An X-Ray Investigation of the Hydrolysis Products of

Mercury(II) In Solution

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X-Ray scattering measurements have been made on concentrated hydrolyzed and non-hydrolyzed mercury(II) perchlorate solutions, prepared by dissolving HgO in $HClO_4$. In an acid solution, the Hg^{2+} ion coordinates about six water molecules at approximately equal distances (2.4 Å). Hydrolysis leads to a shortening of some of these $Hg-O$ bonds and to the formation of polynuclear complexes in which the $Hg-Hg$ distances are 3.64 Å. The average number of mercury atoms bonded to each mercury atom in the solution has been determined as a function of the degree of hydrolysis.

The ionic equilibria in hydrolyzed solutions of mercury(II) salts have been investigated by several workers, and the formation of polynuclear complexes has been suggested.[1] In an attempt to get direct information on the structures of these complexes, X-ray scattering measurements have now been made on hydrolyzed and non-hydrolyzed mercury(II) perchlorate solutions, prepared by dissolving HgO in perchloric acid. Series of solutions have been investigated, in which the total metal concentration and, as far as possible, the perchlorate concentration were kept constant, but the degree of hydrolysis, *i.e.* the amount of dissolved HgO, was varied.

EXPERIMENTAL

Preparation of solutions. The solutions were prepared by heating mercury(II) oxide (Merck *p.a.*) with perchloric acid (Merck *p.a.*) on a water bath, diluting to the required concentration, cooling to room temperature, and adding, to some of the solutions, sodium perchlorate to keep the ClO_4^- concentration constant. The composition of a solution was checked by analyzing for Hg^{2+} and ClO_4^-. Mercury(II) was reduced by H_3PO_3 and precipitated and weighed as Hg_2Cl_2. The amount of perchlorate was determined by passing a portion of a solution through a cation exchanger and titrating the eluent with NaOH. The density was determined with a pycnometer. The compositions of the solutions are given in Table 1.

Three series of solutions with different total concentrations of Hg(II), 2 M, 3.5 M, and 4.6 M, were used. The largest solubility, about 0.25 mol of HgO per mol of Hg(II),

Table 1. Composition of solutions in atoms per stoichiometric unit ($= V$ Å^3).

Solution No.	A1	A2	A3	A4	B1	B2
Conc. of Hg^{2+}	3.50 M	3.50 M	3.50 M	3.50 M	4.54 M	4.64 M
V Å^3	474.37	474.37	474.37	474.37	365.87	357.82
Hg	1.00	1.00	1.00	1.00	1.00	1.00
Cl	2.18	2.18	2.19	1.77	1.65	1.59
O	19.7	19.6	19.4	19.0	15.1	14.8
H	22.0	21.6	21.0	25.2	16.5	16.4
Na	–	0.34	0.55	0.30	–	–

was obtained for the intermediate concentration. For the largest Hg(II) concentration, only hydrolyzed solutions could be prepared — in acid solutions mercury(II) perchlorate crystallized out. For the 2 M solutions, difficulties were encountered because of precipitation of insoluble compounds on the surface of the more hydrolyzed solutions during the X-ray measurements. The results obtained for those solutions that could be measured did not, however, differ from the more concentrated solutions, and will not be discussed further.

The solubility of HgO was limited by the formation of basic salts. Three different phases were found. In order of increasing basicity, they are: triclinic $Hg_5O_2(OH)_2(ClO_4)_4(H_2O)_x$, orthorhombic $Hg_7O_4(OH)_2(ClO_4)_4$, and monoclinic $Hg_2OOHClO_4$. Their structures are closely related. They are all built up from infinite complexes and do not contain any discrete hydroxo complexes. The structure determinations will be published separately.[2,3]

X-Ray scattering measurements. The X-ray scattering was measured from the free surface of the solutions, using MoK radiation. The Bragg-Brentano focusing geometry was used. The diffractometer was essentially the same as described in previous papers,[4] with the X-ray tube and the scintillation counter moving in opposite directions around the sample which was placed with the solution surface on the rotation axis of the diffractometer. A cylindrical radiation shield, provided with a beryllium window, enclosed the sample and hindered evaporation from the surface of the solution. Philips X-ray units PW1010 or PW1130 were used. Monochromatization of the scattered radiation was accomplished by means of a focusing single crystal LiF monochromator, placed on the counter side of the diffractometer. A further monochromatization was achieved by a pulse height discriminator. All measurements were made at 25°C.

The diffractometer is automatic, and measures and prints the time used for counting a preset number of counts (usually 40 000, corresponding to a statistical error of 0.5 %) at discrete values of θ ($2\theta =$ the scattering angle). The intervals in θ were 0.25°, except for the smaller angles ($\theta < 4°$), where an interval of 0.1° was used. The range covered was 1° < θ < 70°. Opening slits of 1/12°, 1/4°, and 1° were used. Scaling factors for converting intensity values to the same slit width were obtained from measurements in overlapping regions. A check on the reproducibility of the intensity values was obtained by remeasuring each slit interval with larger steps in θ. These measurements were always the same within the statistical errors, and no corrections were required.

TREATMENT OF THE DATA

After converting the intensity data to a common slit width, it was corrected for polarization in the sample and in the monochromator. The amount of incoherent radiation slipping through the monochromator was estimated from the spectrum of the X-ray tube and the resolving power of the monochromator. For the outermost angles, it was experimentally determined by comparing the scattered intensity obtained with a Zr filter between the X-ray tube and the

sample with that obtained with the same filter between the sample and the monochromator. For $\theta = 65°$, the amount of incoherent radiation was determined to be about 5 % of the total scattered radiation.

