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On the Polarographic Behaviour of Copper Salts in Solution of Liquid Ammoniates of Ammonium Nitrate and Lithium Nitrate

Polarograficzne zachowanie się soli miedzi w ciekłych amoniakatach azotanu amonu i azotanu litu

Полярографические свойства солей меди в жидких аммиакатах азотнокислого аммония и азотнокислого лита

In aqueous solutions not containing complexing agents the cupric ion gives only one polarographic wave corresponding to the reduction $Cu^{\cdot\cdot} \to Cu^\circ$. In solutions, however, where we have complexing agents as well as cupric ions, the former may: a) give no polarographic wave at all, b) give one wave, c) give two waves.

If, after adding the complexing agent, the copper wave disappears, as happens when KCN is used, then there is formed a complex, and its reduction potential is more negative than that of the discharge potential of the supporting electrolyte. The cupric ions give one polarographic wave in the presence of these complexing agents, which, with cuprous ions, give compounds that are not too stable, e. g. tartaric acid.

Copper gives two polarographic waves in solutions of HCl and chlorides, also in tartrate and citrate solutions of pH more than 7, and also in pyridine solution and in ammonia solutions containing ammonia salts. The formation of two polarographic waves of copper in aqueous solutions $NH_3 — NH_4Cl$ is caused by two cathodic processes, the first, $Cu^{\cdot\cdot} \to Cu^\cdot$, occurring at more positive potentials and the second, $Cu^\cdot \to Cu^\circ$, occurring at more negative ones. In this case we owe the stepwise reduction to the fact that ammonia complexes of cuprous ions are stable.

Liquid ammonia dissolves many cuprous and cupric salts. L a i t i n e n and S h o e m a k e r (1), when polarographically investigating solutions of copper in liquid ammonia, found that copper gives in these conditions two equal waves, the midwave points of which, when referred to Hg pool electrode, have the value $\frac{\Pi_1}{2} = -0,15$ V and $\frac{\Pi_2}{2} = -0,52$ V. They have not studied the polarographic behaviour of cuprous salts.

In our previous papers (2, 3, 4, 5) we showed that liquid ammoniates of ammonium nitrate (Divers Liquid) and lithium nitrate may be successfully used in polarography as solvents and supporting electrolytes. Because of this fact, those liquid ammoniates may be also considered at the given temperature and pressure as saturated salt solutions in the liquid ammonia. Therefore, it is possible to use them as solvents instead of pure liquid ammonia. It is necessary to stress here that, from the point of view of non-aqueous solutions, according to Franklin's theory, liquid ammoniates of ammonium nitrate and lithium nitrate will be of a different character. $NH_4NO_3 \cdot nNH_3$, having a great concentration of positive ions ($NH_4^{\bullet}$) of a solvent (NH_3), ought to show the character of an acid, and $LiNO_3 \cdot nNH_3$ that of a neutral salt. We see this difference when considering the various activities of both ammoniates against metals.

The aim of this paper is to show whether

a) the processes of polarographic reduction of copper in the liquid ammoniates of $LiNO_3$ and NH_4NO_3 will occur analogously to the solutions of liquid ammonia,

b) we shall observe in these solvents the linear relation between the height of the copper wave and its concentration,

c) it is possible to determine in these solutions the existence of cupric salts in the presence of cuprous ones.

THE EXPERIMENTAL PART

NH_4NO_3 chem. pure, from F.O.Ch. Gliwice, was dried in a drying-oven at 110°. $LiNO_3$ was prepared by dissolving Li_2CO_3 chem. pure from F.O.Ch. Gliwice in chem. pure nitric acid, then evaporating to dryness, crystalising and drying at 200°. Anhydrous salts, prepared in such a way, were preserved in a desiccator over concentrated H_2SO_4. Gaseous ammonia, produced in F.Z.A. Tarnów, was taken from pressure steel bottles and dried by going through drying tubes, filled with pieces of solid KOH mixed with flakes of metallic sodium.

The saturation of anhydrous ammonium nitrate or lithium nitrate by ammonia took place in gas-washing flasks Schott-Gen. Jena 172 Gl, in which the outlets were secured by a mercury valve, causing the overpressure of ammonia about 10 mm Hg.

