and the assistance of Drs. G. E. Hilbert and L. B. Howard, as well as valuable discussions with other members of the Staff of the Fixed Nitrogen Research Laboratory.

Summary

Absorption coefficients have been measured in the absorption lying at about 1.5μ due to the N–H group in a number of primary and secondary aliphatic and aromatic amines, and the positions of the maxima of absorption have been determined.

A method is suggested for the utilization of such data, as yet in a somewhat restricted field, for the detection of the presence of N–H groups, and for the approximate determination of the number of N–H groups present per cubic centimeter of a solution as well as the way in which this group is linked in the molecule.

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Complex Compounds in Eder's Solution

BY G. H. CARTLEDGE AND S. L. GOLDHEIM[1]

Several attempts have been made to explain the mechanism of Eder's reaction, $2HgCl_2 + C_2O_4^= \longrightarrow Hg_2Cl_2 + 2CO_2 + 2Cl^-$. Most of the students of this reaction have assumed, as will be pointed out later in the discussion of their work, that the photochemical properties of this solution of oxalate and mercuric chloride are dependent on a mercuri-oxalate complex.

The present work was undertaken in order to determine the nature of the complexes which exist in Eder's solution and the extent to which they form. This information was sought by: (1) experiments on the partition of mercuric chloride between benzene and aqueous oxalate solutions, and (2) determinations of the freezing point depressions in Eder mixtures. Preliminary freezing point experiments made in this Laboratory by Mr. F. B. Slagle showed that the formation of the complex or complexes is attended by a small diminution in the number of molecules.

Since chloride ion is known to have a marked effect on the reaction and is also known to form complexes with mercuric chloride, a careful study of the literature on mercuri-chloro complexes as well as that on mercuri-oxalate complexes was made.

Throughout this work, the ionization of mercuric chloride is neglected,

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[1] This paper is abstracted from the dissertation presented by S. L. Goldheim to the Faculty of Philosophy of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

the figures given by Drucker,[2] $(Hg^{++})(Cl^{-})^2/(HgCl_2) = 0.95 \cdot 10^{-14}$ at 25° and $(Hg^{++})(Cl^{-})/(HgCl^{+}) = 5.3 \cdot 10^{-8}$ at 25°, showing that this assumption is permissible.

Literature

Mercuri-oxalate Complexes.—Roloff[3] attempted to show by the rather dubious ebullioscopic method the presence of complexes such as $(NH_4)_2Hg(C_2O_4)Cl_2$, $(NH_4)_2Hg_2(C_2O_4)_2Cl_2$ and others. Berger[4] assumed the presence of a complex without giving its formula. Bekhterev[5] has also mentioned the presence of complex mercury salts in Eder's solution. Other workers have studied the system $K_2C_2O_4$–HgC_2O_4–H_2O and found definite complexes, which are, of course, solid salts in equilibrium with saturated solutions.

Mercuri-chloro Complexes.—A great mass of conflicting data on these complexes exists. A critical study of forty-four articles on this subject leads to the conclusion that the work of Linhart[6] is the most definite and quantitatively accurate. This work shows that in solutions of mercuric chloride and alkali chloride (represented by MCl) below 40° the following molecular species may exist: $HgCl_2$, Hg_2Cl_4, MCl, M^+, Cl^-, $MHgCl_3$, $HgCl_3^-$, M_2HgCl_4, $HgCl_4^{=}$, MHg_2Cl_5, $Hg_2Cl_5^-$, $M_2Hg_2Cl_6$, $Hg_2Cl_6^{=}$. We neglect any ionization of $HgCl_2$ or Hg_2Cl_4. The proportions of these species in any solution depend chiefly on the concentrations. With the mercuric chloride in excess of the alkali chloride, the complexes are those having the greater proportion of mercury. The equilibrium constants necessary for calculations of these species are known from Linhart's work, which is used as the basis for the present research.

Theoretical

A scheme of complex formation in Eder's solution which would satisfy three points has been sought: first, the distribution experiments; second, the measurements of freezing point depressions; and, third, the known reaction rates, assuming that the reaction is, as has been suggested, a decomposition of the mercuri-oxalate complex.