The outermost range of the scattering curves ($\theta > 50°$) was used for the scaling (Fig. 1). The independent coherent scattering, $\sum n_i f_i{}^2$ was calculated from the scattering factors (f_i), given by Cromer and Waber [5] for the neutral atoms. The scattering factors were corrected for the real and the imaginary parts of the anomalous dispersion according to Cromer.[6] The total amount of incoherent radiation was calculated from the values given in the *International Tables* [7] for Cl, O, and Na. For H, Compton and Allison's [8] values were used, and for Hg, estimates were made with the formula given by Bewilogua.[9]

Reduced intensity functions $i(s) = I - \sum n_i f_i{}^2$ were obtained by taking the difference between the measured intensities after scaling, and the sum of the independent coherent scattering and the incoherent scattering. The radial distribution curves ($D(r)$) were calculated from the reduced intensity functions according to the expression

$$D(r) = 4\pi r^2 \varrho_0 + 2r\pi^{-1} \int_0^{s_{max}} s\, i(s) [f_{Hg}(0)/f_{Hg}(s)]^2 \exp(-ks^2) \sin(rs)\, ds$$

Here, $s = 4\pi \sin\theta/\lambda$, and $f_{Hg}(s)$ is the scattering factor of Hg for a value s. The average scattering density, ϱ_0, is given by the square of the number of electrons per unit volume, which for all solutions was chosen to be the volume containing one Hg atom. The sharpening of the distribution curves obtained by the factor $(f_{Hg}(0)/f_{Hg}(s))^2$ was reduced by the exponential factor $\exp(-ks^2)$. Several different values for k were tried, but the curves given here have all been calculated with $k = 0.012$, which seemed to be the best choice for minimizing false details in the curves without causing appreciable broadening of the peaks.

Pair interaction functions were calculated from

$$i(s) = \sum_n \sum_{\substack{m \\ n \neq m}} f_n f_m \sin r_{nm} s / r_{nm} s \, \exp(-bs^2)$$

Here, r_{nm} is the distance between two atoms n and m, f_n and f_m are the scattering factors, and b is a temperature factor.

Least squares refinements were made by means of the LETAGROP [10] program. A minimum was sought for the function $\sum(|s \cdot i_{obs}| - |s \cdot i_{calc}|)^2$.

The computer programs were written in such a way that the original intensity values and corresponding s values were used throughout the calculations.[11] No averaging in order to eliminate the statistical errors was made.

The following procedure for treating the data was used for all the solutions. After correction for polarization, scaling, and subtraction of incoherent radiation, the reduced intensities were calculated. Values with deviations from surrounding values which were clearly outside the limits, set by the statistical accuracy, were then excluded. Usually about 10 to 20 of the approximately 300 measured points were eliminated in this way. A new scaling was then made, and the radial distribution function was calculated. This usually showed small spurious peaks below 1 Å, which could not correspond to interatomic distances. They probably result from systematic errors corresponding to low-frequency additions to the reduced intensity functions, mainly due to small errors in the
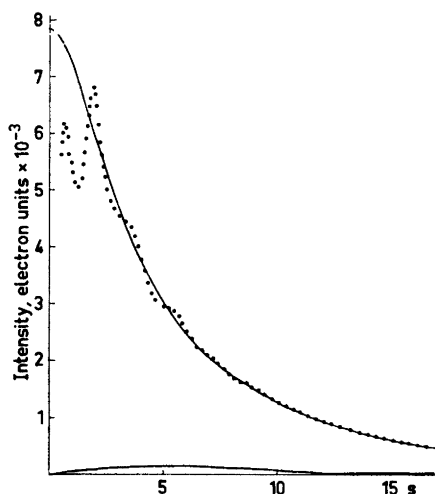
Fig. 1. Survey of the measurements for the solution A4. Observed intensity values, after scaling and correction for incoherent radiation, are indicated by open circles. The upper full-drawn line indicates the independent coherent scattering referred to a stoichiometric unit of solution. The lower line gives the estimated amount of incoherent radiation reaching the counter.
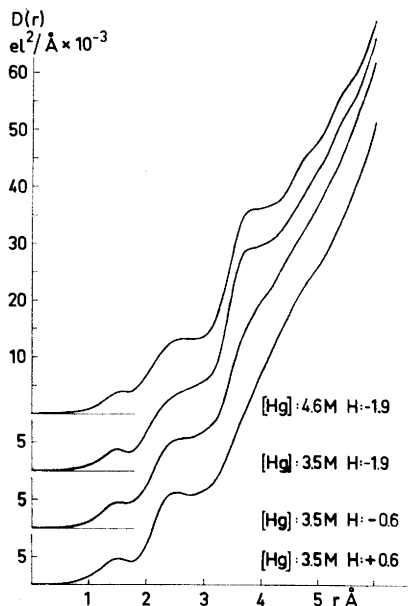
Fig. 2. Radial distribution functions $D(r)$.

scattering factors or in the corrections made for incoherent radiation. The intensity values were corrected for these contributions by a Fourier inversion of the part of the radial distribution curve between 0 and ~ 1 Å. The expected contributions in this region from $O-H$ distances at 1.0 Å and $Cl-O$ distances at 1.45 Å were taken into account. The $i(s)$ values given in Table 2 have been corrected in this way, but no such correction has been applied to the I values in that table. A survey of the measurements for one of the solutions is given in Fig. 1.

ANALYSIS OF THE RADIAL DISTRIBUTION CURVES

Distribution curves, $D(r)$, are shown in Fig. 2, and $D(r) - 4\pi r^2 \varrho_0$ functions in Fig. 3.

For all solutions, a peak occurs at 1.5 Å, which corresponds to the $Cl-O$ distance of the perchlorate group. The acid solution shows only two more marked peaks, one at about 2.4 Å, which is the expected $Hg-O$ distance for

Table 2. Observed intensities after scaling (I) and reduced intensities (i) as a function of $s = 4\pi \sin\theta/\lambda$ for solutions A1, A4 and B2.

