION WAVE

0.001 M hexamminecobaltic chloride, m = 1.67 mg./sec., t = 4.48 sec./drop in 0.1 N KCl (open circuit)

Supp. elect. Nature	Supp. elect. Concn., M	Half-wave potential, $-E_{1/2}$ *vs.* S. C. E.	Slope	i_d, μa	t, sec./drop	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
Potassium nitrate	0.1	0.244 v	0.078	3.22	5.16	1.74
	.9	.268	.088	3.34	4.92	1.82
	$.1^a$	.284	.060	3.07	5.00	1.67
Potassium chloride	0.1	0.255	0.142	3.28	4.96	1.78
	.2	.237	.114	3.16	4.99	1.72
	.3	.204	.117	3.28	4.91	1.79
	.4	.184	.100	3.25	5.03	1.76
	.5	.185	.090	3.23	4.96	1.76
	.8	.192	.068	3.23	4.95	1.76
	.9	.134	.170	3.53	4.89	1.93
	$.1^a$	.279	.060	3.24	4.95	1.76
	$.5^a$	.291	.090	3.19	4.92	1.74
	$.8^a$	.312	.112	3.30	4.90	1.80
Potassium sulfate	0.1	0.456	0.082	2.92	4.83	1.60
	.2	.455	.070	2.95	4.83	1.61
	.3	.465	.070	2.90	4.85	1.58
	.4	.470	.080	2.88	4.86	1.57
Potassium tartrate	0.1	0.305	0.089	2.75	4.83	1.50
	.5	.371	.082	2.45	4.94	1.33
	.9	.378	.080	2.21	5.09	1.20
Potassium citrate	0.1	0.270	0.066	2.59	4.89	1.41
	.5	.356	.065	2.25	4.79	1.23
	.9	.382	.060	1.92	4.95	1.04

[a] In presence of 0.002% methyl red; all other experiments in absence of maximum suppressors.

A slight effect of concentration of supporting electrolyte on the half-wave potential and a pronounced effect on the calculated diffusion coefficient was observed for those electrolytes whose anions have significant coördinating ability.

The standard electrode potential for the reaction

$$Co(NH_3)_6^{+++} + e^- \longrightarrow Co(NH_3)_6^{++}$$

is estimated by Latimer[13] to be about 0.1 volt against the normal hydrogen electrode (−0.15 volt *vs.* S.C.E.). If hexamminecobaltous ion were formed reversibly as a stable reduction prod-

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[9] F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 97 (1945).

[10] F. Buckley and J. K. Taylor, *Trans. Electrochem. Soc.*, **87**, 463 (1945).

[11] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

[12] J. K. Taylor, *Ind. Eng. Chem., Anal. Ed.*, **19**, 368 (1947).

[13] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 201.

TABLE IV

EFFECT OF SUPPORTING ELECTROLYTE ON SECOND REDUCTION WAVE, 0.001 M HEXAMMINECOBALTIC CHLORIDE

Suppl. elect.		Second reduct. wave		First and second reduct. waves combined			
Nature	Concn., M	Half-wave potential, $-E_{1/2}$	Slope	i_d, μa	t, sec./drop	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	Ratio of diffusion coefficients
Potassium nitrate	0.1	1.207 v	0.042	9.52	4.03	5.36	
	.9	1.224	.054	10.46	3.74	5.96	
	.1[a]	1.200	.062	8.89	3.80	5.06	1.00 (base value)
Potassium chloride	0.1	1.203	0.046	9.45	3.78	5.38	
	.2	1.203	.046	9.16	3.82	5.21	
	.3	1.202	.052	9.43	3.76	5.37	
	.4	1.212	.044	9.20	3.87	5.22	
	.5	1.213	.060	9.01	3.71	5.15	
	.8	1.218	.057	8.90	3.64	5.10	
	.9	1.210	.040	9.42	3.68	5.39	
	.1[a]	1.203	.062	9.17	3.84	5.21	1.06
	.5[a]	1.215	.060	8.75	3.71	5.00	0.98
	.8[a]	1.225	.060	8.88	3.63	5.09	1.02
Potassium sulfate	0.1	1.232	0.052	8.36	3.73	4.77	0.89
	.2	1.242	.056	8.16	3.61	4.68	.86
	.3	1.248	.048	7.90	3.60	4.53	.81
	.4	1.253	.043	7.98	3.63	4.57	.82
Potassium tartrate	0.1	1.318	0.083	7.49	3.33	4.35	0.74
	.5	1.435	.100	6.82	3.28	3.98	.62
	.9	1.463	.104	6.11	3.34	3.55	.49
Potassium citrate	0.1	1.422	0.067	6.78	3.39	3.89	.59
	.5	1.519	.089	6.18	2.97	3.66	.52
	.9	1.529	.122	5.11	3.35	2.97	.35

