

THE STRUCTURE OF ANODIC FILMS FORMED ON MERCURY IN HALIDE SOLUTIONS

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Surface films of mercury halides approximately 50-100 Å in thickness have been prepared anodically in solutions of HCl, HBr, HI, KCl, KBr and KI in a concentration range of 2 N to 0.01 N and at current densities of 2.5 mA cm⁻² to 0.025 mA cm⁻². The stripped films have been examined optically and by the electron microscope and the orientations of the crystallites determined in the latter instrument by electron diffraction. The iodide films are mainly of the random Hg₂I₂ salt with some HgO and HgI₂; the chloride and bromide films are arranged invariably with {110} planes parallel to the mercury surface and there is considerable evidence for the interlocking of the crystals at the boundaries. Over most of the preparative conditions the Hg₂Cl₂ and Hg₂Br₂ are skeletal in form apparently penetrated by randomly or linearly disposed irregularly shaped holes.

Hills and Ives,¹ Grahame,² Kolthoff and Lingane,³ Bockris and Parsons,⁴ Heyrovsky,⁵ Haul and Sholtz,⁶ have all shown that there are suggestions of unusual phenomena occurring during the reaction of halide ions at mercury electrodes. Thirsk⁷ showed that in 2 N HCl and with a current density of the order of 2.5 mA cm⁻² a special orientation of electrochemically formed calomel with respect to the mercury surface did in fact exist. In this paper the previous investigation⁷ has been greatly extended and includes reactions in bromide and iodide solutions.

EXPERIMENTAL

The apparatus was similar to that used previously,⁷ the cell consisting of an H-shaped glass vessel with two cylindrical compartments separated by a horizontal tube. The anode compartment, about 3 cm in diameter, contained a mercury pool to which contact was made by means of a sealed-in platinum wire whilst the smaller compartment contained a large platinum electrode.

The mercury was purified by dropping through dilute nitric acid and subsequently re-distilled under a pressure of a few cm of mercury. Solutions were made up from A.R. reagents and distilled water. The hydriodic acid was freshly distilled over red phosphorus. No attempt was made to exclude oxygen from the solutions.

Three different methods were used to strip the anodically formed film. In the first, it was lifted off the mercury surface by means of a fine platinum gauze, washed by floating on to a cleaned water surface and picked up on a microscope slide. The deposit was then dried in a vertical position in a desiccator thus draining away some of the excess mercury adhering to the film. Further drying of the salt for several hours in a vacuum desiccator containing P₂O₅, served also to remove the remainder of the mercury. The dried films were coated with a 1 % collodion solution and stripped off by the Scotch tape method on to copper grids of the type used in the Metropolitan-Vickers E.M.3 electron microscope. Chemical interaction between the copper grid and the mercury halide was prevented by the intervening collodion layer.

This method was reasonably easy to carry out but it was felt desirable to prepare larger areas of the anodic films in a manner which lessened the chance of mechanical distortion. This was particularly important since from previous work⁷ it was to be expected that many of the films would be composed of crystals having a cleavage plane both parallel to and at an angle of 45° to the mercury surface. Two other techniques

were therefore developed. In the first a larger anode compartment of about 100 ml capacity was used in which a perforated porcelain disc having a pore size selected by trial was kept below the surface of about 20 ml mercury forming the electrode, by means of a glass cylinder. When the anodic layer had formed the disc was allowed to rise to the surface of the mercury by carefully lifting the cylinder. With practice, large areas of film could be retained on the surface of the porcelain disc, excess mercury running through the perforations. The film was then washed and mounted as in the first method.

A third method was as follows. After forming the anodic film the solution was removed by means of a pipette and the deposit, still attached to the mercury surface, was washed with conductivity water. The complete cell was then placed in a desiccator in order to dry the film, after which one drop of 1 % collodion solution was run on to the film. After drying slowly for at least 24 h, E.M.3 type copper specimen grids were placed on the deposit and depressed slightly by means of a dissecting needle. The specimen was dried for a further 24 h and then picked up by means of a "ring tool" formed from a platinum loop. These specimens whilst requiring considerable time for preparation were remarkably free from excess mercury and showed little sign of mechanical strain. For optical microscopy, glass cover slips were used in place of the copper grids.

All the films were inspected by electron microscopy and areas of either $10\ \mu$ or $2\ \mu$ in diameter selected for examination by electron diffraction by the insertion of diaphragms into the optical path. By searching the films in this manner a detailed knowledge of the structure of the deposit was built up.

The apparatus used for obtaining constant polarizing currents and for overvoltage measurements was the same as that previously described.⁸ Examination by electron microscopy and electron diffraction was carried out on a Metropolitan-Vickers E.M.3 electron microscope, and optical microscopy by means of a Cooke, Troughton and Simms type 4000 microscope.

