377. *The Formation of Ammonium Amalgam by Electrolysis.*

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Conditions have been investigated under which amalgam formation takes place when solutions of ammonium sulphate are electrolysed with a mercury cathode. At room temperature there is definite evidence of amalgam formation at beyond about pH 4. This can be suppressed by adding impurities such as yellow ammonium sulphide, or by raising the temperature to about 50°. In other respects the conditions for the formation of ammonium amalgam closely resemble those for the formation of potassium amalgam.

Under conditions leading to amalgam formation prolonged electrolysis leads first to a pasty froth of amalgam, and then to a grey-black mass which eventually peptises to a colloidal suspension. The mechanical stability of the froth can be explained by the marked lowering in surface tension and the marked increase in surface viscosity which are observed when amalgam formation takes place.

DURING a series of investigations on pseudometallic groupings (Ubbelohde, *J.*, 1950, 1143; McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191), some of the problems connected with amalgam formation by the ammonium radical have been investigated. Salient facts from the large and rather chaotic variety of investigations on " ammonium " which were published from the mid-nineteenth century onwards are as follows :

(i) The pasty mass which is obtained, for example, when sodium amalgam decomposes an ammonium salt contains gas bubbles, which approximately obey Boyle's law (Routledge, *Chem. News*, 1872, **26**, 211). In the present paper the view is developed that the pasty mass is an example of a froth. Results detailed below explain how this froth is stabilised mechanically.

(ii) The lowering of the freezing point of mercury by the molecule NH_4 (Rich and Travers, *J.*, 1906, **89**, 872) suggests a metallic solute which is stable at least around the freezing point of mercury. For convenience the solutions will be described as amalgams. A tentative view subject to experimental verification is that the molecule NH_4 dissolves in the mercury, as do sodium and potassium, and gives up one *s* electron to the conduction band. Such metallic behaviour would correspond with the general hypothesis about the metallic valency of pseudometallic groupings (Ubbelohde, *loc. cit.*). Symbolically,

$$NH_4 + \underset{\text{excess}}{(Hg)} \xrightarrow{\text{amalgam}} NH_4^+ + e.$$

The molecule NH_4 dissolved in mercury may compactly be referred to as " ammonium " though it must be stressed that the evidence for its existence is at present indirect.

(iii) Amalgams of NH_4 stored for indefinite periods at $-78°$ and then rapidly melted can reduce aqueous potassium iodate. But if the melts are stored for various periods around $-20°$ to $-30°$ a progressive loss of reducing power has been reported, which has been identified (Deyrup, *J. Amer. Chem. Soc.*, 1934, **56**, 2594) with a progressive decomposition in the mercury solution according to the equation :

$$\underset{\text{(amalgam)}}{2NH_4^+ + 2e} \longrightarrow H_2 + 2NH_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

We began the present investigation with the idea that when the ion NH_4^+ is discharged at a mercury cathode the process

$$\underset{\text{at surface of mercury}}{NH_4{}^+{}_{aq.} + e} \longrightarrow \underset{\text{in amalgam}}{NH_4} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

should occur at a rate depending on the current density used. By using sufficiently high current densities, reaction (2) can be made faster than reaction (1) even at room temperature. Under such circumstances increasing concentrations of ammonium should build up in the mercury. Various lines of evidence indicate that this actually appears to take place. However, with increasing concentration of NH_4 in the mercury the concurrent decomposition process produces physical conditions which prevent convenient investigation of metrical parameters of ammonium such as the molecular volume or the electrical conductivity. Results so far obtained are nevertheless of some interest, and are briefly recorded in the present paper.

Five main lines of experimental investigation were pursued in considerable detail.

(1*a*) Solutions of ammonium sulphate were electrolysed at a mercury cathode. When the current was switched off, and the mixture set aside, the stored NH_4 decomposed to give ammonia which was evaluated by titration. Amalgam formation was also verified by testing the reducing power of the cathodic mercury for potassium iodate.

(1*b*) The pH of the electrolyte solution was varied by adding ammonia or sulphuric acid. Various procedures showed that amalgam formation becomes important only at pH $>$ about 5. Amalgam formation was completely suppressed by raising the temperature of the electrolyte to about 50°, or (at pH $\sim$7·4) by adding a few drops of yellow ammonium sulphide in an attempt to poison the mercury surface.

Parallel experiments carried out with solutions of potassium sulphate in place of ammonium sulphate gave closely similar behaviour with respect to the conditions under which amalgam formation occurred.