The following schemes were tried

$$HgCl_2 + 2C_2O_4^{=} \rightleftharpoons Hg(C_2O_4)_2^{=} + 2Cl^- \tag{1}$$
$$Hg_2Cl_4 + 4C_2O_4^{=} \rightleftharpoons Hg_2(C_2O_4)_4^{==} + 4Cl^- \tag{2}$$
$$HgCl_2 + C_2O_4^{=} \rightleftharpoons HgClC_2O_4^- + Cl^- \tag{3}$$
$$HgCl_2 + C_2O_4^{=} \rightleftharpoons HgCl_2C_2O_4^{=} \tag{4}$$
$$Hg_2Cl_4 + C_2O_4^{=} \rightleftharpoons Hg_2Cl_4C_2O_4^{=} \tag{5a}$$
$$2HgCl_2 + C_2O_4^{=} \rightleftharpoons Hg_2Cl_4C_2O_4^{=} \tag{5b}$$
$$Hg_2Cl_4 + C_2O_4^{=} \rightleftharpoons Hg_2Cl_2C_2O_4 + 2Cl^- \tag{6a}$$
$$2HgCl_2 + C_2O_4^{=} \rightleftharpoons Hg_2Cl_2C_2O_4 + 2Cl^- \tag{6b}$$

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(2) Drucker, *Z. Elektrochem.*, **18**, 236 (1912).

(3) Roloff, *Z. physik. Chem.*, **13**, 327 (1894).

(4) Berger, *Rec. trav. chim.*, **40**, 387 (1921).

(5) Bekhterev, *J. Russ. Phys.-Chem. Soc.*, **57**, 161 (1925); *Chem. Abstr.*, **20**, 2459 (1926).

(6) Linhart, THIS JOURNAL, **37**, 258 (1915); **38**, 1272 (1916).

$$2HgCl_2 + 2C_2O_4^{=} \rightleftharpoons Hg_2Cl(C_2O_4)_2^{-} + 3Cl^{-} \quad (7)$$

$$Hg_2Cl_4 + 2C_2O_4^{=} \rightleftharpoons Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^{-} \quad (8a)$$

$$2HgCl_2 + 2C_2O_4^{=} \rightleftharpoons Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^{-} \quad (8b)$$

The distribution measurements lead to equilibrium constants for schemes 1 to 7 showing decided drifts in these values when arranged in the order of varying ratio of bichloride to oxalate. The constant is the same for (8a) and (8b) and shows no drift. Measurements of the freezing point depressions, however, show that (8b) is the correct representation, and an additional reason for adopting this scheme is that this permits an explanation of certain of the reported reaction rate measurements.

In the distribution experiments successive portions of Eder's solution were shaken with benzene until the mercuric chloride in the benzene was in equilibrium with that in the *original* aqueous solution. The concentration in the benzene was determined. Then, knowing the original concentrations of mercuric chloride and potassium oxalate, the following calculations were made. All concentrations are expressed in moles per liter.

As has been stated, the only scheme of complex formation which fits the experimental results is

$$2HgCl_2 + 2C_2O_4^{=} \rightleftharpoons Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^{-} \quad (1)$$

We have at the same time the equilibria

$$2HgCl_2 \rightleftharpoons Hg_2Cl_4 \quad (2)$$

$$HgCl_2 + Cl^{-} \rightleftharpoons HgCl_3^{-} \quad (3)$$

$$Hg_2Cl_4 + Cl^{-} \rightleftharpoons Hg_2Cl_5^{-} \quad (4)$$

$$HgCl_3^{-} + Cl^{-} \rightleftharpoons HgCl_4^{=} \quad (5)$$

$$Hg_2Cl_5^{-} + Cl^{-} \rightleftharpoons Hg_2Cl_6^{=} \quad (6)$$

$$Hg_2Cl_6^{-} + Cl^{-} \rightleftharpoons HgCl_3^{-} + HgCl_4^{=} \quad (7)$$

Equation 7 is included for completeness but does not enter the calculations. Equation 2 fixes a relationship between $HgCl_2$ and Hg_2Cl_4. The remaining five equations contain five unknowns and yield, on inspection, five algebraic equations, containing these. The solution has been carried out, and calculations made on this basis check the results here presented. Because, however, of the large amount of arithmetic involved it has been found more satisfactory to neglect equations 5 and 6 when dealing with solutions of low chloride ion concentration, as is the case in Eder mixtures. Equations 1 to 4 then lead to the following three algebraic equations