RESULTS

Experiments were made in the solutions listed below at three current densities $2.55\ \text{mA cm}^{-2}$, $0.255\ \text{mA cm}^{-2}$ and $0.025\ \text{mA cm}^{-2}$ for polarization times of 6 sec, 60 sec and 10 min with a few exceptions which are noted. The preparations have been numbered for ease of reference and are taken in the order of the highest c.d. first.

HCl: 2 N, 1-3; N, 4-6; 0.1 N, 7-9; 0.01 N, 10-12 (c.d. for 10, $1.25\ \text{mA cm}^{-2}$ for 12 sec).

KCl: N, 13-15; 0.1 N, 16-18; 0.1 N sat. with Hg_2Cl_2 , 16a-18a; 0.01 N, 19-21.

HBr: N, 22-24; 0.1 N, 25-27; 0.01 N, 28-30.

KBr: N, 31, the lower c.d.s failing to give films suitable for collection; 0.1 N, 32-34; 0.01 N, 35-37 (c.d. for 35, $1.0\ \text{mA cm}^{-2}$ for 15 sec).

The iodide films, formed under a much narrower range of conditions, were all prepared at a c.d. of $0.25\ \text{mA cm}^{-2}$: HI; 0.1 N for 2.5 min, 38; 0.01 N for 1 min, 39; KI; 0.01 N for 3.5 min, 40; 0.01 N KI with 0.01 N HNO_3 for 3 min, 41; 0.005 N KI for 5 min, 42.

Polarization curves were recorded for all the conditions of solution concentration and current density. The characteristic features of these overvoltage curves show indirect agreement with earlier work of Rothschild⁹ on the polarizability of the calomel electrode. The iodide films, as is reasonable in view of the loosely organized character of the precipitated salts, show a very irregular rise of overvoltage with time.

The forms of the polarization curves fall roughly into two groups. The majority from bromide and chloride solutions flatten off, as shown in fig. 1(a), at about 2.5 V after a very sharp initial potential rise. Irregularities of the potential which are recorded on further polarization are due to the mechanical breakdown of a film which is rather susceptible to any disturbance of the mercury surface by vibration. Fig. 1(a) is to be associated with the type of film illustrated by fig. 4 and 5 and is relevant particularly to the preparations giving the better developed crystals.

Prep. 11, 12, 15, 18, 21, 36, 37, 38, 39, 40, 41 give a much more gradual rise in overpotential and this is illustrated by fig. 1(b). The short vertical arrows A indicate the points on the voltage-time curve at which the current was normally stopped and the film stripped from the mercury surface. The potential dropped rapidly on the cessation of current to a value 2 or 3 mV above the reversible potential, the final decay taking many hours. This is shown in fig. 1(a) by the path followed by the curve subsequent to the time marked by the arrow B.

Jonsson, Qvarfort and Sillén¹⁰ note the existence of this slightly positive value with freshly precipitated material in their work on the mercury-halogen ion equilibrium and ascribe it to enhanced solubility of the halide due to an assumed very fine grain size. Increased solubility in our investigations could additionally arise from strain in the crystals rather than any unusually small size and large relative surface area. Detailed investigations on this part of the electrochemical behaviour of the system have not been made. The films themselves, apart from a marked solubility noticeable mainly in the more concentrated bromide and iodide solutions, were not affected in structure by standing in the halide solution in as far as this could be detected by electron optical methods.

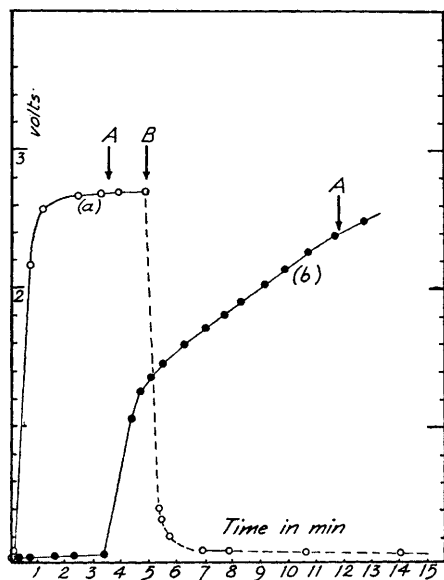


FIG. 1.—Typical anodic polarization curves for mercury in halide solutions. The arrows A show approximately the stage reached when the films were removed. In (a) the change of voltage with time is shown after current interruption at B.

(a) N/10 KBr at c.d. 2.5 mA cm^{-2} , potential against Ag/AgBr electrode.

(b) N/100 HCl at c.d. 0.25 mA cm^{-2} , potential against Ag/AgCl electrode.