(2) From measurements on sessile drops of mercury maintained as cathodes under solutions of ammonium sulphate a large decrease in surface tension was observed under conditions leading to amalgam formation. Under conditions where no amalgam formation occurs the change in surface tension of the mercury on applying a voltage was much smaller. Closely similar behaviour was shown by sessile mercury cathodes under solutions of potassium sulphate.

(3) When a column of mercury in a cylindrical glass tube was covered with a solution of ammonium sulphate and made cathodic, a pronounced " wedge " effect was observed under conditions where amalgam formation occurs. The wedge effect has been described more extensively elsewhere (Johnston and Ubbelohde, *Proc. Roy. Soc.*, 1951, *A*, **206**, 275). Briefly, when mercury in a glass vessel is covered with electrolyte, the familiar contact angle conditions at the mercury/glass/electrolyte interface are completely upset if the negative voltage of the mercury exceeds about 3 v. With more negative potentials, a wedge of electrolyte about 0·01 mm. thick at the base forces itself with apex downwards between the mercury and the glass, to a depth of several cm. This depth ranges from about 1 cm. for magnesium sulphate to 10 cm. for potassium sulphate. It has been observed for the ions Li^+, Na^+, K^+, Mg^{++}, and Ba^{++}, and is not observed for the ions Ag^+, Zn^{++}, Cd^{++}, or OH_3^+. In the case of ammonium sulphate the depth of the wedge was as large as 16 cm.

No wedge effect was observed with NH_4^+ under conditions of temperature or pH where ammonium amalgam formation does not occur.

(4) Measurements of the surface viscosity of a pool of mercury under solutions of ammonium sulphate were made with an oscillating-disc viscometer. When amalgam formation occurred, it was found that the surface viscosity increased much more rapidly for ammonium than for potassium amalgam, indicating a considerable difference in surface properties.

(5) When a mercury cathode was subjected to continued electrolysis under a solution of ammonium sulphate and with conditions suitable for amalgam formation, the accumulating NH_4 gradually built up a sufficient concentration in the mercury to decompose fast enough to form a froth. With a suitable set-up froth-formation pushes part of the amalgam closer to the anode and increases the current density at this part. A progressively more concentrated amalgam grows upwards and changes in appearance from smooth silver to grey, and finally to black. Gaseous decomposition products which accompany this increase of NH_4 concentration break up the grey and black masses. Finally at the parts nearest the anode the break-up leads to disruption to a colloidal suspension.

EXPERIMENTAL.

In each of the following experiments the mercury used was freshly acid-washed and triply distilled. Where necessary, distillation was direct into the evacuated apparatus. The mercury was covered with a fresh sample of electrolyte in each experiment.

Analytical Assessment of the NH_4 *Stored in the Amalgam.*—(*a*) Electrolysis was carried out by using the cell shown in Fig. 1. Anode and cathode compartments were separated by narrow capillaries which acted as diffusion barriers. The total volume of electrolyte (0·1M-ammonium sulphate) in the cathode compartment could be read from the graduations. Froth formation at the cathode was suppressed by vigorous stirring of the mercury to facilitate escape of the gas bubbles. When electrolysis had been allowed to proceed for various periods, with currents ranging from 10 to 20 milliamps., the electrolyte in the cathode compartment was sampled for analysis after mixing. Illustrative results are given in the first line of Table I. The current was then stopped, stirring of the mercury being continued. When decomposition of the stored NH_4 was complete, as shown by cessation of bubble formation, the cathode electrolyte was again mixed and a further sample analysed. Both samples were titrated for alkali content by an accurate semi-micro-technique. The difference between the total ammonia in the cathode compartment before and after decomposition of the amalgam permitted calculation of the NH_4 " latent " at the moment of stopping the electrolysis (line 2 of Table I). The term " latent ammonium " is applied to that quantity of NH_4 which exists in some form of combination with the mercury at the instant when electrolysis is discontinued. During electrolysis the current passed was measured by using a hydrogen coulombmeter in series. An independent check on the accuracy of accounting for all the NH_4 liberated is obtained by comparing the sum of the figures in lines 1 and 2 with those in line 3.

TABLE I.

The storage of " latent " NH_4 *in a mercury cathode during electrolysis.*

(Results are in g.-equivs. $\times 10^{-4}$; pH of solution = 7·4; current = 20 milliamps.)