$$\Sigma HgCl_2 = a + 2b + 2x + y + 2z$$

$$(y)/(a)(2x - y - z) = A$$

$$(z)/(b)(2x - y - z) = B$$

The symbols used in this discussion are: $(HgCl_2)_b$, the concentration in the benzene—experimentally determined; $a = (HgCl_2)_w$, the concentration in the water layer[6]—$a = 11.90(HgCl_2)_b$; $b = (Hg_2Cl_4)$, the concentration of the double molecules[6]—$b = 0.297 \cdot a^2$; $x = (Hg_2Cl_2(C_2O_4)_2^{=})$, the concentration of the oxalate complex; $y = (HgCl_3^-)$; $z = (Hg_2Cl_5^-)$; $\Sigma HgCl_2$, the original formality of mercuric chloride; $\Sigma K_2C_2O_4$, the original formality of potassium oxalate.

At equilibrium the concentration of the chloride ions will then be $(2x - y - z)$, and that of the oxalate ions will be $(\Sigma K_2C_2O_4 - 2x)$.

A and B are constants having the values 9.8 and 37, respectively.[6]

Solving the three algebraic equations (most simply by determinants), we obtain the results

$$
\begin{aligned}
x &= (\Sigma HgCl_2 - a - 2b)(aA + bB + 1)/(2)(2aA + 3bB + 1) \\
y &= (\Sigma HgCl_2 - a - 2b)(aA)/(2aA + 3bB + 1) \\
z &= (\Sigma HgCl_2 - a - 2b)(bB)/(2aA + 3bB + 1)
\end{aligned}
$$

Using the values of x, y and z thus obtained, the equilibrium constant of formation of the oxalate complex may be calculated

$$
\begin{aligned}
K' &= (Hg_2Cl_2(C_2O_4)_2^{=})(Cl^-)^2/(HgCl_2)^2(C_2O_4^{=})^2 \\
&= (x)(2x - y - z)^2/(a)^2(\Sigma K_2C_2O_4 - 2x)^2
\end{aligned}
$$

This constant, K', differs from the true equilibrium constant, K, by a factor due to the activity coefficients of the ions. If the activity coefficient is represented by γ, we will call $\gamma_{Cl^-} = \gamma_I$. To a reasonable approximation, $\gamma_{Hg_2Cl_2(C_2O_4)^-} = \gamma_{C_2O_4^{=}} = \gamma_{SO_4^-} = \gamma_{II}$. We may calculate the ionic strengths[7] of each solution used, and find corresponding values for γ_{Cl^-} and $\gamma_{SO_4^-}$. The constant, K, will then equal $(K')(\gamma_I)^2/(\gamma_{II})$.

In the freezing point experiments, the sum of the freezing point depressions of the separate mercuric chloride and potassium oxalate solutions is compared with the depression of the mixture containing the same concentrations of salts. For every mole of $Hg_2Cl_2(C_2O_4)_2^{=}$, of $HgCl_3^-$, or of $Hg_2Cl_5^-$ that is formed, the sum of all the moles in solution is reduced by one, while the effect on the equilibrium $2HgCl_2 \rightleftarrows Hg_2Cl_4$ is inappreciable (less than 0.001 mole at all the concentrations studied). Hence the product, $(1.86)(x + y + z) = \delta_{\text{calcd.}}$, should give the amount by which the depression calculated on the basis of no complex formation (that is, the sum of the depressions of the separate solutions), exceeds the actual depression. This calculated value of δ may then be compared with the observed value.

Experimental

Materials. Mercuric Chloride.—Baker C. P. salt, labeled as containing 0.001% Fe, was three times recrystallized from water and dried in an oven.

Potassium Oxalate.—Djang[8] has showed that ammonia is present in the precipitate of mercurous chloride when ammonium oxalate is used in Eder's reaction; hence potassium oxalate was used throughout this work. Baker C. P. salt, labeled as containing 0.0006% Fe, was three times recrystallized from water and dried over calcium chloride in a desiccator.

Potassium Iodate.—Kahlbaum best salt was powdered and dried in an oven.

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[7] Lewis and Randall, "Thermodynamics," 1923.

[8] Djang, Dissertation, Johns Hopkins University, 1930.

Benzene.—Baker "Thiophene-free" C. P. benzene was redistilled once in a simple distilling apparatus and the liquid boiling at 80–81° (uncorrected) was used.