In the present experiments the mercury was polarized until the anodic film became visible over all the surface. Calomel films were formed in chloride solutions for all the selected conditions, but due to the ready formation of complex anions we failed to obtain films in N and 0.1 N KBr solutions at the lowest current density and in KI solutions at concentrations greater than 0.01 N. The maximum thickness of a film for each set of conditions was calculated from Faraday's laws and an assumed figure for the density of the deposit. The actual thickness could not be estimated since there was an appreciable and sometimes rapid removal of the deposited mercury compound from the salt/solution interface; a process which, as is usual, became increasingly large for differing halide solutions of the same normality in the order $\text{I} > \text{Br} > \text{Cl}$. This accounted for the impossibility of forming a precipitate at all in the stronger potassium bromide and potassium iodide solutions under low current density conditions. In the majority of cases large areas of the film must have been $< 10^{-6} \text{ cm}$ in thickness and this is confirmed by the electron diffraction patterns.

The value of the equilibrium constant¹⁰ for the reaction $\text{Hg}^{2+} + \text{Hg} = \text{Hg}_2^{2+}$ is 129.2 ± 1.0 and so the mercurous ion would be expected to predominate over the mercuric as the potential-determining ion at the surface. Furthermore, taking the value of the solubility product¹¹ of mercurous chloride as 1.15×10^{-18} , for mercury hydroxide as 1.0×10^{-26} and for mercurous bromide as 5.5×10^{-23} , mercurous chloride should form at the electrode when $[\text{Cl}^-]/[\text{OH}^-] > 10^3$ and mercurous bromide when $[\text{Br}^-]/[\text{OH}^-] > 0.5 \times 10^{-2}$. The effect of pH should be negligible with iodide solutions since the solubility product of mercurous iodide is given by Brodsky¹² as 5.0×10^{-29} . Therefore unless the polarization conditions are productive of an excessive depletion of halide ion at the electrode surface under the conditions of these experiments the mercurous halide rather than mercury oxide would be expected on the anode.

The behaviour of mercury in chloride and bromide solutions was markedly different from that found in iodide solutions. This difference was not expected on purely structural

grounds since the three mercurous halides are apparently very similar. The structure of the compounds may be considered to be based on a tetragonal unit cell, with space group D_{4h}^{17} . Slight differences in recorded cell dimensions occur in the literature; we have used the following data from the A.S.T.M. index; 13 Hg_2Cl_2 , $a_0 = 4.47 \text{ \AA}$, $c_0 = 10.89 \text{ \AA}$; Hg_2Br_2 , $a_0 = 4.65 \text{ \AA}$, $c_0 = 11.10 \text{ \AA}$; Hg_2I_2 , $a_0 = 4.92 \text{ \AA}$, $c_0 = 11.61 \text{ \AA}$.

CHLORIDE AND BROMIDE SOLUTIONS.—Important optical and electron optical details of the film structure are shown in fig. 2-9. An examination of the electron microscope photographs led to the conclusion that over the majority of our selected conditions the halide films grew in the manner shown in fig. 4 and 5. The dark areas are the mercurous halide, the light areas are holes passing right through the film irregularly disposed in fig. 4 but lying along approximately straight lines in fig. 5, both types of growth often being present in the same specimen. Prolonged polarization reduced the areas of the perforations through the film and the method of preparing the specimen for the electron optical examination often led to a considerable disruption of the material so that loosely organized fragments alone were observed. Considerable fine detail occurs; for example, the minute holes, approximately 0.01μ in diameter penetrating the halide in fig. 4, whilst continuous changes in thickness apparently produce the mottled appearance in the film shown in fig. 5. The slight variations in the thickness of the deposit may arise from localized differences in the concentration of the solution due to diffusion.

The general appearance of films similar to those of fig. 5 may be assessed more easily, although the actual holes through the films are no longer resolved, in the optical micrograph, fig. 8. Fig. 8 and 9 were obtained from the same specimen as fig. 5. Fig. 9 shows a rare type of crystal growth found in prep. 33 in which the single crystals are lune-shaped or elliptical. The appearance suggests that they had been formed by a precipitation process analogous to that causing the formation of Liesegang rings. As far as could be ascertained the bands of the crystal were uniform in thickness.

The implication of these observations is that during the formation of the deposit a considerable area at the mercury/solution interface is free from a surface film or one exists of such extreme thinness that either it is too fragile to be separated from the mercury surface although supported by the thicker portions of the surrounding deposit, or that it dissolves during the preparation of the microscope specimen. When it is recalled that the films having this type of deposit sustain an overpotential of the order of 2-3 V it is easy to see that the potential gradient across the deposit is very high and must be particularly great in the region of the mercury/solution interface in the holes in the film.

Deposits containing material of a different character, showing continuous sheets of very thin film as illustrated in fig. 2 were obtained with prep. 3, 7, 9, 12, 18(a), 23 and 31. These films appeared to break down fairly easily and gave areas of loosely organized material consisting of crystals of varying sizes including some quite extensive single crystals. Prep. 18(a) made in the presence of excess calomel consisted solely of this unperforated material. The sheets are slightly uneven with regard to thickness, probably ascribable to local variations in solution concentration during formation.