NH$_4$NO$_3$ was saturated at 0° and LiNO$_3$ at 12°. Liquid ammoniate of ammonium nitrate at this temperature corresponded to the formula NH$_4$NO$_3$ · 2,2NH$_3$ and ammoniate of lithium nitrate to the formula LiNO$_3$ · 2,9NH$_3$. Solutions of CuSO$_4$ in Diver's Liquid were prepared for the quantitative measurement in the following way: the aqueous solution of CuSO$_4$ containing 0,0028 g of copper in 1 ml was dropped, by means of a microburette, in the quantities, 0.1 ml to 1 ml into 50 ml bottles. Next, the water in the solutions was evaporated by long heating at 160°. After cooling to 0°, the bottles were filled with liquid ammoniates of ammonium nitrate or lithium nitrate. The solution of CuSO$_4$ in LiNO$_3$ · nNH$_3$ was prepared in an analogous way, by using aqueous solutions of CuSO$_4$ with 0.01 M concentration. The obtained solutions of CuSO$_4$ in ammoniates contained traces of water. As it was proved, however, the additions to 1% of water to ammoniates had no influence on the shape of polarograms.

For measurements there were used: Heyrovsky's polarograph V 301, lead accumulators, normal capillaries. As to the oscillographic measurements, there was used oscillograph RFT 1KO712 and an attachment containing an amplifying and differentiating system. The attachment was constructed by J. Matysik in the Polarographic Institute in Prague, according to the instruction of dr R. K a l v o d a. By means of this device the curves $\dfrac{dE}{dT}$ versus E were registered when using a dropping electrode. All the measurements were referred to a quiet Hg electrode. For the measurements there was taken 2—3 ml of the suitable solution of CuSO$_4$. NH$_3$ was steadily flowing over the surface of the solution. The temperature of the measurements was for the solutions of NH$_4$NO$_3$ · nNH$_3$ 0°C ± 1°C, m = 5 mg, t = 1,6 sec. The solutions of LiNO$_3$ · nNH$_3$ were polarographically measured at —18°C±1°C, m=5 mg, t = 2.5 sec.

In the case of both solutions there were obtained reproducible polarograms showing two well-shaped waves in the cathodic part (Tabl. 1 and 2). The mid-wave points of both waves had the values $\dfrac{\Pi_1}{2} = -0.19$ V and $\dfrac{\Pi_1}{2} = -0.43$ V for NH$_4$NO$_3$ · nNH$_3$ solutions, and for LiNO$_3$ · nNH$_3$ solutions $\dfrac{\Pi_1}{2} = -0.22$ V and $\dfrac{\Pi_2}{2} = -0.43$ V.

In almost every case the waves had unequal heigths. The first wave was lower than the second one, and the difference of the wave height was decreasing with the increase of CuSO$_4$ concentration. Ratios of wave heights took values from 0.5 : 1 to 1 : 1. At the concentration greater than 2.10^{-3} M CuSO$_4$, the height of the waves was almost equal,

and the second wave showed maximum increasing with the increase of $Cu^{..}$ concentration. The maxima were already damped through the adding of 0.01% gelatin solution in adequate ammoniates. The ratio $\frac{i_d}{c}$ was constant over an applied range of concentrations. In the case of solutions in liquid NH_4NO_3 ammoniate it was stated that $Cu^{..}$ concentration was proportional to the sum of the heights $h_1 + h_2$ of both waves at the range of 4.10^{-4} to 1.10^{-2} M and in the $LiNO_3 \cdot nNH_3$ solutions the height h_2 of the second wave was proportional to the concentration of $Cu^{..}$ at the range 8.10^{-4} to 4.10^{-2} M solutions. The results of the measurements are assembled in Table 1 *).