NH_4 liberated into electrolyte as NH_3 before switching off	2·28	2·07	2·09
NH_4 latent in mercury at instant of switching off	1·00	1·05	1·14
Total NH_4 corresponding with coulombs passed	3·40	3·21	3·21

FIG. 1.

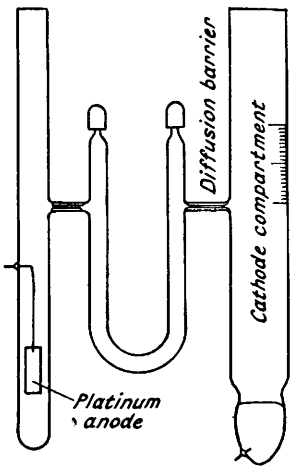
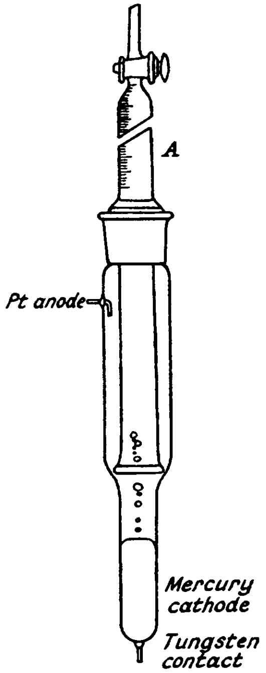


FIG. 2.

Electrolytic cell for discharge pH *experiments.*



(*b*) When the pH of the solution of ammonium sulphate was changed, the ratio of the number of ions forming a mercury amalgam to the number discharged directly at the surface was found to depend on the pH. This was investigated in a cell of the type illustrated in Fig. 2, in which the froth was left unstirred so as to retain as much as possible of any gas formed by decomposition of NH_4 within the mercury. The pH was adjusted by adding the appropriate acid or alkali and was measured externally by means of selected indicators. The hydrogen evolved at the surface of the mercury cathode ascended into the measuring burette at *A* and the volume was compared with the volume of the hydrogen in a sulphuric acid–platinum voltameter in series. By this means continuous records were obtained as electrolysis proceeded. To illustrate the results of a large number of measurements Fig. 3 gives the " latent NH_4 " after passage of 24 coulombs, at room temperature as a function of pH. In the experiments illustrated the current used was 5—10 milliamps. In this case " latent ammonium " is calculated from the hydrogen trapped by the mercury either as metallic ammonium or as bubbles in the froth which result from the decomposition of the NH_4. Since some bubbles of hydrogen escape from the froth, particularly as the concentration of NH_4 increases, this procedure gives a lower limit to the total NH_4 which at some time has been combined in some form with the mercury.

A similar curve obtained by using 0·1M-potassium sulphate is also plotted in Fig. 4. There is of course no froth formation in the case of potassium amalgam. Latent NH_4 was also detected in qualitative confirmatory experiments by switching off and quickly drawing off the *mercury*. Samples of such mercury reduced acid potassium iodate solution. The equation assumed for this reduction was $6H_2O + IO_3^- + 6NH_4 \longrightarrow 6NH_4^+ + I^- + 3H_2O + 6OH^-$. The rate of decomposition and the manipulative difficulties involved made it impossible to use the method quantitatively at room temperature. Deyrup (*loc. cit.*) used it at low temperatures where the decomposition is slower.

(*c*) When a few drops of yellow ammonium sulphide were added to the solution as a possible poison for the mercury surface, entry of NH_4 into the cathode mercury was entirely suppressed as shown in Fig. 3.

(*d*) The gas evolution method described above showed that at 50° electrolysis gave no latent NH_4 at pH = 7·6. Entry of NH_4 into the cathode mercury appears to be suppressed at temperatures only a little above room temperature.

Change in Surface Tension of Mercury when NH_4 *is Deposited by Electrolysis.*—The surface tension of a sessile drop of freshly purified mercury was measured under 0·1M-ammonium sulphate (AnalaR), of pH 7·4, in an apparatus in which the mercury could be made progressively more cathodic (Johnston and Ubbelohde, *loc. cit.*). To prevent the mercury from becoming anodic at any stage, which can lead to oxidation of the surface, a minimum voltage of 1 v. was applied to the drop before it was covered with electrolyte. With applied cathodic potentials of 1—3 v. the change in shape of the sessile drop is small and does not lend itself to very accurate measurements of changes in surface tension. The general effects are in accordance with the Lippmann–Helmholtz curve. But as soon as a critical negative potential greater than about 3 v. was applied to the mercury there was a marked change in shape of the drop, implying a large decrease in the interfacial tension mercury/electrolyte which then underwent little further change on prolonged electrolysis (Fig. 4). Closely similar behaviour has previously been observed with solutions of potassium sulphate (Johnston and Ubbelohde, *loc. cit.*).