In general with the lowering of the current density below 0.025 mA cm^{-2} the crystal size became smaller. At very low current densities of the order of $1 \mu\text{A cm}^{-2}$ the deposit was formed as an intimate mixture of mercury and mercurous halide. It is likely that under these conditions the normal process of crystal growth is being interfered with by the chemical disproportionation of the mercurous ion into the mercuric ion and mercury at a rate which is of the same order as the rate of formation of the mercurous salt.

The description given of the orientations found for mercurous chloride in an earlier paper⁷ apply in all particulars to these preparations; only $\{110\}$ faces are found parallel to the substrate. Mercurous chloride cleaves readily along the $\{110\}$ planes and from our results this also seems true of mercurous bromide. This property had in some cases given rise to examples of what Wilman¹⁴ has described as rotational slip; twinning, either singly or repeated was often observed on $\{112\}$ planes perpendicular to the surface.

It has been proposed⁷ that the $\{110\}$ orientation might be assisted by some hexagonal arrangement of the mercury atoms in the liquid mercury surface. This atomic arrangement was suggested in two earlier papers on the structure of the surface of mercury by Berdennikov, Bresler, Zel'manov and Shtrauf.¹⁵ According to these workers, liquid crystals occur at the mercury surface giving spot patterns by electron diffraction, formed as hexagonal crystals having basal planes parallel to the surface. The spacing, 3 \AA , coincides with the period along the hexagonal axis for crystals of solid mercury. In their more recent investigation and summary Bailey, Fordham and Tyson¹⁶ do not support the view that liquid crystals of this type exist at the clean mercury surface. If this is so

then nucleation of the salt in the correct orientation may be initiated by a hexagonal packing arrangement in the liquid surface.

In these present experiments the very large numbers of films examined and the more elaborate techniques employed in removing the films from the mercury surface made it possible to differentiate the artefacts produced by the mechanical strain occurring during the removal of the orientated deposit from the structural characteristics of the deposits themselves.

For example, in fig. 3 the diffraction pattern shown was selected from a number obtained with the electron beam perpendicular to the plane of an apparently extensive single crystal, prep. 36. The actual arrangement was of a single crystal sited above a distorted region consisting of crystals rotated on an axis parallel to the electron beam, that is an axis perpendicular to the $\{110\}$ cleavage plane so that the c_0 -axes lie at angles of up to 30° from the c_0 -axis of the large single crystal. The single crystal gives rise to the strong spot pattern, the distorted region to the arced pattern, whilst the strong primary spots themselves give rise to arcs, each diffracted beam acting as a primary source. From a consideration of the operations involved in setting up the specimens for examination, the intensity of the arcs and an absence of additional relatively strong single crystal patterns, it is easily deduced that the distorted area lies at what was the salt/mercury interface; this distortion almost certainly arose when the film was stripped.

The only evidence found in chloride and potassium bromide solutions for the presence of an oxide or oxyhalide of mercury was in the case of prep 12 and 19 where traces of HgO were observed by diffraction. Otherwise all diffractions could be indexed assuming a more or less polycrystalline deposit in the orientation described above. The preparations in hydrobromic acid gave, rather surprisingly, faint diffractions that could be indexed as HgO over a rather wider range of conditions. This occurred with prep. 22, 28, 29, 30. It is possible that the oxide formed during the drying out of the film.

Frequently, examination by electron diffraction showed in addition to the well-marked boundaries of crystals, an example of which is seen in fig. 5, indeterminate areas marking the overgrowth, at the junction, of material in differing orientations. These orientations, however, also correspond to crystals having a common axis normal to the film, but in a range of azimuths about this axis. Fairly well-defined areas of this type are to be seen in fig. 4.

An analysis was therefore carried out on the nature of the orientations occurring at the junctions. Since the $\{110\}$ plane represented the only lattice net parallel to the surface of the mercury, positions of minimum potential energy would be determined by the repeated occurrence of certain angles between the same lattice row in the $\{110\}$ planes in adjacent or overlapping crystals.

The types of diffraction pattern analyzed in order to define these orientations are shown in fig. 6 and 7 from prep. 17(a) and 33. The area examined in fig. 6 overlapped a strongly marked boundary like that shown in fig. 5 and corresponds to two crystals orientated with the c_0 axes at $59^\circ 49'$. Fig. 7 shows, because of the double diffraction, that one crystal interleaves with or is superposed on a second; the respective c_0 axes of parallel $\{110\}$ faces being at 89° and the type of growth similar to that of fig. 4.