Table 1.

| 'Solvent | No. | Molar Concentration of $Cu^{..}$ | Sensitivity | Heights of waves in mm | | | |
| | | | | without gelatin | | with gelatin | |
				h_1	$h_1 + h_2$	h_1	$h_1 + h_2$
$LiNO_3 . nNH_3$	1	$8 \cdot 10^{-4}$	1:10	4	10	—	—
	2	$4 \cdot 10^{-4}$	1:10	5	13,3	5	13
	3	$9 \cdot 10^{-4}$	1:10	14	29	14.5	30
	4	$2.4 \cdot 10^{-3}$	1:10	35	70	37.5	72.5
	5	$5.25 \cdot 10^{-3}$	1:20	40	80	40	80
	6	$7.9 \cdot 10^{-3}$	1:100	12	24	12	24
	7	$1.68 \cdot 10^{-2}$	1:100	27	54	25	51
$NH_4NO_3 . nNH_3$	8	$1 \cdot 10^{-3}$	1:10	14	43	—	—
	9	$4.3 \cdot 10^{-3}$	1:150	—	13.3	—	—
	10	$8.5 \cdot 10^{-3}$	1:70	28	58	27	56
	11	$1.3 \cdot 10^{-2}$	1:150	—	38	—	37
	12	$2 \cdot 10^{-2}$	1:150	29	58	—	—
	13	$2.2 \cdot 10^{-2}$	1:150	—	62	—	—

Ammonia cuprous complexes are stable compounds, e. g. the dissociation constant of $Cu(NH_3)_2^{.}$ is $1.35.10^{-1}$. We could expect that cuprous compounds solutions in liquid ammoniates would be stable and would give a characteristic polarographic wave identical or not identical with the second wave of cuprous ions reduction. In such a case it would be possible

to determine $Cu^{..}$ and $Cu^{.}$ concentrations in a solution containing cuprous and cupric salts.

In order to prove that we are right in our opinions there were made some polarographic measurements of cuprous salt solutions CuCl, CuJ,
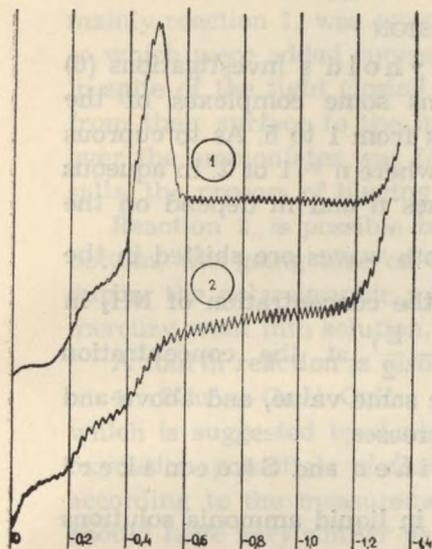
Fig. 1. Polarograms of 10^{-3} M CuSO₄ solution in $NH_4NO_3 \cdot nNH_3$ 1 — without gelatin 2 — with gelatin
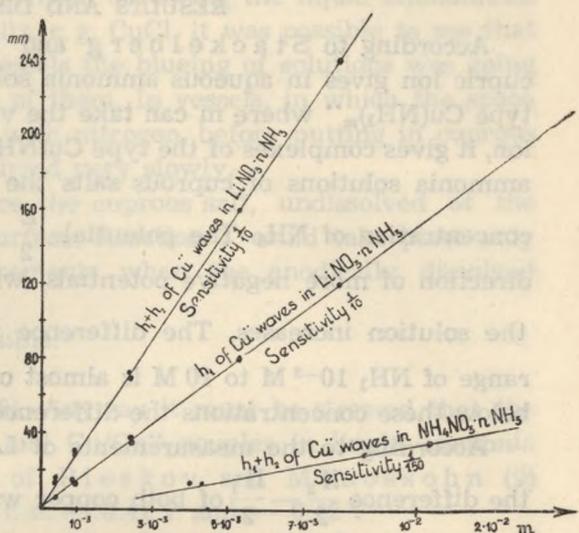
Fig. 2. Wave height - concentration relationships for $Cu^{..}$ salts solutions in $NH_4NO_3 \cdot nNH_3$ and $LiNO_3$ nNH₃

Cu(CNS) in both liquid ammoniates (c = 1.10^{-3} M). The salts used dissolved comparatively slowly and sparingly in $NH_4NO_3 \cdot nNH_3$ and $LiNO_3 \cdot nNH_3$. During dissolving the solutions became greenish, passing to blue. CuCl dissolved the most quickly (blue colour at the end); CuCNS dissolved very quickly (dirty green colour) and CuJ dissolved very slowly

Table 2.