[a] In presence of 0.002% methyl acid; all other experiments in absence of maximum suppressors.

uct, the half-wave potential would be very nearly equal to the standard potential. Actually, all the observed values are more negative, and the slopes of the curves indicate irreversible behavior in all cases. If it were assumed that the half-wave potential is reversibly determined by the ratio of hexamminecobaltic and hexamminecobaltous ion concentrations but that the latter is very small owing to rapid decomposition, then the observed half-wave potential would become more positive than the standard potential. Probably the hexamminecobaltous ion does not exist in sufficient concentration at the electrode surface to be potential determining, and the electrode reaction is best pictured as a reduction accompanied by a simultaneous aquation of the cobaltous ion, in agreement with Willis, Friend and Mellor.[5] The second stage of reduction is that of the aquated cobaltous ion except in tartrate and citrate media when stable cobaltous complexes exist.

To account for the effect on the diffusion current, it is proposed that in sulfate, citrate and tartrate solutions a "super-complex" is formed in which the hexamminecobaltic ion acts as the central ion. Ions of the supporting electrolyte are thought to be clustered about the central complex by an electrostatic attraction similar to that postulated in the ion-pair concept of Bjerrum[14,15] and of Fuoss and Kraus.[16,17] The original complex may be thought to be solvated in the same sense of the hydration in water solution of a metallic ion such as an alkali metal ion, which has little or no tendency for covalent bond formation. In the super-complex here proposed, the ions of the electrolyte may replace some of the molecules of water in the outer layer about the complex. The stronger the electrostatic and ion-dipole attraction between the central complex ion and the clustering ions, the more firmly they would be attracted. This would encumber the complex ion as it diffuses to the electrode, thus making it diffuse more slowly, and would cause the electron to have added difficulty in getting to the center to effect reduction, thereby making reduction harder and the half-wave potential more negative. We might have such ions present in sulfate medium, for example, as $[Co(NH_3)_6]SO_4{}^+$, $[Co(NH_3)_6](SO_4)_2{}^-$, and so forth.

Brintzinger and co-workers have mentioned similar "multi-shelled" complex compounds.[18-21] Kiss and Czegledy,[22] by a study of extinction curves of a number of the multi-shelled complexes

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[14] J. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[15] J. Bjerrum and Falkenhagen, "Electrolyte," Verlag von S. Hirzel, Leipzig, 1932, p. 257.

[16] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

[17] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

[18] H. Brintzinger and H. Osswald, *Z. anorg. allgem. Chem.*, **223** 253 (1935).

[19] H. Brintzinger and H. Osswald, *ibid.*, **224**, 283 (1935).

[20] H. Brintzinger and F. Jahn, *ibid.*, **230**, 176 (1936).

[21] H. Brintzinger and F. Jahn, *ibid.*, **231**, 281 (1937).

[22] A. Kiss and D. von Czegledy, *ibid.*, **239**, 27 (1938).

have presented evidence of ionic bonding for sulfate and secondary phosphate ions in the second sphere. Results of their work were not conclusive with other electrolytes.