	A1		A4		B2																	
s	I	i(s)	I	i(s)	I	i(s)	s	I	i(s)	I	i(s)	I	i(s)	s	I	i(s)	I	i(s)	I	i(s)	I	i(s)
0.426	4252	−4367	5458	−2186	5089	−2359	5.867	2706	86	2594	90	2531	75	12.422	898	−2	894	−7	877	0
0.457	4405	−4193	5483	−2144	5186	−2245	5.940	2682	100	2547	78	2490	67	12.477	890	−2	895	1	−	−
0.488	4447	−4129	5562	−2047	5254	−2159	6.013	2643	94	2485	49	2429	39	12.531	887	2	883	−5	868	5
0.518	4636	−3916	5545	−2045	5280	−2114	6.085	2586	76	2443	40	2399	40	12.585	878	−1	880	1	854	−2
0.549	4819	−3709	5756	−1813	5457	−1919	6.158	2536	61	2391	19	2338	10	12.640	867	−5	873	1	843	−1
0.580	5130	−3372	5953	−1594	5730	−1624	6.230	2507	67	2353	13	2313	15	12.693	867	2	−	−	845	1
0.611	5471	−3002	6081	−1444	5796	−1557	6.302	2461	54	2293	− 17	2251	− 17	12.747	859	1	860	2	844	8
0.642	5685	−2760	−	−	6124	−1195	6.374	2412	38	2265	− 15	2220	− 16	12.800	850	−2	855	2	827	−2
0.673	6241	−2175	6088	−1389	6222	−1064	6.446	2365	23	2214	− 37	2194	− 16	12.855	849	4	853	8	830	7
0.703	6416	−1967	6015	−1437	6398	− 873	6.518	2342	31	2197	− 26	2162	− 20	12.906	839	0	835	−3	823	6
0.734	6768	−1585	5868	−1558	6551	− 685	6.589	2288	8	2164	− 31	2124	−32	12.959	833	0	−	−	812	2
0.765	7024	−1296	5872	−1527	7509	100	6.661	2248	− 2	2154	− 14	2076	− 53	13.011	832	3	831	6	−	−
0.796	7294	− 993	5859	−1512	6391	− 792	6.732	2211	− 9	2128	− 14	2071	− 32	13.063	817	−4	831	13	802	3
0.827	7313	− 959	5552	−1792	8386	− 771	6.804	2176	− 15	2091	− 25	2037	− 40	13.115	810	−4	822	10	790	−3
0.858	7175	− 799	5603	−1712	6141	−997	6.875	2160	− 3	2077	− 14	2053	1	13.167	807	−1	813	8	791	4
0.888	7359	− 823	5523	−1751	6131	− 968	6.946	2110	− 25	2058	− 7	2031	4	13.218	806	4	801	1	773	−2
0.919	7293	− 853	5396	−1858	5919	−1151	7.017	2095	− 13	2043	3	2005	2	13.269	794	−2	800	7	780	4
0.950	7429	− 679	5296	−1927	5779	−1260	7.087	2071	− 10	2042	26	1976	− 3	13.320	788	−2	788	0	−	−
0.981	7253	− 817	−	−	5473	−1536	7.158	2027	− 29	2017	24	1966	11	13.371	785	0	781	−1	761	−3
1.012	7222	− 709	5227	−1931	5514	−1463	7.228	2002	− 28	1978	7	1941	8	13.421	778	−1	774	−1	755	−4
1.042	7262	− 729	5154	−1971	5382	−1564	7.299	1981	− 24	1965	17	1924	13	13.471	773	−1	772	2	−	−
1.073	7239	− 712	5185	−1906	5340	−1573	7.369	1959	− 21	1930	4	1895	6	13.521	770	2	736	−8	750	2
1.104	7235	− 675	5055	−2002	5163	−1716	7.439	1928	− 28	1911	7	1884	18	13.571	764	1	759	0	742	−1
1.135	7089	− 779	−	−	5255	−1591	7.509	1898	− 34	1890	8	−	−	13.620	758	.1	747	−7	745	9
1.166	7299	− 526	5057	−1930	5104	−1708	7.579	1874	− 35	1865	4	1803	− 22	13.669	756	4	742	−5	740	8
1.196	7099	− 685	5054	−1897	5011	−1766	7.648	1860	− 26	1837	− 3	1810	6	13.718	750	3	743	1	740	13
1.227	7211	− 529	5049	−1866	5063	−1679	7.718	1839	− 24	1790	− 30	1779	− 5	13.766	744	2	729	−8	734	1
1.258	−	−	4979	−1899	5137	−1569	7.787	1819	− 21	1786	− 14	1741	− 23	13.815	744	8	736	4	725	1
1.289	7015	− 659	4990	−1851	5087	−1582	7.856	1793	− 26	1773	− 7	−	−	13.863	732	1	718	−9	715	3
1.320	−	−	5105	−1698	5013	−1621	7.925	1779	− 18	1722	− 39	1709	− 15	13.911	733	7	718	−4	709	1
1.350	6984	− 578	5094	−1671	5119	−1478	7.994	1759	− 17	1709	− 32	1693	− 22	13.958	723	7	724	7	703	5
1.361	−	−	5135	−1592	5229	−1330	8.063	1745	− 13	1681	− 41	1666	− 20	14.005	720	3	719	7	700	1
1.412	−	−	5126	−1562	5158	−1363	8.132	1732	− 3	1662	− 42	1640	− 28	14.052	715	3	712	5	702	9
1.443	6931	− 516	5235	−1414	5269	−1215	8.200	1704	− 11	1652	− 34	−	−	14.099	712	5	717	9	697	7
1.473	−	−	5382	−1228	5424	−1022	8.268	1697	2	1640	− 28	1622	− 9	14.145	708	6	699	0	686	2
1.504	6970	− 361	5446	−1125	5546	− 862	8.336	1668	− 7	1614	− 37	1597	− 17	14.191	−	−	702	9	688	8
1.535	−	−	5588	− 942	5518	− 850	8.404	1668	2	1610	− 23	1597	0	14.237	704	11	695	6	677	1
1.566	−	−	5695	− 795	5699	− 631	8.472	1646	9	1591	− 25	1593	13	14.283	692	3	691	8	676	4
1.596	6968	− 244	5836	− 614	5672	− 619	8.540	1630	11	1597	− 3	1571	8	14.328	692	7	673	−1	668	1
1.627	−	−	5981	− 429	5824	− 428	8.607	1614	14	1601	19	1536	− 11	14.373	684	4	676	1	665	2
1.658	7028	− 64	6058	− 311	5907	− 306	8.675	1600	17	1569	2	1534	6	14.418	679	3	675	4	661	1
1.689	−	−	6175	− 153	5979	− 194	8.742	1583	19	1556	6	1527	13	14.463	678	6	671	5	658	3
1.719	−	−	6249	− 39	6221	88	8.809	1564	16	1532	− 4	1508	10	14.500	671	6	671	6	652	0
1.750	7088	117	6408	161	6295	201	8.876	1545	15	1531	12	1489	2	14.551	669	5	660	2	652	4
1.781	−	−	6551	344	6320	266	8.942	1528	13	1512	7	1468	0	14.595	664	4	654	0	643	−1
1.811	6989	139	6571	405	6294	279	9.009	1507	25	1500	10	1457	5	14.638	658	2	655	4	644	4
1.842	−	−	6758	633	6396	421	9.141	1480	15	1492	31	−	−	14.681	655	4	652	6	640	4
1.903	6841	112	6696	653	−	−	9.207	1464	12	1466	20	1420	11	14.724	651	3	644	1	634	1