Solutions.—Mercuric chloride solution was made up to the approximate concentration desired and standardized against potassium iodate according to the method of Jamieson.[9]

Potassium oxalate solution was made up approximately and standardized against potassium permanganate in the usual manner.

Potassium iodate solution was made up accurately according to Jamieson's directions.

Apparatus and Methods.—The distribution experiments were carried out in a water thermostat, painted black, kept out of direct sunlight, and regulated to 25.00 ± 0.02°. It was found convenient to shake the solutions in foil-covered hydrogenation bottles of about 250-cc. capacity. The thick walls of these diminish the possibilities of sudden temperature changes. The bottles were fitted with spring-clamped porcelain plugs, as caps, firmly seated in the necks of the bottles by means of chamois-skin washers. Such an arrangement allowed fast work with little loss of benzene by evaporation. Both aqueous and benzene layers were removed by *blowing* out in a pipet.

Two series of freezing point experiments were made, one set carried out in a one-pint Dewar flask, according to the method suggested by Richards;[10] and the other set done by the Beckmann method as usually described.[11]

Potassium oxalate concentrations were determined in the usual manner with potassium permanganate, duplicate titrations being run in practically all cases.

The analyses for mercuric chloride were in most cases made by the potassium iodate method of Jamieson, which was found by check experiments to be very satisfactory. In the freezing point experiments with pure mercuric chloride the analyses were made by measuring the density of a 10-cc. portion and reading off the molality from a curve prepared from figures collected by Comey.[12] Two of these analyses were checked by the sulfide method. In a few other cases the sulfide method was used.

The mode of procedure in the distribution experiments was as follows: 100 cc. of benzene and 50 cc. of the Eder mixture, of known concentration in mercuric chloride and potassium oxalate, were put in the bottles in the thermostat and shaken for two hours. After standing for another half to three-quarters hour, the bottom (aqueous) layer was blown out in a pipet, and a fresh 20-cc. portion of the Eder mixture added. This process was repeated until the benzene had been shaken with four portions of solution, preliminary experiments having shown that four successive shakings were needed to ensure equilibrium conditions. Shaking was found more satisfactory than stirring, equilibrium being reached in equal times. After the last shaking, the solutions again stood half to three-quarters of an hour in order to settle, and a 25-cc. sample of the benzene layer was carefully blown out from as near the top as possible. This sample was evaporated over a lamp bulb in a stream of air, fifteen to twenty minutes being required and check experiments showing that there was no detectable loss of mercuric chloride. A test with potassium permanganate showed that no detectable amount of potassium oxalate went into the benzene. The mercuric chloride left on evaporation of the benzene was determined by the Jamieson method.

Results

The results of the distribution experiments are given in Table I. The symbols used as column headings are explained on page 3585. Set A

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(9) Jamieson, "Volumetric Iodate Methods," 1926.

(10) Richards, THIS JOURNAL, **25**, 291 (1903).

(11) Findlay, "Practical Physical Chemistry," p. 113.

(12) Comey, "Dictionary of Solubilities," 1921.

TABLE I

The explanation of the column headings is given on page 3585. The averaged results of Experiments 1 and 2 are repeated under Sets B and C, in parentheses, for purposes of comparison.

