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Vernadskii Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow

Institute of Nuclear Physics, Moscow State University

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Some Electrochemical Properties of Mercury

E.F.Speranskaya and T.G.Pokhvalitova

The first information about the application of mercury as an electrode material dates back to the end of the 19th century[1]. At the same time it was noted that mercury is not an indifferent metal and is capable of reacting with a number of ions in solution. Further extensive application of mercury as an electrode material stimulated systematic investigation of its electrochemical properties: electrocapillary phenomena at the mercury-solution interface, equilibrium and steady-state potentials, kinetics and mechanism of the discharge-ionisation process at the equilibrium and steady-state potentials, and reducing and other properties of mercury. These questions are discussed in the present review. The bibliography comprises 65 references.

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I. ELECTROCAPILLARY PHENOMENA AT THE MERCURY–SOLUTION INTERFACE

The electrical double layer arising under equilibrium conditions at the mercury–solution interface is known to consist of anions in the liquid component, the surface of the mercury being positively charged relative to the liquid. The displacement of the potential towards negative values leads to a decrease of the concentration of anions in the double layer. On further displacement of the potential, the charge of the double layer is reversed. The change in potential and the associated charge reversal of the double layer alters the surface tension of mercury.

The first measurement of the surface tension of mercury as a function of the applied potential was made by Lippman[2] with the aid of the capillary electrometer of his design. Paschen[3] and then Gouy[4,5] made systematic studies on the surface tension of mercury as a function of the potential in solutions of different electrolytes (hydrochloric acid, sulphuric acid, nitric acid, potassium hydroxide, etc.) and determined the form of the capillary curve. In all cases the dependence of the surface tension of mercury on the applied potential was represented by a curve passing through a maximum. The maximum surface tension corresponds to the zero charge of the mercury surface. The surface tension and correspondingly the surface energy of the electrode are a maximum at this point.

Adsorption of anions displaces the electrocapillary maximum towards more negative potentials, while adsorption of cations has the opposite effect. Anions can be arranged in the same depolarising effect sequence as that of their effect on the surface tension of mercury. Thus, in the series of anions $NO_3^- < SO_4^{2-} < Cl^- < Br^- < < CN^- < S^{2-}$ their depolarising effect increases from NO_3^- to S^{2-} and the shift of the electrocapillary maximum of mercury towards negative potentials increases in the same direction.

The nature of the anion influences not only the equilibrium or steady-state potential of mercury but also the essential features of the potential-determining process. Members of the Soviet electrochemical school have played

a considerable role in the study of this problem. By deepening and extending their studies in this field, Soviet electrochemists have arrived at important conclusions concerning the nature of these phenomena and their influence on the kinetics of electrode processes.

II. EQUILIBRIUM POTENTIALS OF MERCURY

One of the most important electrochemical characteristics of mercury are the potentials of the equilibrium system comprising mercury and a solution of its ions. The potential jump at the metal–solution interface is known to be established and stabilised by the mutual compensation of two opposed processes:

$$M^0 \rightleftarrows M^{n+} + ne .$$

On the other hand the potential jump can also occur as a result of the adsorption of ions and dipolar molecules. The effect of the last process is shown when the metal ions are absent from the solution. In the presence of the metal ions an equilibrium state is established, characterised by the equality of the rates of two opposed processes. The potential of such an electrode can be calculated from the familiar Nernst formula. The simultaneous occurrence of side reactions brings the electrode to a new state, which can be called the steady state.

The first reliable data on the equilibrium potential of the system $Hg-Hg_2^{2+}$ were obtained by Brodskii[6-8]. From measurements of the e.m.f.'s of the concentration cells $Hg\,|\,Hg_2(NO_3)_2,\ c_n\,|\,KNO_3,$ sat. $|\,Hg_2(NO_3)_2,\ c_1\,|\,Hg$, he determined fairly accurately the activity coefficient of Hg_2^{2+} ions. The normal potential of the system $Hg-Hg_2^{2+}$ was calculated from the formula

$$\varphi^0 = \varphi - \frac{RT}{2F}\ln f c ,$$

where c is the concentration of Hg_2^{2+} ions and f their activity coefficient. According to Brodskii's data, the potential φ^0 of this system at 19.2°C is 0.804 V (relative to the normal hydrogen electrode).