1.965	6639	30	6632	670	6366	549	9.273	1451	14	1449	17	1411	16	14.767	−	−	646	7	630	1
2.041	6336	− 153	6427	566	6144	426	9.338	1437	15	1440	22	1398	17	14.809	643	3	639	4	623	−2
2.118	6040	− 330	6092	332	5842	222	9.404	1423	16	−	−	1374	7	14.851	641	4	634	3	617	−5
2.195	5809	− 443	5779	118	5586	62	9.469	1416	23	−	−	1373	19	14.893	637	4	628	0	619	1
2.271	5643	− 492	5563	2	5553	− 74	9.534	1360	1	1396	18	1368	27	14.934	633	4	622	−3	613	−2
2.348	5556	− 464	5343	− 120	5137	− 194	9.599	1367	3	1385	20	1336	8	14.975	632	6	615	−6	−	−
2.424	5441	− 464	5173	− 193	4887	− 355	9.664	1359	7	1381	28	1325	11	15.016	625	2	610	−7	608	1
2.501	5356	−425	4956	− 314	4774	− 370	9.726	1347	9	1351	11	1322	20	15.057	622	3	617	3	601	−3
2.577	5364	− 316	4864	− 312	4675	− 378	9.795	1359	12	1343	11	1292	5	15.097	618	5	605	−6	601	0
2.653	5333	− 237	4749	− 334	4634	− 328	9.857	1315	3	−	−	1283	6	15.137	614	2	600	−7	596	−2
2.729	5343	− 119	4705	− 285	−	−	9.921	1306	7	1296	−	1263	−2	15.177	607	−2	602	−2	591	−4
2.806	5329	− 28	4621	− 280	4472	− 313	9.984	1269	2	1283	−8	−	−	15.216	602	−3	602	1	589	−3
2.882	5334	82	4623	− 190	4469	− 220	10.048	1253	−12	1272	−7	1228	−14	15.255	601	−2	594	−4	582	−6
2.958	5276	125	4529	− 197	4482	− 131	10.111	1256	−5	1256	−11	1220	−10	15.294	598	−1	594	0	578	−3
3.034	5284	233	4495	− 145	4391	− 140	10.175	1240	−10	1244	−7	1217	−1	15.333	596	0	590	−	581	−1
3.110	5198	244	4503	− 54	4356	− 94	10.238	1230	−8	1241	−3	1210	4	15.371	590	−3	591	3	585	5
3.186	5087	229	4433	− 42	4315	− 55	10.300	1226	−1	1233	−3	1155	−1	15.409	589	−1	580	−5	575	−1
3.262	5020	256	4450	55	4300	8	10.363	1208	−3	1223	2	1182	−2	15.447	588	1	585	2	578	4
3.337	4921	247	4389	73	4273	58	10.425	1201	−3	1208	−2	1171	−2	15.484	584	1	580	1	575	4
3.413	4807	222	4323	84	4256	115	10.488	1195	2	1218	19	1174	11	15.521	581	0	574	−3	573	4
3.489	4634	136	4315	151	4212	114	10.550	1183	3	1200	11	1154	2	15.558	−	−	574	0	567	1
3.564	4472	59	4303	212	4161	164	10.611	1171	0	−	−	1141	−	15.595	575	−1	579	8	564	1
3.640	4383	52	4216	197	4110	184	10.673	1180	−1	−	−	1133	2	15.631	573	1	574	5	562	2
3.715	4224	− 26	4145	197	4075	216	10.735	1155	5	1161	5	1126	5	15.667	−	−	559	−7	552	−3
3.791	4112	− 60	4067	186	4016	216	10.796	1141	2	1148	2	1109	2	15.702	572	4	568	4	553	−2
3.866	4003	− 92	3963	150	3904	177	10.857	1138	7	−	−	1119	18	15.738	−	−	567	7	545	−8
3.941	3902	− 118	3856	107	3802	138	10.917	1122	3	1140	13	1107	15	15.773	565	2	558	0	556	6
4.017	3807	− 140	3730	45	3661	59	10.978	1115	6	1120	3	1091	9	15.807	562	3	560	4	539	−9
4.092	3742	− 135	3642	19	3561	19.	11.038	1095	−5	−	−	1072	−1	15.876	558	−2	−	−	538	−4
4.167	3644	− 164	3525	− 37	3457	− 26	11.099	1091	·2	−	−	1055	1	15.910	547	−5	−	−	539	−2
4.242	3576	− 165	3400	− 103	3332	− 94	11.159	1083	3	1094	7	1055	1	15.943	551	1	552	6	534	−4
4.316	3520	− 155	3326	− 119	3252	− 118	11.218	1078	6	1088	11	1056	12	15.976	550	2	543	−1	542	6
4.391	3455	− 156	3240	− 149	3169	− 146	11.278	1065	4	1063	−5	1038	3	16.009	544	−1	539	−2	533	4
4.466	3387	− 161	3137	− 197	3089	− 173	11.337	1053	−1	1058	−1	1026	0	16.042	541	−3	541	0	531	0
4.541	3238	− 159	3115	− 166	3026	− 183	11.339	1043	3	−	−	1011	−6	16.074	540	−1	539	2	531	1
4.615	3295	− 133	3024	− 204	2971	− 188	11.455	1045	11	1035	−5	1004	−4	16.106	540	−1	531	−4	523	−5
4.690	3244	− 127	2980	− 196	2956	− 152	11.514	1033	7	1022	−9	997	−3	16.138	535	−2	537	4	524	−1
4.764	3226	− 88	2976	− 150	2921	− 140	11.572	1017	0	1022	−1	988	−4	16.169	−	−	524	−7	519	−4
4.838	3183	− 75	2966	− 112	2900	− 113	11.630	1010	1	1008	−6	975	−8	16.200	527	−5	525	−1	522	1
4.912	3145	− 60	2952	− 77	2881	− 85	11.688	1005	3	995	−10	966	−9	16.231	530	1	525	−2	518	−2
4.986	3125	− 28	2913	− 70	2873	− 48	11.746	999	7	995	−2	955	−12	16.262	524	−4	519	−6	515	−2
5.060	3110	8	2925	− 12	2853	− 24	11.804	983	0	986	−2	−	−	16.292	526	0	518	−5	508	−4
5.134	3083	29	2902	9	2848	13	11.861	974	−2	−	−	951	0	16.322	518	−7	521	−1	514	0
5.208	3039	35	2897	48	2824	32	11.918	970	3	950	−13	941	−2	16.351	525	3	517	−2	508	−4
5.282	3025	67	2862	54	2815	64	11.975	958	−2	953	−10	937	2	16.380	516	−5	513	−5	514	4
5.355	2969	57	2904	138	2817	106	12.032	951	−1	951	−4	932	4	16.409	516	−3	510	−5	−	−
5.429	2947	80	2848	122	2796	124	12.088	938	−5	935	−12	917	−3	16.438	514	−3	512	0	510	3
5.502	2949	126	2815	128	2765	131	12.144	940	4	937	−1	900	−12	16.466	509	−7	514	2	−	−
5.575	2879	98	2748	100	2729	132	12.200	931	2	921	−10	903	−2	16.494	511	0	513	3	504	1
5.649	2860	121	2742	132	2716	156	12.256	927	3	932	3	890	−7	16.522	509	−3	507	−1	−	−
5.722	2813	114	2698	115	2624	99	12.312	909	−5	910	−6	894	3	16.549	504	−6	505	3	500	0
5.795	2746	87	2618	80	2582	92	12.367	905	−2	912	4	892	9							