No.	$\Sigma HgCl_2$	$\Sigma K_2C_2O_4$	$(HgCl_2)_b$	a	b	x	y	z	(Cl^-)	$(C_2O_4^=)$	K'
					Set A						
1	0.1069	0.0969	0.00619	0.0736	0.00161	0.0102	0.0083	0.00068	0.0115	0.0765	0.042
2	.1069	.0969	.00610	.0726	.00156	.0106	.0086	.00070	.0119	.0757	.051
3	.0713	.0969	.00408	.0485	.00070	.00790	.0050	.00027	.0105	.0811	.056
4	.0535	.0969	.00317	.0378	.00042	.00576	.0031	.00013	.0083	.0854	.039
5	.0356	.0969	.00213	.0254	.00019	.00410	.0016	.00005	.0065	.0887	.036
6	.0104	.0969	.000749	.00890	.000024	.00069	.00011	.000001	.00127	.0955	.0015
7	.0104	.0969	.000752	.00895	.000024	.00065	.00010	.000001	.00119	.0956	.0013
					Set B						
(1	.1069	.0969	.00615	.0731	.00159	.0104	.0085	.00069	.0117	.0761	.047)
8	.1065	.0495	.00678	.0806	.00193	.00734	.0062	.00056	.0079	.0348	.059
9	.1065	.0099	.00746	.0889	.00234	.0042	.0037	.00037	.0043	.0015	4.5
10	.1030	.00959	.00756	.0900	.00241	.0027	.0024	.00024	.0027	.0043	.134
					Set C						
11	.0609	.1412	.00328	.0390	.00045	.00810	.0044	.00019	.0116	.1250	.045
12	.0713	.1292	.00397	.0473	.00066	.00844	.0053	.00028	.0114	.1123	.039
(1	.1069	.0969	.00615	.0731	.00159	.0104	.0085	.00069	.0117	.0761	.047)
13	.1425	.0646	.00877	.1043	.00323	.0100	.0095	.0011	.0093	.0446	.042
14	.0535	.0485	.00373	.0444	.00059	.00298	.00178	.000088	.0041	.0425	.014
					Set D						
		$\Sigma(NH_4)_2C_2O_4$									
15	.0686	.1946	.00323	.0384	.00044	.0113	.0061	.00026	.0162	.1720	.068
16	.1236	.1168	.00644	.0765	.00174	.0147	.0122	.00104	.0162	.0874	.087

includes solutions in which the potassium oxalate concentration was constant; Set B, those in which the mercuric chloride concentration was constant; and Set C, those in which the concentrations were varied simultaneously, Experiments 11, 12, 1, 13, having the total salt concentration constant. Set D includes experiments with ammonium oxalate.

The ionic strengths of the solutions used in these experiments vary from 0.04 in No. 9 to 0.42 in No 11. Inasmuch as the ion activity coefficients are not well known for the higher values of the ionic strength, the correction of K' to K will not be made in the present paper. A rough calculation, however, shows that the value of K is approximately 0.1.

In Table II are presented the freezing point depressions of pure mercuric chloride and pure potassium oxalate solutions. The results for the potassium oxalate solutions by the Beckmann method are given uncorrected for the supercooling; in the final calculations this error cancels out. In each set of the table, the first column is the concentration in moles per liter, and the second column is the observed freezing point depression.

TABLE II

Mercuric chloride		Potassium oxalate					
		(Beckmann method)		(Richards method)		(Richards method)	
Concn.	ΔT	Concn.	ΔT	Concn.	ΔT	Concn.	ΔT
0.0485	0.089°	0.018	0.098°	0.0243	0.121°	0.110	0.499
.0623	.113	.054	.268	.0344	.166	.140	.627
.0778	.138	.108	.509	.0480	.232	.163	.728
.0920	.167	.180	.815	.0621	.293	.189	.841
.118	.209	.198	.896	.0848	.397		

TABLE III

(1) No.	(2) ($HgCl_2$) moles/liter	(3) ΔT_1[a]	(4) ($K_2C_2O_4$) moles/liter	(5) ΔT_2[b]	(6) Calcd. ΔT $\Delta T_1 + \Delta T_2$	(7) Obs. ΔT	(8) δ
B 1	0.180	0.325°	0.018	0.098°	0.423°	0.396°	0.027°
B 2	.162	.293	.036	.181	.474	.442	.032
B 3	.144	.260	.054	.268	.528	.493	.035
B 4	.117	.211	.081	.389	.600	.565	.035
B 5	.099	.178	.099	.470	.648	.617	.031
B 6	.090	.162	.108	.509	.671	.643	.028
B 7	.072	.129	.126	.588	.717	.688	.029
B 8	.054	.096	.144	.664	.760	.744	.016
B 9	.036	.064	.162	.740	.804	.798	.006
B 10	.018	.032	.180	.815	.847	.843	.004
R 11	.081	.147	.038	.183	.330	.317	.013
R 12	.073	.132	.068	.319	.451	.434	.017
R 13	.049	.089	.023	.112	.201	.194	.007
R 14	.048	.085	.088	.410	.495	.483	.012
R 15	.046	.083	.043	.209	.292	.284	.008
R 16	.053	.095	.049	.234	.329	.319	.010
R 17	.028	.050	.105	.482	.532	.530	.002

[a] Read from Curve II of Fig. 1. [b] Read from Curves III or IV of Fig. 1.