Fig. 3.

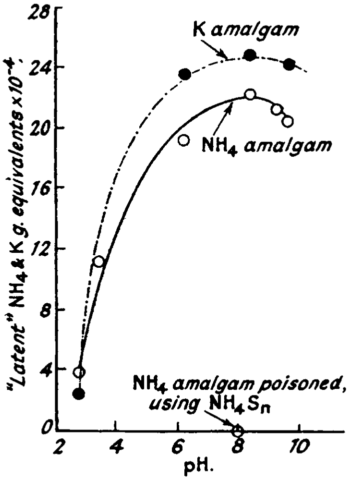
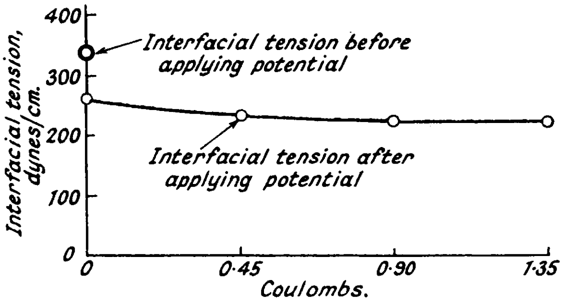


Fig. 4.

Change in interfacial tension during electrolysis.



The " Wedge " Effect at a Mercury Cathode due to Amalgamation of NH_4.—An electrolytic cell was prepared as described elsewhere (Johnston and Ubbelohde, *loc. cit.*). 0·1M-Ammonium sulphate was electrolysed with a platinum anode and a mercury cathode. At <3 v. only the usual electrocapillary effects were observed. At potentials greater than three volts a wedge of electrolyte penetrated *between* the mercury and the glass wall of the cell to a depth of 4 cm. Electrolysis at a potential of 5 v. increased the depth of penetration to 16 cm. This wedge effect was most marked for the pH range 6—9. It was inhibited at a pH <4. It was also inhibited at pH 7·6 by raising the temperature to 50°, or by adding a few drops of yellow ammonium polysulphide as poison, *i.e.*, under conditions where amalgam formation is suppressed.

Increase in Surface Viscosity on Formation of Amalgams.—The construction of a practicable surface viscometer was made extremely difficult both by the high density of the mercury and the penetration, during electrolysis, of electrolyte between mercury and any surface which passes through the mercury/electrolyte interface, on account of the wedge effect. The glass oscillation viscometer finally designed after numerous trials is illustrated in Fig. 5. A large logarithmic decrement of torsional oscillations was found after switching on a current under conditions leading to ammonium amalgam formation (pH 7·4) (cf. Fig. 6). Essentially the experiments involved observation of the amplitudes of successive oscillations of the viscometer, using a lamp and scale. Since electrolysis was progressive, no high-precision observations were made on the *frequency* of oscillation, so that it was not possible to determine whether the period of oscillation increased as amplitude decreased, *i.e.*, whether there was a non-Newtonian component in the viscosity.

The marked increase of surface viscosity, before any visible swelling of the amalgam owing to froth formation can be noted, is correlated with the immediate change in surface tension and the wedge effect after application of the voltage requisite for formation of ammonium amalgam. To test for possible chance contamination by surface-active impurities similar experiments were carried out with potassium sulphate as electrolyte. The results are also plotted in Fig. 6, and show no evidence of marked decrement. In the later stages of electrolysis of ammonium salt solutions, thixotropic stiffening of the mercury by froth formation enhances the damping enormously, but no measurements could be carried out in this region.

Effect of Prolonged Electrolysis.—Prolonged electrolysis transforms the mercury foam to a spongy grey mass. At the point on the cathodic pool of mercury nearest to the anode, where the current density was highest, grey growths appeared, the parts nearest the anode soon becoming black and then dispersing to form a suspension. When the electrolyte was withdrawn and centrifuged at this stage irregular microscopic particles were found in the deposit. The nature of this colloid is still uncertain.

DISCUSSION.