water molecules in the first coordination sphere of the Hg^{2+} ion, and one, very broad peak, at about 4.2 Å, which probably is an indication of a second coordination sphere. When the solution is hydrolyzed, there are two main changes in the distribution curves, which is best seen from Fig. 3. A new peak appears
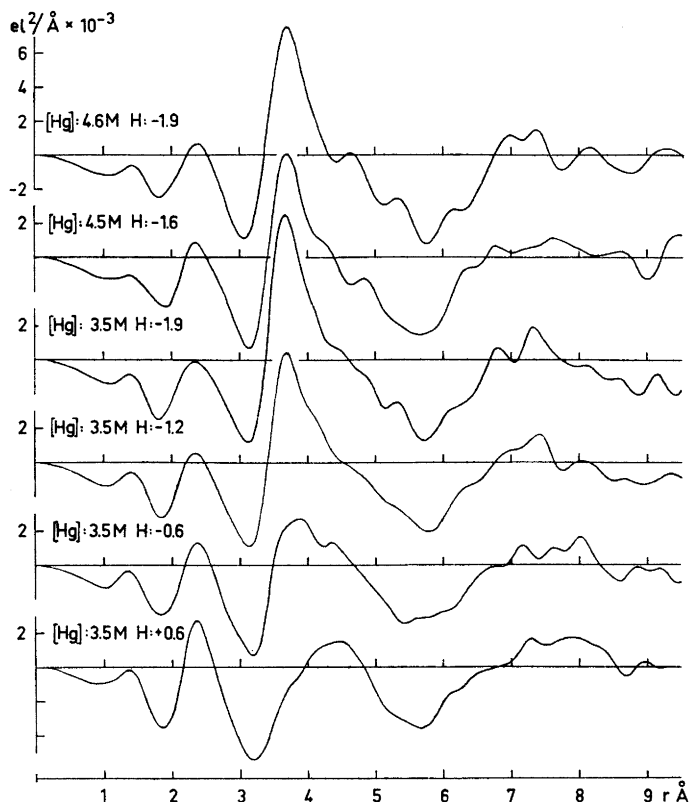
Fig. 3. Functions $D(r) - 4\pi r^2 \varrho_0$