Salt	Solvent	Supporting Electrolite	$\frac{II_2}{2}$	$\frac{II_1}{2}$	$\frac{II_1}{2} - \frac{II_2}{2}$
CuSO₄	water	1M NH₃–1M NH₄Cl	−0.24	−0.50	−0.26
CuSO₄	NH₃	(C₄H₉)₄NJ	−0.15	−0.52	−0.37
CuSO₄	LiNO₃ · nNH₃	—	−0.22	−0.43	−0.21
CuCl	,,	—	0.00	−0.24	−0.23
CuCNS	,,	—	+0.13	−0.14	−0.27
CuJ	,,	—	−0.16	−0.36	−0.20
CuSO₄	NH₄NO₃ · nNH₃	—	−0.19	−0.43	−0.24
CuCl	,,	—	−0.02	−0.26	−0.24
CuJ	,,	—	+0.01	−0.23	−0.24
CuCNS	,,	—	+0.03	−0.20	−0.23

with a light blue colour. The polarograms of the three solutions were almost identical and they showed two waves with midwave points shifted in the direction of more positive potentials.

The addition of $CuSO_4$ to these solutions did not cause the occurrence of new waves, only the increase of both previous ones.

RESULTS AND DISCUSSION

According to Stackelberg and Freyhold's investigations (6) cupric ion gives in aqueous ammonia solutions some complexes of the type $Cu(NH_3)_m^{\cdot\cdot}$ where m can take the values from 1 to 5. As to cuprous ion, it gives complexes of the type $Cu(NH_3)_n^{\cdot}$ where n = 1 or 2. In aqueous ammonia solutions of cuprous salts the values n and m depend on the concentration of NH_3. The potentials $\dfrac{E}{2}$ of both waves are shifted in the direction of more negative potentials, while the concentration of NH_3 in the solution increases. The difference $\dfrac{E_2}{2} - \dfrac{E_1}{2}$ at the concentration range of NH_3 10^{-2} M to 10 M is almost of the same value, and above and below these concentrations the difference decreases.

According to the measurements of Laitinen and Shoemaker[1] the difference $\dfrac{\Pi_2}{2} - \dfrac{\Pi_1}{2}$ of both copper waves in liquid ammonia solutions is equal to —0.37 V and in the case of both our $CuSO_4$ solutions this difference is —0.21 V for $LiNO_3 \cdot nNH_3$, and —0.24 V for $NH_4NO_3 \cdot nNH_3$. It would point not only to the smaller solvatations of ions $Cu(NH_3)_m^{\cdot\cdot}$ and $Cu(NH_3)_n^{\cdot}$ in both ammoniates, than in liquid ammonia, but also to the fact that m and n have smaller values.

The great ionic strength of the investigated solutions (Lingane (7)) would allow us to suppose that midwave potentials of copper ought to have smaller values than happens in liquid ammonia solutions yet only $\dfrac{\Pi_1}{2}$ for copper in the liquid ammoniates has the smaller value, than $\dfrac{\Pi_1}{2}$ for copper in the liquid ammonia. The second midwave point of $CuSO_4$ solution of $NH_4NO_3 \cdot nNH_3$ has a greater value, as well as in $LiNO_3 \cdot nNH_3$ than in the liquid ammonia. The fact that the addition of cupric salts to the cuprous salt solutions in both liquid ammoniates caused only the increase of both waves, was a sufficient proof that cuprous salts in the studied solutions were oxidated up to the cupric ones. The shifting of midwave points, in the direction of more positive values, was caused by the change of the potential of the quiet Hg electrode (the least changes occurred with Cl', the greatest with CNS'). The causes of oxidation may be found in three possible reactions:

1. $6Cu^{\cdot} + 3O_2 + 2NH_3 \rightarrow 6Cu^{\cdot\cdot} + 6OH' + N_2$
2. $2Cu^{\cdot} + NO_3' + 2NH_4^{\cdot} \rightarrow 2Cu^{\cdot\cdot} + NO_2' + 2NH_3 + H_2O$
3. $2\ Cu^{\cdot} + 2Hg^{\cdot\cdot} \rightarrow 2Cu^{\cdot\cdot} + Hg_2^{\cdot\cdot}$

$Hg_2^{\cdot\cdot} + 2NH_3 \rightarrow HgNH_2^{\cdot} + Hg + NH_4^{\cdot}$

No doubt the oxygen in the air was the chief oxidating agent and mainly reaction 1. was occurring. When observing the liquid ammoniates to which were added cuprous salts, e. g. CuCl, it was possible to see that in spite of the tight closing of vessels the blueing of solutions was going from their surface to the inside of them. In vessels, in which the space over the ammoniates was filled with nitrogen, before putting in cuprous salts, the process of blueing occurred very slowly.