The notation introduced by Wilman¹⁴ in his studies of orientation phenomena of this type has been used in tabulating data from a study of the jointing of adjacent crystals. Rectangular axes a and b were chosen corresponding to the $[1\bar{1}0]$ and c_0 lattice rows in the $\{110\}$ planes and δ is defined so that the rotation of two adjacent sheets, initially parallel, through angles of $\delta/2$ in opposite direction from the parallel azimuth would cause the $[u_1v_1]$ and $[u_1\bar{v}_1]$ rows to coincide along the initial a axis and two rows $[u_2v_2]$ and $[\bar{u}_2v_2]$ to coincide along the initial b axis so that

$$\tan \frac{\delta}{2} = \frac{v_1b}{u_1a} = \frac{u_2a}{v_2b}.$$

Values of δ have been listed in table 1 for HCl and KCl and table 2 for HBr and KBr . The entries have been restricted to angles occurring at least twice and the probability of their representing a related orientation is thus high. The fractions v_1/u_1 and u_2/v_2 are within 1 % of the estimated value of $(a/b) \tan \delta/2$ or $[(b/a) \tan \delta/2]$ respectively, assuming no change in lattice parameter.

BEHAVIOUR IN IODIDE SOLUTIONS.—The films were very different from the bromide and chloride. The loosely organized deposit, formed only in dilute solutions, were very difficult to mount in a form suitable for electron optical studies. It was seen by low power optical microscopy that their green colour was due to finely dispersed mercury



FIG. 2.— Hg_2Cl_2 formed in N/100 HCl at a c.d. of 0.025 mA cm^{-2} for 10 min; electron microscopy $\times 16,000$.

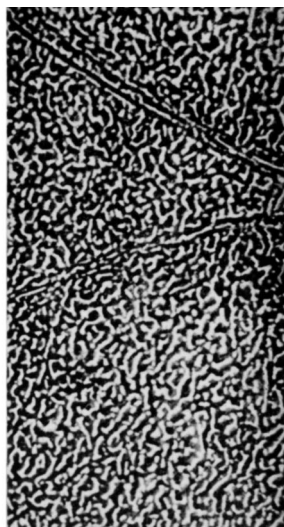


FIG. 4.— Hg_2Cl_2 formed in 2N HCl at a c.d. of 2.5 mA cm^{-2} for 6 sec; electron microscopy $\times 7,200$ showing skeletal form with irregularly distributed holes.

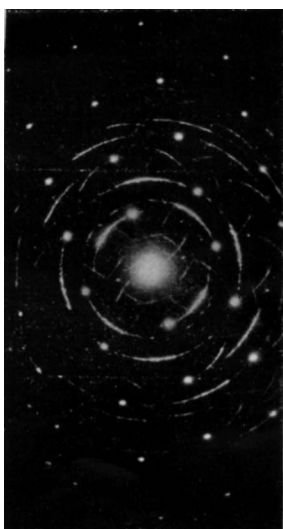


FIG. 3.—Electron diffraction pattern from Hg_2Br_2 formed in N/100 KBr at a c.d. of 0.25 mA cm^{-2} for 60 sec; single crystal, with a distorted region giving arcs by double diffraction; beam \perp to the plane of the film.

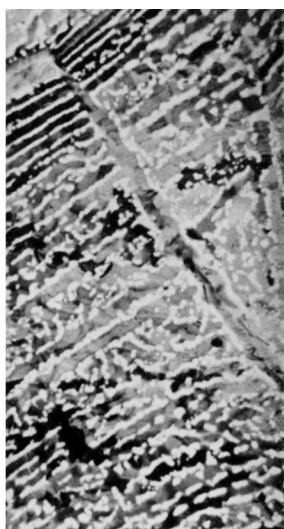


FIG 5.— Hg_2Br_2 formed in N/10 KBr at a c.d. of 0.25 mA cm^{-2} for 60 sec; electron microscopy $\times 3,400$ showing skeletal form with linearly distributed holes.

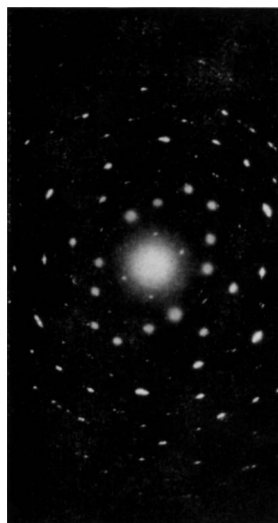


FIG. 6.—Electron diffraction pattern from Hg_2Cl_2 formed in N/10 KCl sat. with Hg_2Cl_2 at a c.d. of 0.25 mA cm^{-2} for 60 sec. Two single crystals with an angle $59^\circ 49'$ between c_0 axes, $\{110\}$ faces parallel to substrate, beam \perp to the plane of the film.