at 3.6 Å, and a marked change occurs in the peak corresponding to the first coordination sphere of the Hg^{2+} ion.

The 3.6 Å peak obviously represents Hg – Hg interactions in polynuclear hydrolysis complexes. It is close to the shortest of the Hg – Hg distances found in the basic mercury(II) perchlorates.[2,3] The 2.4 Å peak is not well resolved in the $D(r)$ curves (Fig. 2). With increasing hydrolysis, it broadens and becomes less and less separated from the light atom interactions at about 3 Å.

The differences are more clearly brought out by using the distribution curve of the acid solution as an approximate reference line, and subtracting it from those of the hydrolyzed solutions. The resulting curves are given in Fig. 4. The effect of the second coordination sphere, which obscures the Hg – Hg peak in Fig. 3, is then largely eliminated, as it does not differ much for the different solutions. The resulting Hg – Hg peak seems to be symmetrical, and thus probably represents a single Hg – Hg distance in the complexes. The size of the peak corresponds to an average of about one Hg atom bonded to each Hg in the most hydrolyzed of the solutions. There are no clear indications of longer Hg – Hg distances.

The changes within the first coordination sphere of the Hg^{2+} ion are clearly seen in the difference curves in the 1.5 to 2.5 Å region, to which only $Hg-O$ interactions should contribute. Contributions from ClO_4 groups at 1.5 Å ($Cl-O$) and 2.4 Å ($O-O$) are the same as in the acid solution, and cancel out. For those solutions in which the ClO_4 concentrations are slightly lower (Table 1), the differences have been compensated by adding calculated contributions from $Cl-O$ and $O-O$ interactions. Light atom interactions, primarily $O-O$ contact distances, are small in this region, and should not differ significantly for the different solutions. Thus the positive peaks at 1.95 Å and the negative peaks at 2.35 Å in Fig. 4 can be uniquely ascribed to changes in $Hg-O$ in-
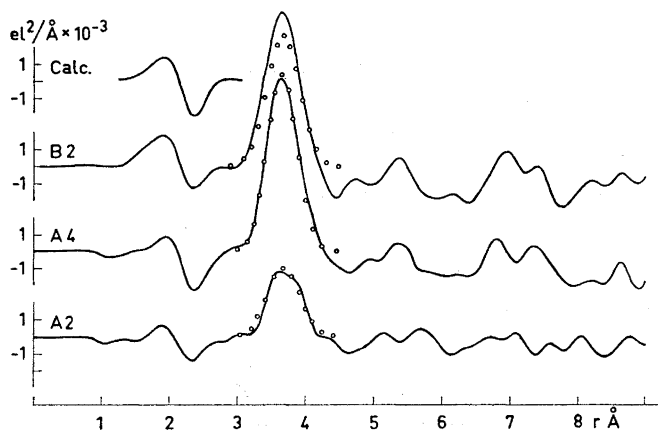
Fig. 4. Difference functions obtained by subtracting the curve for the acid solution in Fig. 3 from the corresponding curves for the hydrolyzed solutions. The calculated curve at the top of the drawing was obtained by subtracting the peak shape for six $Hg-O$ interactions at 2.34 Å from that for two $Hg-O$ at 2.0 Å, and four $Hg-O$ at 2.5 Å and multiplying the result with 0.7, to correct for the presence of unhydrolyzed Hg^{2+}. The dots indicate peak shapes for $Hg-Hg$ interactions, calculated with the use of the parameters from the least squares refinement.

teractions. The occurrence of these peaks shows that in the hydrolyzed solutions, $Hg-O$ distances must occur, which are shorter than about 2.1 Å, and which are not present in the acid solution. The negative peak at 2.35 Å indicates that in comparison with the acid solution, fewer and slightly longer distances occur in this region.

An analysis of the $Hg-O$ peak in the distribution curve for the acid solution, made by comparison with calculated $Hg-O$ peak shapes, assuming different temperature factors for the $Hg-O$ interaction, shows no indication of the presence of diaquo ions. This is illustrated in Fig. 5, which compares the experimental $D(r)$ curve for the acid solution with calculated $Hg-O$ peaks in the 1.5 to 2.5 Å region. The experimental curve has the same shape as that calculated for six oxygen atoms at equal distances (2.34 Å). It differs clearly from the shape calculated for two oxygens at 2.0 Å and 4 oxygens at 2.5 Å, which are the approximate distances expected for a diaquo ion. Similar results

el²/Å × 10⁻³
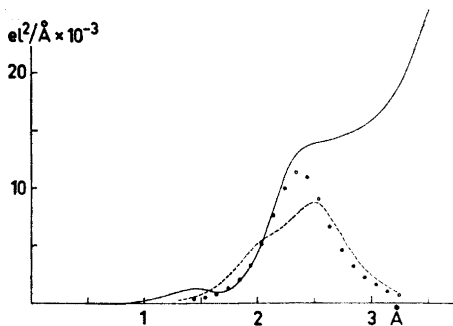
Fig. 5. A comparison of the experimental $D(r)$ curve for the acid solution (after subtraction of contributions from distances in the perchlorate groups) with calculated peak shapes for two different assumptions about the distribution of water molecules in the first coordination sphere of the Hg^{2+} ion. Open circles represent the calculated shape for six water molecules at 2.34 Å ($b = 0.01$), and the dashed line gives the expected shape for two water molecules at 2.0 Å and four molecules at 2.5 Å.

have previously been reported by van Eck,[12] who measured the X-ray scattering from 2 M solutions of $Hg(BF_4)_2$. He concluded that in these solutions, the Hg^{2+} ion was octahedrally coordinated by six water molecules at 2.33 Å.

The change in the coordination around the mercury ion caused by the hydrolysis and illustrated by the difference curves in Fig. 4 can now be explained as the result of a shortening of some of the Hg – O bonds. The observed difference curves can be closely reproduced by assuming that in the hydrolysis products, about two Hg – O bonds are shortened to 2.0 – 2.1 Å, and the remaining four bonds lengthened to about 2.5 Å (Fig. 4), compared with the approximately equal distances of 2.3_4 Å around the unhydrolyzed Hg^{2+} ion. Although the estimate of the number of bonds affected by these changes is at best approximate, the estimates of the resulting distances are more exact, since even small changes in the assumed distances cause drastic changes in the calculated difference curves, which are clearly inconsistent with those observed.

ANALYSIS OF THE REDUCED INTENSITY FUNCTIONS

For a closer analysis of the Hg – Hg interactions, the intensity curves are more suitable than the distribution curves, in which the presence of the broad background peak from the second coordination sphere interferes with the Hg – Hg peak. The broad peak corresponds to highly damped contributions to the intensity function, while the sharp Hg – Hg peak results from contributions over a much larger range of s values. This makes a separation of the two contributions possible by a direct analysis of the $i(s)$ values, for example by means of a least squares procedure. Such an analysis also has the advantages that the direct connection to the measured data allows an estimate of the statistical errors in the parameters, and each intensity value can be given a weight corresponding to its statistical accuracy.