The results of freezing point determinations on Eder mixtures are given in Table III. Experiments by the Beckmann method are marked B; those by the Richards method are marked R.

It will be noticed that experiments 1 to 10 are for solutions of constant total molality. Figure 1 presents in graphical form the results in Table II, suitable for interpolation and use in Table III as explained.

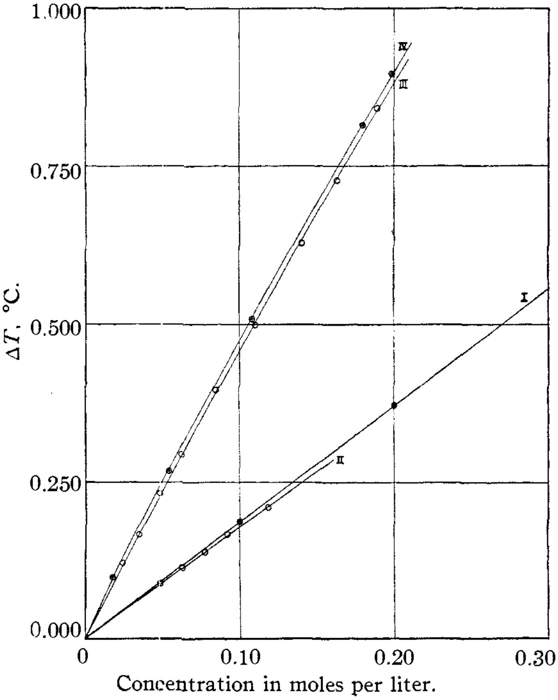

Fig. 1.—I, Theoretical non-electrolyte; II, mercuric chloride; III, potassium oxalate, Richards method; IV, potassium oxalate, Beckmann method.

The calculated values of δ are now compared in Table IV with the observed values from Column 8, Table III. The calculated values are found from Table I, from which (see page 3586) $\delta_{\text{calcd.}} = (1.86)(x + y + z)$.

TABLE IV

No. of expt.	$\delta_{\text{calcd.}}$	No. of expt.	$\delta_{\text{obs.}}$
Table I 1	0.036°	Table III 5	0.031°
Table I 3	.025	Table III 7	.029
Table I 4	.017	Table III 16	.010
Table I 5	.011	Table III 17	.002
Table I 6	.001	Table III 10	.004
Table I 11	.024	Table III 8	.016
Table I 12	.026	Table III 7	.029
Table I 13	.038	Table III 3	.035
Table I 14	.009	Table III 15	.008

Discussion

The results show that in the distribution experiments duplicate runs agree within about 1% in the measured concentration of mercuric chloride. On account of the subtractions involved in the calculations experimental errors are multiplied fifteen or twenty-fold in the final value of K'. Errors are introduced into K' also by the fact that the constants A and B are known to only two-place accuracy, and that the activity coefficients are not known. The calculations are least accurate when the oxalate-ion concentration is very low, as in Experiments 9 and 10 of Table I. Another factor that is beyond our control is the hydrolysis of the mercuric chloride. Considering only the experiments in which neither component is present in greater than three to one excess over the other, the values of K' show no drift as the concentration ratio is varied, whereas decided drifts are obtained when other schemes of formulation are tried. Thus, if we arrange the significant experiments of Table I in order of decreasing ratio of bichloride to oxalate, taking average values of K' for runs having approximately equal ratios of the formalities, we obtain the values of K': 0.050, 0.047, 0.056, 0.039, 0.045, 0.036, when $\Sigma HgCl_2/\Sigma K_2C_2O_4$ varies from 2.2 to 0.37. According to scheme 4 (page 3585) the corresponding values of the constant are: 9.5, 6.3, 5.8, 4.6, 4.5, 4.4. When the concentration ratio differs widely from unity it is most likely that the composition of the complex changes, as is known to be the case with the chloro complexes.

The agreement between the calculated and observed values of δ (Table IV) is also satisfactory, these being obtained from differences of measurements which are hardly accurate to more than 0.003°. Furthermore, these values are compared in solutions of only approximately the same composition and, of course, at two different temperatures, 0 and 25°. Thermal effects, however, on solutions of this type of complex should be relatively small in the neighborhood of room temperature. The observed values of δ are all less than would be expected if the complex had the formula $HgCl_2C_2O_4^{=}$.