It might be noted that a possible explanation based upon displacement of part or all of the coördinating groups of the original complex by electrolyte ions was ruled out for a number of reasons. First, ammonia is known to form a very stable covalent bond to cobalt (III), whereas sulfato complexes are in general much less stable. Second, from the point of view of super-complexing, which is electrostatic in character, the divalent ions such as the sulfato ion would be expected to show the clustering behavior more readily than univalent ions such as chloride, nitrate, or perchlorate, a prediction which is in accord with the experimental result. Third, the color stability of the solutions provides a reason for discounting a theory based upon displacement of the ammonia molecules in the original complex, inasmuch as displacement of coördinating groups might reasonably be expected to cause a change of color; actually no such color change occurs. Fourth, the size and charge of the ion that would result from such a displacement should lead to less hydrated ions; for example, if a sulfate ion replaced two ammonia molecules, the resulting ion would be a univalent cation which would be less highly hydrated than the original trivalent ion and, hence, would be expected to diffuse more rapidly; if two sulfate ions replaced four ammonia molecules, a univalent negative ion would result, again with a higher diffusion rate, which would orient differently with respect to the dropping mercury electrode and might be expected to be more easily reduced if indeed any change would result; the experimental result is in the opposite direction.

Summary

1. Capillary active substances such as gelatin and octyl alcohol were found to shift the half-wave potentials for the first reduction step of the hexamminecobaltic ion to more negative potentials.

2. The optimum drop rate for most favorable conformity with the Ilkovic equation was established.

3. Supporting electrolytes of good coördinating ability were found to shift the half-wave potential for the first reduction step of the hexamminecobaltic ion to more negative potentials and to decrease the diffusion rate of the cobaltic complex. A "super-complex" of anions of the indifferent electrolyte clustered about the central complex by electrostatic and ion-dipole attraction is postulated.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Polarography in Liquid Ammonia. II. The Electron Electrode[1]

BY H. A. LAITINEN AND C. J. NYMAN[1a]

The electrode reactions which might occur at a cathode on electrolysis of anhydrous liquid ammonia solutions have been summarized by Makishima.[2] For a platinum electrode, metal deposition, reduction in valence state of the metal ion, hydrogen discharge, and electron dissolution are possible processes. The dissolution of electrons was observed by several investigators when a salt solution, whose ions were non-reducible, was electrolyzed with a platinum cathode. On electrolysis of solutions of tetramethylammonium chloride and hydroxide and tetraethylammonium chloride between platinum electrodes at -34°, Palmaer[3] obtained in each case a blue solution, which he attributed to the electron or to the "free alkylammonium radical." Similar observations were made by Kraus[4] and by Schlubach.[5] Forbes and Norton[6] have prepared solutions of tetramethyl-, tetraethyl-, tetrapropyl-, tetrabutyl-, trimethylbutyl-, triethylbutyl-, tripropylbutyl-, tributylmethyl-, tributylethyl- and diethyldibutylammonium ions and electrons by electrolysis of the iodides of these ions between platinum electrodes. Cady[7] and Kraus[8] found on electrolysis of sodium solutions between platinum electrodes that the transfer of electrons from the electrode to the solution was the only cathodic process which occurred and that the opposite transfer was the only anodic process which occurred.

All the processes listed for a platinum cathode can also occur at a dropping mercury cathode. In addition, there is the possibility of amalgamation of the cation of the salt solution, as is known to be the case with the alkali metal ions.[1] For electrons to enter solution from the surface of a dropping mercury cathode, the potential of electron dissolution must be more positive than the amalgamation potential of the cation of the salt solution.

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(2) S. Makishima, *J. Faculty Eng. Tokyo Imp. Univ.*, **21**, 115 (1938).

(3) W. Palmaer, *Z. Elektrochem.*, **8**, 729 (1902).

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(5) H. H. Schlubach, *Ber.*, **53**, 1689 (1920).

(6) G. S. Forbes and C. E. Norton, THIS JOURNAL, **48**, 2278 (1926).

(7) H. P. Cady, *J. Phys. Chem.*, **1**, 707 (1897).

(8) C. A. Kraus, THIS JOURNAL, **30**, 1323 (1908); **36**, 864 (1914).