Theoretical intensity values were calculated as a sum of pair interaction functions. A Hg – O distance at 2.4 Å, a Hg – Hg distance at 3.6 Å, and another Hg – O distance at 4.2 Å, approximating the many different Hg – O interactions in that region, were included. To this was added contributions from the perchlorate ions, assuming the ClO_4 group to be a regular tetrahedron with a Cl – O distance of 1.45 Å. For each pair interaction, three parameters
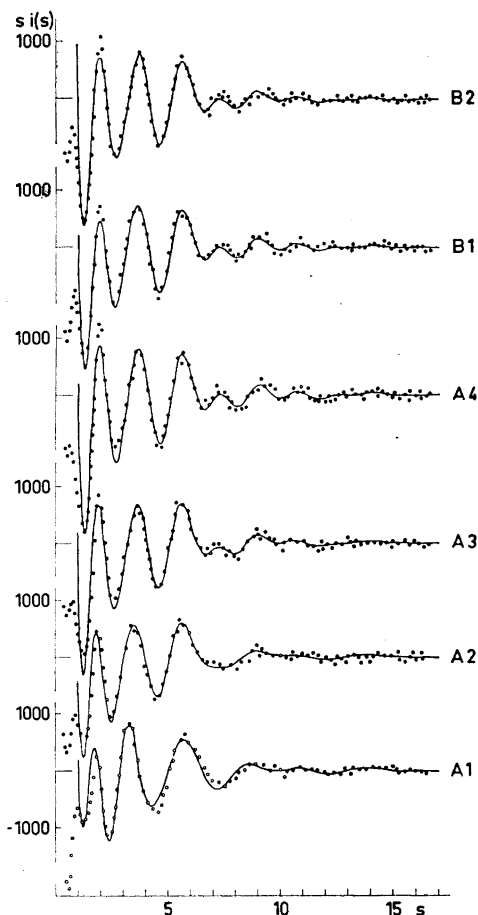
Fig. 6. Reduced intensity functions, $i(s)$, after multiplication by s, referred to a stoichiometric unit of solution, containing one mercury atom. About one third of the number of observed values, chosen at random, are indicated. The full-drawn curves represent $i(s)$ values calculated with the parameters from the least squares refinement.
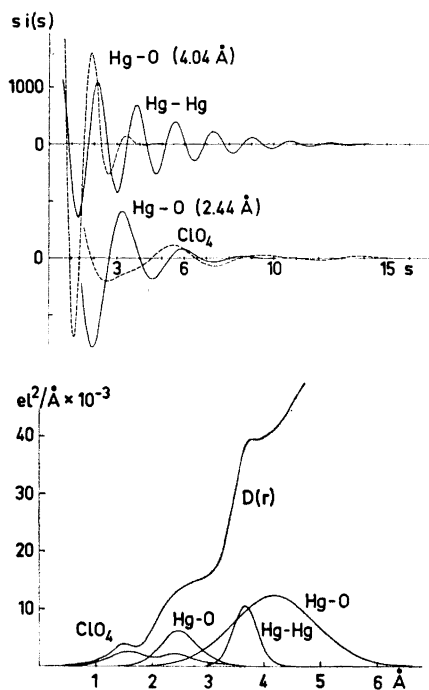
Fig. 7. Calculated $s\ i(s)$ values and peak shapes for the interactions included in the least squares refinement of the scattering data from solution A4. The calculations are based on the parameters in Table 3.

were introduced: the distance, the number of interactions, and a temperature factor. These were refined, as was also a scaling factor, by a least squares procedure, to get the best agreement between observed and calculated intensities.

The refinement was carried out in several steps. Firstly, the intensity values for $2.7 < s < 16$ were used, to refine the short $Hg - O$ and the $Hg - Hg$ interactions with no other $Hg - O$ distances included. The region $1 < s < 16$

was then used to refine simultaneously the Hg – Hg distance and the longer
Hg – O distance (4.2 Å), keeping other parameters constant. This refinement
converged, indicating that the two interactions could be resolved. Finally,
the region $2.5 < s < 14$ was used to refine the Hg – Hg and the short Hg – O

Table 3. Result of the least squares refinement of the $i(s)$ curves. d = distance in Å, n = number of distances per Hg atom, b = temperature factor. Standard deviations are given within brackets.

Soln. No.	Hg – Hg			$(Hg – O)_1$			$(Hg – O)_2$		
	d	n	b	d	n	b	d	n	b
A1	–	–	–	2.42(1)	5.7(3)	0.019(2)	4.10(2)	18.4(6)	0.29(2)
A2	3.69(3)	0.24(4)	0.018(5)	2.41(1)	5.4(4)	0.030(5)	4.17(4)	20.4(10)	0.34(3)
A3	3.66(2)	0.45(5)	0.018(6)	2.43(2)	6.5(5)	0.047(7)	4.09(3)	21.2(9)	0.31(3)
A4	3.63(1)	0.50(4)	0.014(3)	2.44(1)	6.8(2)	0.052(2)	4.04(3)	17.1(6)	0.24(2)
B1	3.65(1)	0.36(3)	0.010(3)	2.43(1)	6.0(5)	0.043(6)	4.06(3)	16.0(5)	0.24(2)
B2	3.65(1)	0.49(4)	0.017(3)	2.41(1)	4.9(4)	0.036(3)	4.08(3)	15.3(7)	0.26(2)

distances without varying the parameters of the longer Hg – O distance, the
contributions of which are very small in this region of the intensity curves.
The refinements were continued until the shifts were well below the calculated
standard deviations.