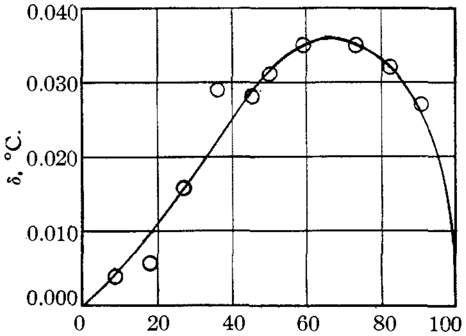

Fig. 2.

The variation in the value of δ with the ratio of bichloride to oxalate in solutions whose gross formality is constant is particularly striking. This variation is shown graphically in Fig. 2, from which it is evident that the greatest decrease in the freezing-point lowering occurs with an excess of bichloride. This is undoubtedly due to the effect of the mercuric chloride in forming chloro complexes, which is to be expected from a formulation such as the one here proposed, but not if the complex is formed by the reaction $HgCl_2 + C_2O_4^= \rightleftarrows HgCl_2C_2O_4^=$ in which no chloride ions are liberated.

The scheme of complex formation presented on page 3585 is thus in good agreement with experiment, such an agreement not being found for any of the other formulations which were tried. It will be convenient to remember that in the original Eder solution, as usually made up (Expt. 15, Table I), the concentration of the complex $Hg_2Cl_2(C_2O_4)_2^=$ is approximately 0.01 molar.

Discussion of the Rate of the Eder Reaction.—The mercuri-oxalate complex which has been shown to exist in Eder's solution may be made the basis of an explanation of the reaction rate measurements.

Roseveare,[13] Roseveare and Olson,[14] and Wyckoff and Baker[15] have found that the rate of Eder's reaction is proportional to the first power of the mercuric chloride concentration under certain conditions. This is to be expected from a consideration of the equilibrium equation. If we assume that no excess of chloride ion is initially present, the formation of a complex mercuri-chloro-oxalate ion liberates two chloride ions, so that, as a first approximation, the chloride-ion concentration is twice the concentration of the complex ion. We have, therefore

$$\begin{aligned}(Hg_2Cl_2(C_2O_4)_2^=) &= K(HgCl_2)^2(C_2O_4^=)^2/(Cl^-)^2 \\ &= K(HgCl_2)^2(C_2O_4^=)^2/4(Hg_2Cl_2(C_2O_4)_2^=)^2\end{aligned}$$

from which, for a given oxalate concentration, $(Hg_2Cl_2(C_2O_4)_2^=) \propto (HgCl_2)^{2/3}$. Since our measurements show that, within limits, the free $HgCl_2$ is proportional to the total mercury present (Expts. 1 to 5, Table I), in the early stages of the decomposition reaction the rate should be roughly proportional to somewhat less than the first power of the concentration of mercuric chloride. This was found to be the case for both the thermal and x-ray photolytic reactions. When chlorides are initially present the order of the reaction as to mercuric chloride should increase, according to our formulation. This appears to be the case, since the results of Roseveare and Olson (Ref. 14, Tables II and III) agree better with a second order equation than with a first order one when considerable potassium chloride is present. The presence of high concentrations of chlorides so complicates the problem, however, that we cannot be certain what the results mean. It appears most likely that the composition of the mercuri-chloro-oxalate complex changes when chlorides are present in considerable concentration. Not only so, but the kinetic relationships are also complicated by salt effects quite apart from the specific action of the chloride ions, as has been shown for Eder's reaction by Berger.[4]

(13) Roseveare, THIS JOURNAL, **52**, 2617 (1930).

(14) Roseveare and Olson, *ibid.*, **51**, 1716 (1929).

(15) Wyckoff and Baker, *Am. J. Roentgenol. Radium Therapy*, [6] **22**, 551 (1929).

Particularly interesting results are obtained, however, when we consider the order of the reaction with respect to oxalate ion. Roseveare and Olson found that the rate varies as the second power of the oxalate-ion concentration in the absence of oxygen, but in two experiments run with the solutions saturated with oxygen, the reaction became first order with respect to the oxalate concentration. Likewise, Roseveare found a first-order rate with respect to oxalate in the x-ray photolysis in the *absence* of oxygen. Dhar[16] also found the reaction to be monomolecular as to both mercuric chloride and potassium oxalate with no chloride added and with an indefinite concentration of oxygen (solutions previously saturated with carbon dioxide). These conflicting results are clarified by considering the different conditions under which the rates were measured.