Reaction 2. is possible because the cuprous salt, undissolved at the bottom, was going blue on its surface. Reaction 3. could take place only during the polarographic measurements, when the anodically dissolved mercury went into solution.

A fourth reaction is also possible.

4. $2Cu^{\cdot} \rightarrow Cu + Cu^{\cdot\cdot}$
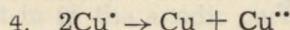
which is suggested by J o l l y (8). Anyway it must be stressed that the oxydation potentials of Cu/Cu$^{\cdot}$ and Cu/Cu$^{\cdot\cdot}$ couples in liquid ammonia according to the measurements of P l e s k o v and M o n o s s o h n (9) should have very similar values i. e. — 0.41 V and — 0.42 V.

We do not regard this problem of the behaviour of cuprous salts in both ammoniates examined as solved, and we shall come back to this theme next time. On the one hand, it seems that cuprous salts are in these conditions very little soluble, and, on the other hand, cuprous ions in the solutions used are very stably complexed.

It seems strange and difficult to explain that the heights of both waves corresponding to the successive reduction of copper ions are not equal for diluted solutions of $CuSO_4$ or cuprous salts in both ammo-niates. According to M a a s e n (10) both waves in aqueous $NH_3 — NH_4Cl$ solutions are equal, though the interpretation of polarograms is not quite convincing. K o l t h o f f (11) speaks in his book also about two equal waves of copper in these conditions. H e y r o v s k y (12), in his mono-graph on applied polarography, is of the same opinion. But the example given by him (determination of copper and zinc) seems to contradict it, for the first wave of copper is distinctly lower than the second one (Abb. 68).

Previously we tried to explain the case of the inequality of waves by migration currents, or by the different diffusion coefficients of Cu$^{\cdot\cdot}$ and Cu$^{\cdot}$ ions. In solving this problem we were helped by the microscopic observation of mercury drops, dropping from capillary dipped in aqueous solution of cupric salts. When using $CuCl_2$ solution it was possible to

see distincly that the increasing mercury drop lost its brightness. In the field of microscopic observation, we could see, that, during the dropping of mercury, there appeared little cloudlets in the solution, formerly quite clear. They were in the shape of flat rings similar to „tobacco smoke rings". Mercury gathering at the bottom of the vessel was covering itself with grey film, which did not allow the particular drops to join together. The shaking of pure mercury with solutions of $Cu(NO_3)_2$, $CuSO_4$, $CuCl_2$, $CuBr_2$ showed that all the solutions except that of copper intrate became turbid. After 12 hours shaking $CuBr_2$ solution was quite discoloured, $CuCl_2$ only partially, and $CuSO_4$ preserved its colour. In the first case the discolouring of the solution was accompanied by the formation of a yellow-green precipitate (Hg_2Br_2 + CuBr); in the second, by a white one (Hg_2Cl_2 + CuCl), and in the third there appeared white turbidity (Cu_2SO_4 + Hg_2SO_4).

So it is quite clear that we are dealing here with the reduction of

$$2\,Cu^{\cdot\cdot} + 2\,Hg \rightarrow 2\,Cu^{\cdot} + Hg_2^{\cdot\cdot}$$
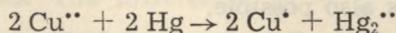
The possibility of this reaction is mentioned only by B o u s-s i g a u l t (13) in his paper on amalgamation of silver ores. This reaction, which seems to be contrary to the values of standard reduction potentials, occurs as the result of the precipitating of cuprous and mercurious salts of low solubility.