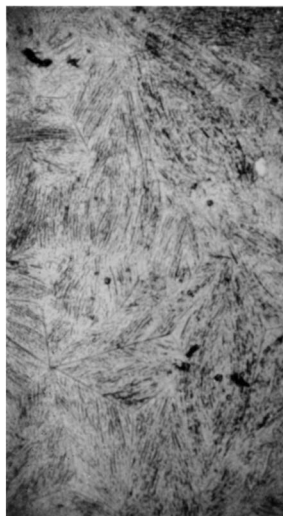


FIG. 8.— Hg_2Br_2 formed in N/10 KBr at a c.d. of 0.25 mA cm^{-2} for 60 sec; optical microscopy $\times 375$, showing the disposition of linearly distributed holes (see fig. 5).

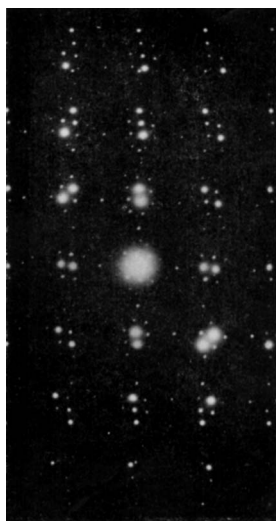


FIG. 7.—Electron diffraction pattern from Hg_2Br_2 formed in N/10 KBr at a c.d. of 0.25 mA cm^{-2} for 60 sec. Double diffraction with two interleaved single crystals with an angle of 89° between c_0 axes, $\{110\}$ faces parallel to substrate, beam \perp to the plane of the film.

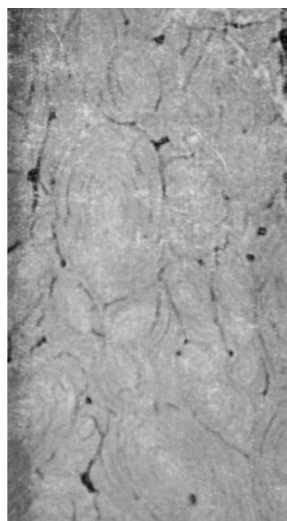


FIG. 9.— Hg_2Br_2 formed in N/10 KBr at a c.d. of 0.25 mA cm^{-2} for 60 sec; optical microscopy $\times 625$ showing lune or elliptical shaped single crystals.

sited in a yellow-green precipitate and, as in the case of chloride and bromide preparations made at current densities of the order of $1 \mu\text{A cm}^2$, it was found very difficult to remove the element and leave the inorganic salt. When this was possible such areas as were successfully examined by electron microscopy showed in the main very fine needle-shaped crystals; very infrequently fragments of crystals showing a skeletal type of growth were observed. There was no evidence for $\{110\}$ interfacial orientations.

DISCUSSION

We have in these results good evidence for the coherence of the growing crystals of the bromide and chloride at the boundaries under a wide range of conditions. This feature of the overgrowth together with the surface orientation accounts in a very plausible manner for some of the observations on the nature of the surface films found in the ref. (1)-(7). For example, it is easy to visualize the growth of the "tubes" described by Bockris and Parsons.⁴

TABLE 1.— Hg_2Cl_2 FORMED IN HCl AND KCl ; ANGLES δ BASED ON THE ROTATION OF A RECTANGULAR NET WITH $a = 6.32 \text{ \AA}$, $b = 10.89 \text{ \AA}$ WHERE

$$\tan \frac{\delta}{2} = \frac{v_1 b}{u_1 a} = \frac{u_2 a}{v_2 b}.$$

H = high c.d. (2.5 mA cm^{-2}), M = medium c.d. (0.25 mA cm^{-2}), L = low c.d. (0.025 mA cm^{-2})

δ	$\frac{v_1}{u_1}$	$\frac{u_2}{v_2}$	HCl		KCl	
			[electrolyte]	c.d.	[electrolyte]	c.d.
$3^\circ 20'$	1/60	1/20			N	M
					0.01 N	L
5°	1/39	3/40	N	H	0.1 N*	M
			0.1 N	M		
6°	1/33	2/21	N	H		
			0.01 N	L		
$6^\circ 38'$	1/30	1/10	N	H	0.1 N*	M, L
$8^\circ 40'$	2/45	13/100	2 N	H		
			N	M		
			0.1 N	M		
$9^\circ 50'$	1/20	3/20	0.1 N	H	N	H
					0.1 N	L
$12^\circ 40'$	2/31	6/31	0.1 N	H	0.1 N*	M
38°	1/5	3/5	2 N	H	0.1 N	L
			N	M		
			0.1 N	H, M		
$39^\circ 40'$	7/33	31/50			N	M
					0.1 N*	M
$48^\circ 30'$	13/50	7/9	N	L	0.1 N	M
$59^\circ 49'$	1/3	1	2 N	H, L	N	M
twin			N	M	0.1 N*	H, M, L
			0.1 N	M		
			0.01 N	M, L	0.01 N	L
69°	2/5	6/5	0.1 N	M	0.01 N	L
72°	3/7	5/4			N	M
					0.1 N*	L
90°	29/50	43/25	N	M		
			0.1 N	L		

* potassium chloride electrolyte in equilibrium with solid mercurous chloride.