From our equilibrium equation $(Hg_2Cl_2(C_2O_4)_2^{=}) = K(HgCl_2)^2(C_2O_4^{=})^2/(Cl^-)^2$, the reaction rate with respect to the oxalate concentration should have different values according as the chloride ion accumulates during the reaction or else remains more or less fixed. As previously pointed out (page 3592, *et seq.*), if no chloride ion is initially present the concentration of the complex ion varies as $(HgCl_2)^{2/3}(C_2O_4^{=})^{2/3}$, or, the initial reaction rate should be less than first order with respect to oxalate. This situation prevails when the mercury is not present in considerable excess and no potassium chloride is added; under these conditions, the initial chloride-ion concentration is equal to twice the concentration of the complex. Now these are exactly the conditions under which the oxygen experiments of Roseveare and Olson and the x-ray photolysis of Roseveare were carried out. On the other hand, if chloride ion is added to the reaction mixture, the additional chloride ion liberated in the formation of the complex is inappreciable and the concentration of the complex varies as the square of the oxalate-ion concentration. Also, if no potassium chloride is added but mercuric chloride is used in considerable excess, the chloride ion initially liberated is extensively removed by the formation of chloro complexes, so that in this case also the rate should vary as the square of the oxalate ion concentration.

From the results of our distribution experiments it is uncertain whether the same mercuri-chloro-oxalate complex persists as the oxalate–mercury ratio deviates widely from unity, but it is significant that the kinetic measurements reveal just the variation in reaction order that our formula leads us to expect. If the formula were $HgCl_2C_2O_4^{=}$, as proposed by Roseveare, the maximum concentration of complex for a given total salt concentration should occur when the mercuric chloride and potassium oxalate were present in equimolal proportions; whereas, according to our measurements, the maximum formation of complexes occurs on the mercuric chloride side of metathetical equivalence.

(16) Dhar, *J. Chem. Soc.*, **111**, 690 (1917).

Summary

1. The results of experiments on the partition of mercuric chloride between aqueous potassium oxalate and benzene are presented.

2. The freezing point depressions of mercuric chloride and of potassium oxalate solutions and of mixtures of these have been determined.

3. It is shown that calculations from the distribution and freezing point experiments lead to the following scheme of complex formation in Eder's solution:

$$2HgCl_2 + 2C_2O_4^{=} \rightleftarrows Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^-$$
$$HgCl_2 + Cl^- \rightleftarrows HgCl_3^-$$
$$Hg_2Cl_4 + Cl^- \rightleftarrows Hg_2Cl_5^-$$

4. This scheme is shown to be in harmony with reaction rate measurements on Eder solutions over a corresponding range of concentrations.

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A Study of Polarization Currents Due Solely to Changes in Electrode Area[1]

BY KENNETH E. GLIDDEN[2] AND W. A. PATRICK

Introduction

The purpose of this investigation was to study the adsorption of mercurous ions at a mercury surface by measuring the current flowing between two mercury electrodes immersed in a mercurous sulfate solution while one of the electrodes was undergoing a slow definite increase in area. Similar studies have been made in the past, but always under conditions that made the interpretations of results quite difficult.

Heyrovský and co-workers have used the dropping mercury electrode to investigate a variety of chemical problems. Semerano gives a discussion of the work of these investigators using the polarograph, an instrument for the automatic recording on photographic paper of the current–voltage curves obtained with the dropping mercury cathode.[3] Frumkin and Schofield[4] have used the dropping mercury electrode to verify the Lippmann equation. Frumkin measured the current caused by a stream of mercury drops falling through the various solutions used, while Schofield actually measured the amount of mercurous salt which was removed from a solution by an expanding mercury surface.

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(1) From a dissertation submitted by K. E. Glidden to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the Doctor of Philosophy Degree, June, 1932.

(2) Brown Company Fellow in Chemistry.

(3) Semerano, "Il Polarografo, sua Teoria e Applicazioni" (The Polarograph, Its Theory and Applications), Libreria Editrice A. Draghi, Padova, Italy, 1932.

(4) Frumkin, *Z. physik. Chem.*, **103**, 55 (1922); Schofield, *Phil. Mag.*, I, 641 (1926).