ELECTROSYNTHESIS OF ORGANIC AMALGAM FROM TETRAETHYLAMMONIUM TETRAFLUOROBORATE IN AQUEOUS MEDIUM

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Received January 1, 1994
Accepted August 20, 1994

The electroreduction of neutral aqueous solutions of 0.1 – 0.5 M Et_4NBF_4 on a mercury cathode at room temperature at –2.8 – –2.4 V produces a black precipitate of Et_4N . Hg_x with simultaneous evolution of hydrogen (the pH value increases to 12). No anodic oxidation of the amalgam has been observed in the interval of 0 – 2.8 V. The composition of the precipitate, collected by filtration under nitrogen, has been determined from the decrease of Et_4N^+ in the solution after electrolysis and from analysis of mercury in the binary compound Et_4N . Hg_x. The value $x = 2.9 \pm 0.8$ has been found.

The term organic amalgam denotes a binary compound R/Hg_x of an organic radical and mercury, which species have been studied for as long as 180 years[1]. A frequent type of preparation of these compounds consists in the reduction of corresponding quaternary salts on a mercury cathode in anhydrous medium with cooling: under such conditions the amalgam is formed as a black precipitate covering the electrode. Because of the low conductivity of the solution electrolyzed at low temperature, the voltage in the electrolyzer usually is 20 to 30 V. The ratio of constituents [organic residue R (Bu = C_4H_8, Alk = C_nH_{2n}, Et = C_2H_5) and mercury] has until recently been studied without any definite idea about the structure of amalgam, and the ratios R : Hg found vary from 1 : 12 to 1 : 7 (ref.[2]). A more recent paper[3] reports the ratio $Bu_4N^+ : Hg = 1 : 4$. The respective compound was found[3] to undergo an exchange reaction with $NaPF_6$ in acetonitrile to give the sodium amalgam $NaHg_4$, which proved the character of organic amalgam as a Zintl salt containing the Hg_4^- anion. At present, numerous papers by Kariv-Miller dealing with amalgams from alkylpyrrolidinium provide evidence for the presence of the Hg_5^- anion in the compounds discussed[4,5]. Hence the reduction of tetraalkylammonium salts proceeds according to the equation

$$Alk_4NA + e^- + x\,Hg \longrightarrow Alk_4NHg_x + A^- \quad , \qquad (A)$$

formally expressing the reduction of mercury to a Zintl anion. In the equations given, Alk_4N can represent any molecular moiety with quaternary nitrogen atom, e.g. a part of aromatic skeleton. The anodic oxidation of amalgam (which forms a fine deposit on the electrode) represents a regeneration of the ammonium cation[5].

$$Alk_4NHg_x - e \longrightarrow Alk_4N^+ + x\, Hg \qquad (B)$$

The character of Hg–N bond can vary from purely covalent one to purely ionic one, which follows from the properties of Zintl salts[6]. The expected reactivity of organic amalgams makes itself felt by their decomposition both in air and in inert atmosphere. In the latter case, an alkyl is split off from the quaternary cation and the respective tertiary amine, elementary mercury, and alkane are formed[4]. In air the amalgams undergo oxidation: its first step involves an electron transfer from the Zintl anion to oxygen[5,7], and the following steps lead to the replacement of this anion by carbonate and separation of elementary mercury. Organic amalgams are heterogeneous objects including the reactant solution and mercury, and in their analyses one attempts to remove the mercury inclusions first of all[1]. The content of mercury in the amalgam is then determined gravimetrically from the decrease of electrode mercury[3]. The quaternary or ammonium ion are determined in the amalgam precipitate after its decomposition with acid and oxidation with air[8,9]. Kariv-Miller uses the data about the charges consumed by the formation of amalgam in anhydrous medium, i.e. the charge for generating a mercury coating on platinum electrode by the reduction of Hg(II) and that for generating the amalgam on the mercury-coated platinum by the reduction of organic cation[4,5]. The chemical analogy with sodium amalgam is reflected by the reactions of organic amalgams with proton donors HA where hydrogen is liberated[1,5]:

$$Alk_4NHg_x + HA \longrightarrow Alk_4NA + 1/2\ H_2 + x\, Hg\ , \qquad (C)$$

here also H_2O can play the role of the proton donor HA. The reaction (*C*) can also take place on a mercury dropping electrode, which means the regeneration of electroactive compound Alk_4N^+ from its reduction product Alk_4NHg_x by action of proton donor and, hence, the condition of a catalytic current of evolution of hydrogen in the presence of a nitrogen base[10]. This was verified[9] in the case of diaminoacridines, which are reduced to amalgams with $x = 4.5$. From this reasoning follows a question concerning the stability of organic amalgams in aqueous medium at room temperature. Therefore, the present work deals with generating the amalgam in aqueous medium and analyzing its composition.