There are limits to the extent to which correlation may be made between the electron microscope image and the diffraction pattern. Due to the rotation of the electron beam by the objective and projector lenses, diffraction pattern and optical picture cannot be spacially related, unless some recognizable feature of the electron optical projection has been previously associated with a certain crystal orientation. For example, the linear portions of the skeletal crystal

TABLE 2.— Hg_2Br_2 FORMED IN HBr AND KBr ; ANGLES δ BASED ON THE ROTATION OF A RECTANGULAR NET WITH $a = 6.56 \text{ \AA}$; $b = 11.10 \text{ \AA}$ WHERE

$$\tan \frac{\delta}{2} = \frac{v_1 b}{u_1 a} = \frac{u_2 a}{v_2 b}.$$

H = high c.d. (2.5 mA cm^{-2}), M = medium c.d. (0.25 mA cm^{-2}), L = low c.d. (0.025 mA cm^{-2})

δ	$\frac{v_1}{u_1}$	$\frac{u_2}{v_2}$	HBr		KBr	
			[electrolyte]	c.d.	[electrolyte]	c.d.
13°	1/15	6/31	0.1 N	H, M		
$15^\circ 30'$	2/25	3/13	N	L	0.1 N	M
			0.01 N	H		
17°	3/34	16/63	N	L		
			0.1 N	M	0.1 N	H, M
			0.01 N	H		
			0.1 N	H	0.1 N	M
19°	1/10	2/7	0.01 N	M		
			N	H	N	H
$20^\circ 30'$	3/28	4/13			0.1 N	M
$27^\circ 30'$	1/7	5/12	N	H	N	H
			0.01 N	H		
29°	3/16	7/16	0.01 N	H	N	H
					0.1 N	M
42°	5/22	13/20	0.1 N	M	0.1 N	H, M
45°	12/49	7/10	0.1 N	M	0.1 N	M
			0.01 N	M		
50°	11/40	15/19	0.01 N	H	0.1 N	M
53°	5/17	11/13	0.1 N	H	0.1 N	M
$59^\circ 40'$ (twin)	17/50	36/37	0.1 N	H	0.1 N	H, M
					0.01 N	M
$64^\circ 30'$	16/43	15/14	0.1 N	H, M	0.1 N	M
			0.01 N	H, M		
78°	11/23	11/8	N	H	0.1 N	M
			0.1 N	M		
			0.01 N	M		
			0.01 N	M		
89°	7/12	5/3	0.01 N	M	0.1 N	M
90°	10/17	17/10			N	H
					0.1 N	M

shown in fig. 5 cannot necessarily be related to some particular crystal axis in the basic tetragonal cell. Certain features may assist in the correlation; for example, the presence of a crystal boundary between two skeletal crystals similar to those in fig. 5 and a pattern of the type of fig. 6 would yield the desired information; or a marked crystal habit may effect the shape of the reciprocal lattice spots obtained by the high-resolution electron diffraction¹⁷ enabling a decision to be made connecting the internal arrangement of portions of the specimen with the external form. There is an alternative method which should be feasible

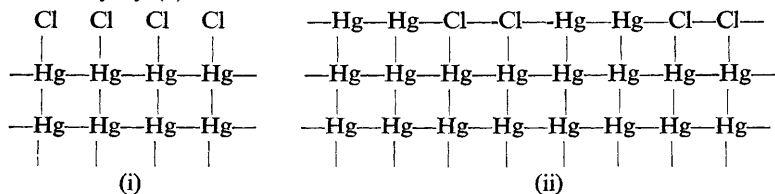
in connection with this type of orientation problem. The conversion of the microscope pattern to that of electron diffraction is carried out in the E.M.3 instrument by altering the strength of a single lens, the first projector. It should be possible to calculate the related rotation ϕ of the pattern by an estimate of the value of the expression $\phi = (e/8mV)^{\frac{1}{2}} \int_{-\infty}^{\infty} H_s ds$, where e and m are the electronic charge and mass, V the accelerating potential and H_s the field of the lens. The most convenient way of doing this at a constant accelerating voltage would seem to be by a direct calibration of the rotation with variation in lens current for a specially selected specimen having a known orientation of artefact with crystallographic direction and using the relation $\phi \propto I/V$, where I is the lens current.

A rather disappointing feature of this work has been that, despite the very large number of specimens which have been very carefully examined, little correlating evidence of this type has been found. The crystals are too thin to make use of a polarizing microscope and efforts to grow thicker crystals for this purpose have so far been unsuccessful.