Comparison between Potassium and Ammonium Amalgam.—The experiments described above show that the behaviour of ammonium discharged at a mercury cathode is initially closely similar to that of potassium. The chief difference is that surface effects due to $(NH_4)Hg_x$ are somewhat more pronounced. In another publication (Johnston and Ubbelohde, *loc. cit.*) reasons are given in support of the view that there is strong positive adsorption of alkali metals at the interface between amalgam and electrolyte. This positive adsorption must be even more marked for ammonium, as might be expected if the electron polarisability of this group is rather bigger than in the case of potassium. At the same time the possibility cannot be wholly excluded that mercury–hydrogen or mercury–nitrogen–hydrogen complexes are also formed at the surface of ammonium amalgams. These might account for the much greater surface viscosity compared with potassium amalgams, and for the ultimate break up of the ammonium amalgam into colloidal suspension. Explosive mercury–ammonia complexes have been reported but their chemistry is still obscure (Sempley, *Chem. Eng. News*, 1947, **25**, 213B). Against this possibility of a permanent chemical change of the mercury atoms at the surface is the observation that the sessile drops return to the normal surface tension of mercury once the NH_4 has decomposed.

FIG. 5.
Disc viscometer.

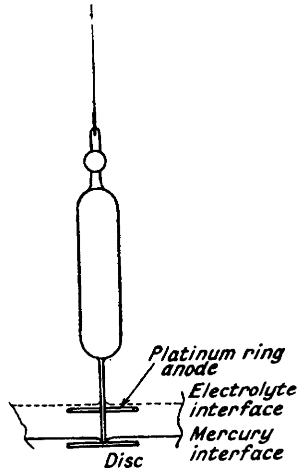
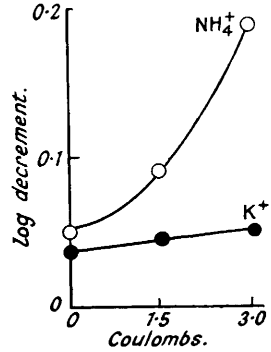


FIG. 6.



Formation and Mechanical Stability of the Froth.—Extrapolation of the results of Deyrup (*loc. cit.*) to room temperature suggests that the ammonium amalgams now obtained decompose more slowly. This may in part be due to the precautions taken to avoid atoms which might be catalytically active from getting into the mercury cathode So long as there is undecomposed ammonium in the mercury the experiments can be interpreted on the view (*a*) that this maintains the surface properties of the amalgam by maintaining an adsorbed layer of NH_4 whose concentration does not vary rapidly with the concentration of NH_4 in the bulk of the mercury, because of the strong positive adsorption, and (*b*) that bubbles of gas are formed continually within the mercury. It has been shown that, in general, froth formation is favoured by low surface tension. Froth stability is aided by high surface viscosity of the liquid phase (Clarke, *D.S.I.R. Chem. Res. Spec. Rept.* No. 6., H.M.S.O., London, 1947). Both these factors must contribute to the mechanical stability of ammonium amalgam, which is almost pasty in consistency.

Effects of Surface Conditions on the Formation of Ammonium Amalgam by Electrolysis.— Competing discharge mechanisms at the mercury cathode can be written as :

$$\mathrm{OH_3^+} + e \xrightarrow{1(a)} \mathrm{OH_3} \xrightarrow{1(b)} \tfrac{1}{2}\mathrm{H_2} + \mathrm{H_2O}$$

$$\mathrm{NH_4^+} + e \xrightarrow{2(a)} \left\{ \begin{array}{l} \mathrm{NH_4} \xrightarrow{2(b)} \tfrac{1}{2}\mathrm{H_2} + \mathrm{NH_3} \\ \mathrm{NH_4} + x\mathrm{Hg} \xrightarrow{2(b')} \text{ammonium amalgam} \end{array} \right.$$

with analogous reactions for K^+. Since increasing the acidity has much the same effect in preventing the formation of potassium or ammonium amalgam (Fig. 3), this effect of pH is probably caused by the increased concentration of OH_3^+ favouring discharge process 1(*a*). Rise of temperature prevents the formation of ammonium amalgam, but it is not clear whether this is on account of a relative enhancement of reactions 1(*a*), 1(*b*), and 2(*b*) with respect to 2(*b'*) at the surface of the mercury, or whether the amalgam merely decomposes much faster within the mercury solution. The effect of a poison such as yellow ammonium sulphide in suppressing reaction 2(*b'*) is curious, and its interpretation is reserved pending investigation.

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