EXPERIMENTAL

Chemicals

Et_4NBF_4 was synthesized from Et_4NBr and tetrafluoroboric acid, purified by repeated recrystallization from methanol, and dried in vacuum (the melting point above 300 °C). The other chemicals used were commercial reagents of p.a. purity grade and were used without special modifications. The thin layer chromatography was carried out on Silufol (Kavalier, The Czech Republic) with a mixture of propanol, ammonia, and water (1 : 1 : 1) and detection with ninhydrine.

Electrolyses and Measurement of Current Intensity–Voltage Curves on Mercury Large-Area Cathode

A vessel of 10 cm^3 volume contained mercury (at the bottom of 4 – 5 cm^2 surface) as the working electrode and a platinum gauze separated by sintered glass as an auxiliary electrode. The reference electrode was a calomel electrode with saturated NaCl solution (NaSCE) with an electrolytic bridge filled with Et_4NBF_4 solution of the same concentration as that of the solution electrolyzed. The potentiostat used was an OH 405 model (Radelkis, Hungary), and the voltage imposed was measured by means of a digital multimeter VDM1 Mesit (Uherske Hradiste, The Czech Republic). The solution was deareated and stirred in a stream of nitrogen. The current intensity–voltage curves were measured in two ways: by automatically scanning the potential at the rates of 0.5 and 10 mV s^{-1} with recording by means of an XY 4103 apparatus (Laboratorni pristroje Prague, The Czech Republic), and by more slowly adjusting (by hand) the potential changes by 100 mV steps with 1 min electrolysis time and measuring pH after each voltage adjustment. For the syntheses of amalgams, the electrolyses were carried out at –2.8 V for a period of 3 min. The cyclic voltammetry was performed with a dropping mercury electrode at the flow rate of 0.688 mg s^{-1} for a 50 cm mercury column with an uncontrolled drop time of 8.7 s. The apparatus used: PRG 4 (Taccusel, France) with a memory oscillograph Tektronix model 5103N. The electrolyses were carried out in a dust-free box under nitrogen in order to ensure separation of the amalgam non attacked by oxidation. By the nitrogen added, the oxygen concentration in the box was lowered below 1%. The oxygen content was measured with an SF6 Tester PL3 apparatus[11].

Estimation of Et_4NBF_4 Reactant Decrease after Electrolysis

Method 1. The mass decrease of Et_4NBF_4 was determined gravimetrically as a difference of its content in 5 cm^3 solution after electrolysis and after filtering off the organic amalgam precipitate and that in 5 cm^3 solution before the electrolysis. The decrease was greater than 1 mg in all the cases. The electrolyte was dried in air at 100 °C 30 min.

Method 2. Using a conductometric titration of Et_4N^+ and BF_4^-, the content of tetraalkylammonium ion was determined in the solution after filtering off the amalgam: the titrant 0.032 M $NH_4[Cr(NH_3)_2(SCN)_4] \ . \ H_2O$ [Reinecke salt – ammonium diamminetetrakis(thiocyanato–N)chromate(1–) monohydrate], the product tetraethylammonium diamminetetrakis(thiocyanato–N)chromate(1–) (ref.[12]). A sample of Et_4NBF_4 solution was diluted 50 times, and the titration course was monitored after 1 cm^3 additions using a Philips PW 9509 conductometer with a PW 9571/00 probe (working frequency 2 000 Hz). The BF_4^- anion was determined by means of a precipitation titration with 4.500 M KCl using 50 μl additions and conductometric indication with the above-mentioned apparatus. During the titration, the solution was cooled with a mixture of water and ice to decrease the solubility of KBF_4.

Determination of Mercury Content in Amalgam

Method 1. The mercury mass decrease was followed indirectly gravimetrically after the electrolysis. With the initial amount of 60 g (± 1 mg) mercury, the decrease after electrolysis was in tens of mg.

Method 2. Mercury was determined by extraction titration in a mineralized sample according to Frideberg[13]. The amalgam on filter paper (with the paper) was spilt with an 80 °C hot mixture of 4 cm^3 diluted (1 : 3) HNO_3 and 2 cm^3 37% HCl and left to cool 1 h. The sample was diluted to 500 cm^3 after adjusting its pH at a value of 1 – 2 with concentrated aqueous ammonia. It was titrated with a 10^{-4} M dithizone solution in CCl_4 standardized with $HgSO_4$ of known concentration. The $HgSO_4$ standard was treated by the same mineralization procedure as were the amalgam samples. The reagent solution is green, and a red brown complex is formed after the extraction of Hg(II), hence the equivalence can also be estimated visually.