With iodide solutions the $\{110\}$ interface orientation was completely absent and the crystals were mixtures of mercurous iodide, mercuric iodide and mercuric oxide. The complete absence of the orientation that was invariably present with the chloride and bromide preparations was most striking. Possible reasons for this may be the relative instability of the mercurous iodide in the presence of excess iodide ion, the related conversion to metallic mercury and the mercuric salt breaking down the regular crystalline growth at an early stage, the formation of mercuric oxide preventing regular crystal growth, or the large change in the inter-halogen spacing in the mercurous salt. The latter increases on going from the mercurous chloride to the bromide and the iodide from 3.33 Å to 3.40 Å and 3.55 Å, and this may just be sufficient to prevent the iodide pair, under the conditions of preparation, from being located within three adjacent mercury atom pairs still sited in the liquid mercury, although this process readily occurs with the smaller chloride and bromide atoms. An attempt was made to prevent the formation of oxide by using hydriodic acid and by means of potassium iodide solutions acidified with nitric acid. The presence of N/100 nitric acid in the KI solutions apparently prevented oxide and to a great extent mercuric iodide formation; in hydriodic acid both were still formed. In neither type of solution was there evidence of any preferred orientation of the deposit.

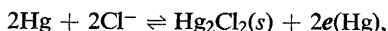
The results indicate conditions under which anomalous surface tension effects at mercury surfaces would be expected; it is not so easy, however, to state in what respect the observations clarify the mechanism of the reversible metal/metal salt electrode.

Hills and Ives recently suggested¹ that for the calomel electrode, equilibrium was reached through a "chloro-mercury" intermediary which was formulated diagrammatically in their paper as in (i) below. Our results point rather definitely to a primary layer being formed on the mercury surface which may be represented approximately by (ii):



We can therefore consider the surface polarized by the presence of an orientated layer of calomel; further passage of current can only take place by ionic migration through or by disruption of this film. Breakdown of the film results in the passage of mercurous or possibly Hg_2Cl^+ ions into the solution and film thickening takes

place by deposition of mercurous chloride on the portions of the unimolecular layers of calomel still attached to the mercury surface. The areas from which the ions leave the mercury form the base of the holes through the deposits observed in the stripped film. The equilibrium state first reached when the surface is completely polarized essentially corresponds to the reaction



the ready formation of the solid being peculiar to the plane orientated with respect to the substrate.

Nevertheless it is thought that, in spite of the interesting speculations that can be made from the results, other reversible mercury electrode systems must be similarly studied before a complete analysis is attempted. In the one other case for which we have data, that of the mercury/mercurous sulphate electrode,¹⁸ no detectable surface film is formed, the salt lying loosely on the surface in the form of minute needles, and here it would seem that the traditional explanation of the control of potential by the activity of the mercurous ion in equilibrium with the anion and precipitated salt is quite natural. Our method of surface examination would, however, fail to detect the presence of a sulphate complex analogous to the "chloromercury" structure postulated by Hills and Ives and a crystal growth mechanism similar to that with bromides and chlorides permitting a thicker film to form does not in this case exist.

We would like to thank Miss Isobel Burton for her valuable assistance in the preparation of some of the films examined during the course of this investigation.

¹ Hills and Ives, *J. Chem. Soc.*, 1951, **70**, 311.

² Grahame, *Chem. Rev.*, 1947, **41**, 283.

³ Kolthoff and Lingane, *Polarography* (Interscience, New York, 1946), p. 322.

⁴ Bockris and Parsons, *Nature*, 1947, **160**, 232.

⁵ Heyrovsky, *Faraday Soc. Discussions*, 1947, **1**, 212.

⁶ Haul and Sholtz, *Angew. Chem. A*, 1948, **60**, 65.

⁷ Thirsk, *Proc. Physic. Soc. B*, 1953, **66**, 129.

⁸ Lal, Thirsk and Wynne-Jones, *Trans. Faraday Soc.*, 1951, **47**, 70.

⁹ Rothschild, *Proc. Roy. Soc. B*, 1938, **125**, 283.

¹⁰ Jonsson, Qvarfort and Sillén, *Acta Chem. Scand.*, 1947, **1**, 461.

¹¹ Gatty and Spooner, *The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions* (Clarendon Press, 1938), pp. 115, 126.

¹² Brodsky, *Z. Elektrochem.*, 1929, **35**, 833.

¹³ A.S.T.M. index.

¹⁴ Wilman, *Proc. Physic. Soc. A*, 1951, **64**, 331.

¹⁵ Berdennikov, Bresler, Zel'manov and Shtrauf, *Physik. Z. Sowjet*, 1933, **4**, 873; *Zhur. Fiz. Khim.*, 1934, **5**, 584.

¹⁶ Bailey, Fordham and Tyson, *Proc. Physic. Soc.*, 1938, **50**, 63.

¹⁷ Cowley, Rees and Spink, *Proc. Physic. Soc.*, 1951, **64**, 609. Butler and Thirsk, *Acta Cryst.*, 1952, **5**, 288.

¹⁸ Boulton and Thirsk, in preparation.