In these cases the solubility products have at 25°C the following values:

CuCl	$1.8 \cdot 10^{-7}$	Hg_2Cl_2	$2.0 \cdot 10^{-18}$
CuBr	$5.3 \cdot 10^{-9}$	Hg_2Br_2	$1.3 \cdot 10^{-21}$
Cu_2SO_4 about	$5 \cdot 10^{-4}$	Hg_2SO_4	$6.3 \cdot 10^{-7}$

Considering these data, it is clear why the apparent velocity of the formation of precipitates increases in the terms $CuBr_2$, $CuCl_2$, $CuSO_4$.

This reaction of $Cu^{\cdot\cdot}$ ions reduction by means of metallic mercury is the direct cause of the fact that, in diluted solution of copper salts, the first wave is always smaller. Because the mercury drop comes into contact with $CuSO_4$ solution, there follows an immediate partial reduction and decrease of $Cu^{\cdot\cdot}$ ions concentration.

This phenomenon probably appears in ammonia aqueous solutions as well as in the liquid ammoniates applied by us. It must be stressed that in the latter solutions reduction reactions of $Cu^{\cdot\cdot}$ ions on the drop of mercury are accompanied by dismutation of formed mercurious compounds and by the slow reaction of dissolving and oxidating cuprous salts. The primary reaction is certainly quicker than the secondary one. L a i t i n e n and S h o e m a k e r in the mentioned investigations on the polarographic behaviour of copper salts in liquid ammonia, when

working on the thermodynamic criterion of reversibility of electrode reduction,

obtained (T = 237°) for the first wave the value 0.049 V, for the second 0.066 V. According to them these values showed the reversibility of the process $Cu^{\cdot\cdot} \to Cu^{\cdot}$.

It often happens that the slope of plot $\log \dfrac{i_d - i}{i}$ versus E is in agreement with the theoretical values for reversible processes, and in spite of it the process is irreversible. Better results are achieved by means of the oscillopolarographic method used also by us. The oscillographic curves obtained, $\dfrac{\alpha\,E}{\alpha\,T}$ versus E, were photographed when using the dropping electrode. The pure liquid ammoniates of lithium and ammonium nitrate gave identical oscillopolarograms without any disturbances (Phot. 1). The oscillopolarograms of $CuSO_4$ solutions (Phot. 2 and 3) gave in the first and second ammoniates two sharp cuts-in and one cut-in in the anodic part, which showed that the process $Cu^{\cdot} \to Cu^{\circ}$ corresponding to the second wave is irreversible.

An analogous picture was given by solution CuCl in Diver's Liquid (Phot. 4). In order to make sure that our interpretation of reversibility of the first electrode process was right, there was made a set of oscillographic measurements of $CuSO_4$ solutions, to which were added increasing quantities of NH_4CNS. The received oscillopolarograms indicated a gradual disappearance of the first cathodic cut-in with a dipping and shifting of the anodic one in the direction of more negative potentials. It would show that in these conditions there occurs the decomposition of $Cu(CNS)_2$, as well in aqueous solutions. It is difficult to interpret the fact that the addition of gelatin to $CuSO_4$ solution in both liquid ammoniates is the cause of disappearance of the anodic cut-in on the oscillopolarogram (Phot. 2a).

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STRESZCZENIE

W pracy tej autorzy wykazali iż roztwory soli miedziowych w ciekłych amoniakatach NH_4NO_3 i $LiNO_3$ dają dobrze wykształcone fale polarograficzne odpowiadające procesom redukcji $Cu^{..} \rightarrow Cu^{.}$ oraz $Cu^{.} \rightarrow Cu^{\circ}$. Pierwsza z tych fal w roztworach rozcieńczonych $Cu^{..}$ 10^{-3} M jest zawsze niższa od fali drugiej. Pomiędzy sumą wysokości obu fal a stężeniem zachodzi zależność linearna. Sole miedziawe w roztworach stosowanych ciekłych amoniakatów ulegają utlenieniu i roztwory te dają analogiczny obraz polarograficzny jak sole miedziowe z tym, że $\frac{II}{2}$ obu fal są przesunięte w kierunku potencjałów bardziej dodatnich na skutek zmiany potencjału Hg elektrody spoczynkowej. To, że pierwsza fala odpowiadająca redukcji $Cu^{..} \rightarrow Cu^{.}$ jest niższa od fali drugiej, autorzy tłumaczą reakcją redukcji zachodzącą na kropli rtęci.

$$2\,Cu^{..} + 2Hg \rightarrow Cu_2^{..} + Hg_2..$$
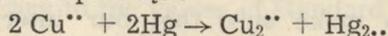
Autorzy uzasadniają słuszność tej reakcji na przykładach.