RESULTS AND DISCUSSION

Electrogeneration of Amalgam by Reduction of Et_4NBF_4 in Aqueous Medium

The conditions of formation of the black precipitate during electrolysis of 0.1 – 0.5 M Et_4NBF_4 solutions were found by measuring the potentiostatic current intensity–voltage curves (Fig. 1). The curves were obtained with the use of a large-area mercury cathode by changing the potential by 100 mV jumps with 60 s waiting at the preceding value. The evolution of hydrogen was observed from −1.5 V (against NaSCE). In this potential region the maximum current intensity is produced. In the potential region at the current intensity increase after the maximum, a black precipitate is formed on the electrode (denoted by an arrow in Fig. 1) during the measurement of *I–E* curves. At this potential, due to evolution of hydrogen the pH value is high enough (Fig. 1) to ensure the stability of the amalgam formed. The reduction of tetraethylammonium ions accom-

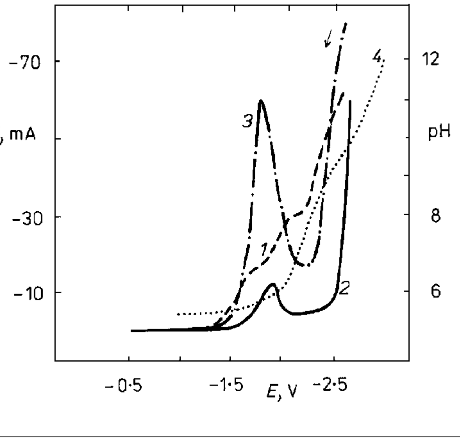

FIG. 1
Current intensity–voltage curves (*1* – *3*) obtained with large-area mercury cathode (5 cm^2) in aqueous solutions of Et_4NBF_4, and pH vs voltage dependence (*4*) obtained at the conditions of curve *3*. The potential of working cathode against NaSCE was changed by 100 mV jumps after 60 s waiting, measured at room temperature at 0.05 M (*1*), 0.1 M (*2*), and 0.5 M (*3*) Et_4NBF_4 concentrations. The arrow denotes the potential of precipitation of amalgam during recording the current intensity–voltage curve

panied by evolution of hydrogen gives a cathodic peak on the cyclic voltammogram (Fig. 2) whose exponent of the dependence of current intensity upon the polarization rate is 0.33 in the interval from 5 to 100 V s^{-1}. The signal of anodic oxidation of the reduction product (i.e. the amalgam) is absent in the whole range of potentials. A similar course of cyclic voltammogram was published for the reduction of tetrabutylammonium salt, which forms an unstable amalgam on the mercury electrode in the medium of dimethylformamide[14]. Stable amalgams usually are oxidable anodically (*B*), as it can be deduced from cyclic voltammograms in nonaqueous[14] or aqueous[9] media. The potential of formation of the precipitate depends on the Et_4NBF_4 concentration and on the polarization rate of the large-area cathode. The effects of these two factors can be seen in Figs 3*a* and 3*b*. From the course of these dependences it can be seen that at a lower polarization rate (curves *1*) the autoinhibition effect of the highest concentration makes itself felt by a decrease of current intensity and a shift of voltage toward more negative values. At a higher polarization rate (curves *2*), obviously the electron transfer to Et_4N^+ becomes rate limiting and the concentration of electroactive compound looses its effect. Hence the formation of amalgam is a result of a slow electron transfer to the substance in absorbed state according to the gross Eq. (*A*). After precipitation of the amalgam it is necessary for pH to increase to 12, which necessitates a certain potential conditioning the rate of evolution of hydrogen. The attempt at adjusting pH and monitoring only the reduction of tetraethylammonium was not successful – additions of both NaOH and Me_4NOH caused an immediate formation of white precipitate due probably to lowered solubility of Et_4NBF_4 at this pH. On the basis of the data given, we selected the following conditions for formation of a compact precipitate: the potential of –2.4 V for potentiostatic electrosynthesis of the amalgam, the concentration of 0.5 M Et_4NBF_4, and the electrolysis time of 3 min. A prolonged electrolysis time resulted in a decrease of the

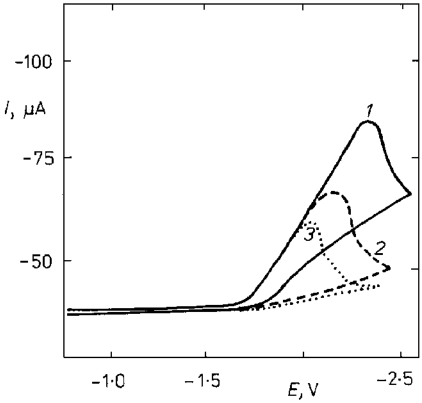

FIG. 2
Cyclic voltammograms of 0.1 M Et_4NBF_4 on mercury dropping electrode. Time of drop 2 s, delay 1 s, polarization rate 100 V s^{-1} (*1*), 20 V s^{-1} (*2*), 5 V s^{-1} (*3*)

precipitate amount, and standing of the precipitate in nitrogen atmosphere with unplugged voltage had the same result. This change in the appearance of reaction mixture probably reflects the decomposition of the amalgam by reductive splitting of Et_4N^+, and this problem was not studied any further. When isolating the amalgam from the reaction mixture we tried to avoid reactions which could complicate its analysis, hence we separated the amalgam under nitrogen (to avoid its oxidation) after a short electrolysis (to avoid its dilution by decomposition reactions).