The parameters of the Hg – Hg interaction, which are the ones of interest,
did not vary significantly between the different refinement steps. The final
parameters and the standard deviations are given in Table 3. The agreement
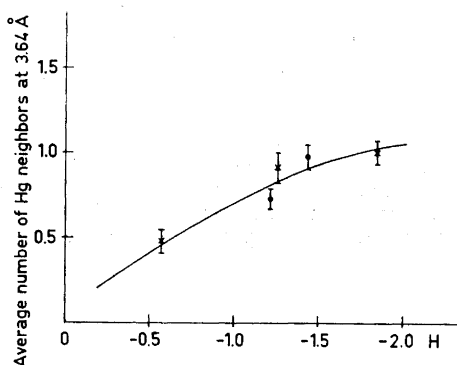
Fig. 8. Number of Hg neighbors at 3.64
Å around each Hg atom as a function of
H, the analytical hydrogen ion excess
(referred to a 3.5 M solution). Observed
values are indicated by crosses (3.5 M
solutions) or dots (4.6 M solutions). The
standard deviation, calculated in the least
squares refinement, is given for each point.

between observed and calculated intensities is shown in Fig. 6. The average
number of Hg neighbours at 3.64 Å from each Hg atom is given in Fig. 8 as
a function of the degree of hydrolysis. For the most hydrolyzed of the solutions
(A4), the contributions of the various interactions to the intensity curves and
their corresponding peak shapes are compared in Fig. 7.

DISCUSSION OF THE RESULTS

The hydrolysis of the mercury(II) solutions has a rather small effect on the scattering curves, because only low-nuclear complexes seem to be formed, and because concentrations of the hydrolysis complexes are small. Even in the most hydrolyzed of the solutions, about one third of the mercury should still be unhydrolyzed, according to the stability constants given by Ahlberg.[13] In the $D(r)$ curves (Fig. 2), no well-resolved peaks are present, which can be used to follow the changes.

However, by working in solutions with, as nearly as possible, the same compositions, the small differences, caused by the hydrolysis, can be analyzed, since contributions to the scattering from distances other than those involving Hg atoms should be fairly constant for the different solutions. The difference curves in Fig. 4. should then give the best representation of the changes. This should be true at least for the 2 to 2.5 Å region, where Hg $-$ O interactions are the main contributors. The splitting up of the Hg $-$ O distances in the hydrolysis complexes, compared with the more equal distances around the unhydrolyzed Hg^{2+} ion, is shown clearly by the distribution functions and especially by the difference curves. In the least squares refinement, this change in coordination is seen mainly as an increased temperature factor for the single Hg $-$ O interaction introduced (Table 3).

In the region 3.5 to 4 Å, where the Hg $-$ Hg distance in the hydrolysis complexes appears, a great many other distances also contribute, and it seems likely that those related to a second coordination sphere around the Hg atom could to some extent change with hydrolysis. In a polynuclear complex, well-defined longer Hg $-$ O distances must occur within the complex, which are not present around an unhydrolyzed Hg^{2+} ion, and these differences may affect the Hg $-$ Hg peaks in the difference curves. A least squares refinement of the parameters of the Hg $-$ Hg interaction, using the observed intensity values, should be less sensitive towards such changes, because the spread of distances within the second coordination sphere should lead to highly damped contributions to the intensity function, and also because such changes at least to some extent can be taken up by the parameters introduced. On the other hand, these second-coordination sphere interactions have been approximated by a single Hg $-$ O interaction with a large temperature factor, which may not correspond to the actual distribution of distances.

Other distances than those now used for the refinement can be introduced in the least squares procedure by using reasonable assumptions for their distributions. It seems preferable, however, to exclude such contributions when refining the intensity values, and to minimize the erros made by not using the first part of the intensity curves, where these interactions have their main contributions. The good agreement between observed and calculated intensities down to values of $s = 1$, as shown in Fig. 5, supports the assumption that no great errors are made by the exclusion of other distances in the solutions. As a further check on the number of Hg $-$ Hg interactions obtained in the refinements (Table 3), corresponding peak shapes were calculated and were compared with the difference curves (Fig. 4), Although the least squares refinements and the difference curves should be differently affected by systematic errors,

the agreement is good. The error estimates made in the least squares process thus seem to be reliable.

CONCLUSIONS

According to the X-ray measurements, two main changes occur when a solution of mercury(II) perchlorate is hydrolyzed. The coordination of the mercury ion is changed, leading to a shortening of some of the $Hg - O$ distances within the first coordination sphere. Polynuclear complexes are formed, in which the $Hg - Hg$ distances are 3.64 Å. In the most hydrolyzed of the solutions investigated, corresponding to a removal of about 0.5 hydrogen ions per hydrated mercury(II) ion, each mercury atom is bonded to an average number of about one other mercury atom. Taking into account that about one third of the mercury in this solution, as calculated from the stability constants given by Ahlberg,[13] is still unhydrolyzed, the average number of Hg atoms bonded by each Hg atom in the hydrolysis complexes is larger than one. Thus the condensation does not stop at dinuclear complexes. However, since longer $Hg - Hg$ distances are not clearly indicated in the radial distribution curves, the dominating complexes in the solutions must still be of a low nuclearity.

An interpretation of the results in terms of possible structures of the hydrolysis complexes can be made by combining information obtained from the X-ray scattering measurements with that from equilibrium measurements and crystal structure determinations, and will be given in a following paper.

REFERENCES

1. Sillén, L. G. and Martell, A. E. *Stability Constants*, Spec. Publ. No. 17, The Chemical Society, London 1964.
2. Johansson, G. and Jelen, A. *To be published.*
3. Johansson, G. and Hansen, E. *To be published.*
4. Johansson, G. *Acta Chem. Scand.* **20** (1966) 553.
5. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
6. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
7. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
8. Compton, A. H. and Allison, S. K. *X-Rays in Theory and Experiment*, Van Nostrand, New York 1935.
9. Bewilogua, L. *Phys. Z.* **32** (1931) 740.
10. Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1085.
11. Johansson, G. Programs with accession Nos. 6037 and 6038 in *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., 1966.
12. van Panthaleon van Eck, C. L., Wolters, H. B. M. and Jaspers, W. J. M. *Rec. Trav. Chim.* **75** (1956) 802.
13. Ahlberg, I. *Acta Chem. Scand.* **16** (1962) 887.