Р Е З Ю М Е

В этой работе авторы выказали, что растворы солей меди в жидких аммиакатах NH_4NO_3 и $LiNO_3$ дают хорошо образованные полярографические волны, которые отвечают восстановлению $Cu^{..} \rightarrow Cu^{.}$ и $Cu^{.} \rightarrow Cu$. Первая волна в разбавленных растворах $Cu^{..} < 10^{-3}$ M всегда является меньше другой. Между суммой высоты воли а концентрацией происходит линейная зависимость.

Соли меди одновалентной в применяемых растворах жидких аммиакатов окисляются, а растворы их дают такую же самую полярограмму как соли Cu^{++}, разница состоит только в передвижении $\frac{II}{2}$ волн в сторону более положительного потенциала вследствие изменения потенциала ртутного электрода. То, что первая волна, которая отвечает восстановлению $Cu^{..} \rightarrow Cu^{.}$ является меньше другой волны авторы объясняют происхождением реакции восстановления на капли ртути

$$2Cu^{..} + 2Hg \rightarrow Cu^{..}_2 + Hg_2^{..}$$

Авторы сущность этой реакции обосновывают примерами.
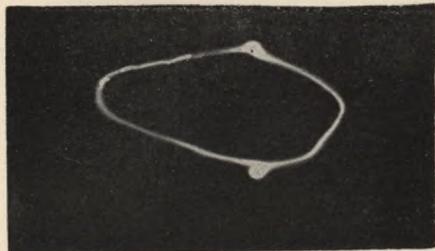
Phot. 3
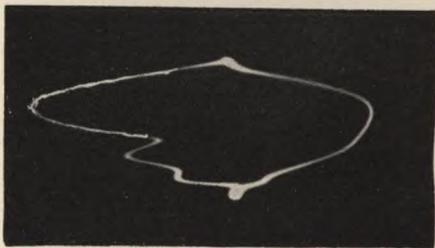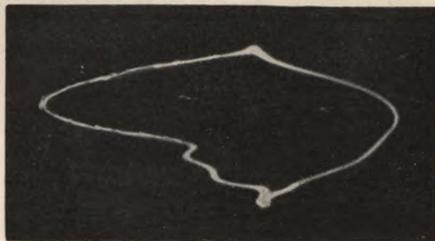
Phot. 2a
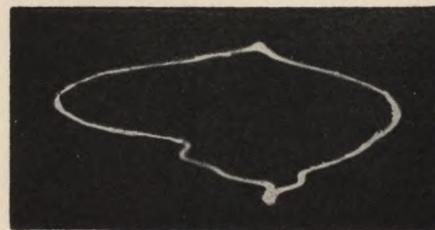
Phot. 6
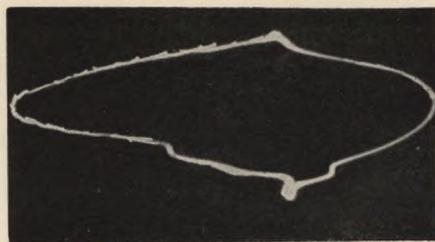
Phot. 2

Phot. 5

Phot. 1

Phot. 4

Phot. 1. pure $NH_4NO_3 \cdot nNH_3$ or $LiNO_3 \cdot nNH_3$
Phot. 2. 10^{-4} M $CuSO_4$ in $NH_4NO_3 \cdot nNH_3$
Phot. 2a. the same solution with addition of gelatin.
Phot. 3. 10^{-4} M $CuSO_4$ in $LiNO_3 \cdot nNH_3$
Phot. 4. ca 10^{-2} M $CuCl$ in $NH_4NO_3 \cdot nNH_3$
Phot. 5, 6. 10^{-4} M $CuSO_4$ in $NH_4NO_3 \cdot nNH_3$ with progressive additions of NH_4CNS

Oscillopolarograms $\dfrac{dE}{dT}$ — E. Dropping electrode

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