Determination of Stoichiometric Factor x by Analysis of Amalgam Et_4NHg_x *and of Reaction Mixture after Electrolysis*

After a three-minute electrolysis of 0.5 M Et_4NBF_4 at −2.4 V, the separated black precipitate of amalgam was filtered off in a dust-free box under nitrogen. The solution after electrolysis was submitted to thin-layer chromatography and the reactant Et_4NBF_4 was only detected. Therefore we can expect that the amalgam collected by filtration represents a sample with a fixed stoichiometric ratio of $Et_4N^+ : x$ Hg corresponding to the composition of amalgam. Potential decomposition reactions of amalgam, particularly the intramolecular reductive splitting off of C_2H_5 radical, will affect the Et_4N^+ content in the amalgam rather than the content of mercury in it. Therefore we determined the content of tetraethylammonium ions in the solution after electrolysis which was lowered by transition of the ions into the precipitate. The concentration of tetrafluoroborate anion after separation of amalgam was the same as that before the electrolysis, which was found by the titration with KCl solution. Hence, the formation of Hg_x^- anion will probably induce a transition of the respective amount of Na^+ cations from the calomel electrode, the M.w. ratio of these cations (Et_4N^+ and Na^+) being approximately 5 : 1. In air, the amalgam is decomposed within about 4 min to give colloi-

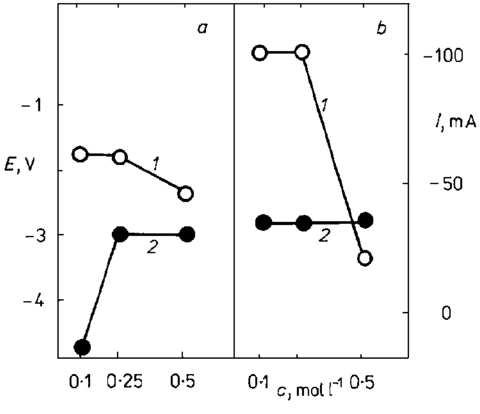

FIG. 3
Effect of Et_4NBF_4 concentration upon potential (*a*) and current intensity (*b*) of working cathode at the moment of precipitation of amalgam. The surface of working electrode 4 cm^2, volume of solution 10 cm^3, polarization rate 0.5 mV s^{-1} (*1*) or 10 mV s^{-1} (*2*)

dal mercury. The treatment of amalgam with HNO_3 and HCl produces Hg(II) whose content was determined by extraction titration. In a parallel analysis we determined the decrease of mercury in the cathode gravimetrically. Hence the analysis of amalgam was always carried out by two methods of determination of each component of this binary compound (see Experimental). The difference between the determinations of Et_4N^+ by gravimetry and by precipitation titration was 10% at the most. The difference between the determinations of mercury by gravimetry and by extraction titration was 25% at the most. If in the parallel analyses we take the highest and the lowest values of the factor x, we obtain the following values x for three samples with the best agreement between the determinations: (2.7; 2.7), (5.0; 3.0) and (2.2; 1.8). The mean value x from these data is 2.9 ± 0.8. The stoichiometric factors found in the most recent literature most often attain the value of 5 (for 6 kinds of quaternary cations[14]). The value of 4 was found for the amalgam from tetrabutylammonium[3], and the values of 4 – 5 were found for diaminoacridines in aqueous medium[9]. Lower values than the old findings of $x = 10 - 13$ are considered more correct[14], being conditioned by fulfilling of structural requirements in crystalline amalgams covering a platinum electrode by a compact layer. The composition of amalgams not deposited on an electrode but precipitated in the solution can be affected by its greater heterogeneity. It can be stated that the composition of amalgam from tetraethylammonium found in the present work is constant – on the whole – and reproducible to the extent usual with these compounds. The stability in aqueous solution is obviously given by the shift of pH to more alkaline region as a consequence of the evolution of hydrogen which proceeds in this case at more positive potentials than those of the amalgam formation proper.

The authors are indebted to Dr L. Pribyla, Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Brno for lending the Tester of oxygen, and to Dr E. Novacek, Department of Organic Chemistry, Masaryk University, Brno for the synthesis of Et_4NBF_4.

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Translated by J. Panchartek.