Three potential-determining processes are usually considered for the system mercury–solution:

$$Hg^{2+} + 2e \rightleftarrows Hg^0 ,$$
$$Hg_2^{2+} + 2e \rightleftarrows 2\,Hg^0 ,$$
$$2\,Hg^{2+} + 2e \rightleftarrows Hg_2^{2+} .$$

The potential of the mercury electrode in a solution of a mercurous salt is

$$\varphi_{Hg,\,Hg_2^{2+}} = \varphi^0_{Hg,\,Hg_2^{2+}} + \frac{RT}{2F}\ln a_{Hg_2^{2+}} .$$

Expressing the ionic activity $a_{Hg_2^{2+}}$ in terms of the activity product of, for example, mercurous chloride, and the activity of chloride ions, we obtain the expression

$$\varphi_{Hg,\,Hg_2Cl_2} = \varphi^0_{Hg,\,Hg_2Cl_2} - \frac{RT}{F}\ln a_{Cl^-} ,$$

where φ^0_{Hg,Hg_2Cl_2} is the normal potential of the calomel electrode (corresponding to unit activity of chloride ions).

Thus it has come to be assumed that the system $Hg-Hg_2^{2+}$ is potential-determining for the calomel electrode. However, the equilibrium in solutions of mercurous salts in the presence of certain anions (halide, cyanide, etc. ions) is more complex than is usually assumed[10]. Ogg[11] established that, when a solution of mercuric salt is shaken with metallic mercury, divalent mercury is not quantitatively converted into the monovalent form, but the following equilibrium is set up:

$$Hg_2^{2+} \rightleftarrows Hg^0 + Hg^{2+} .$$

In the presence of a large excess of chloride, the equilibrium is displaced to the right owing to the formation of the weakly dissociated complex $HgCl_4^{2-}$:

$$Hg_2Cl_2 + 2\,Cl^- \rightleftarrows HgCl_4^{2-} .$$

Richard and Archibald[12] showed that the solubility of calomel increases in direct proportion to the square of the concentration of chloride in agreement with the above equation. It follows from this that the potential of the calomel electrode must depend on the activity of mercurous and mercuric ions and is given by the equation[10]:

$$\varphi = \varphi^0_{Hg/Hg_2^{2+},\,Hg^{2+}} + \frac{RT}{2F}\ln\frac{a^2_{Hg^{2+}}}{a_{Hg_2^{2+}}} .$$

In the presence of an excess of chloride ions, the concentrations of mercurous and mercuric ions are low and almost equal to their activities. Then

$$\varphi = \varphi^0_{Hg/Hg_2^{2+},\,Hg^{2+}} + \frac{RT}{2F}\ln\frac{[Hg^{2+}]^2}{[Hg_2^{2+}]}$$

or

$$\varphi = \varphi^{\circ}_{Hg/Hg_2^{2+},\,Hg^{2+}} + \frac{RT}{2F}\ln\frac{[Hg^{2+}]}{[Hg_2^{2+}]} + \frac{RT}{2F}\ln[Hg^{2+}] .$$

The concentration ratio $[Hg^{2+}]/[Hg_2^{2+}]$ is constant[11] and equal to 1/120. Consequently

$$\varphi = \varphi^0 + \frac{RT}{2F}\ln[Hg^{2+}],$$

i.e. the potential of the mercury electrode in a solution of a mercurous or mercuric salt must be determined by the equilibrium concentration of mercuric ions. Accordingly there should exist not three standard potentials but only one, arising in consequence of the following potential-determining process:

$$Hg^{2+} + 2e \rightleftarrows Hg_2^{2+} .$$

This type of equilibrium is also established in the presence of other ligands (Br^-, I^-, CN^-, SCN^-). The potentials of mercury in the presence of a number of complex-forming ions were measured by Tarayan and Ekimyan[13], Burriel-Marti et al.[14], Bagotskaya[15], and others.

In alkali solutions monovalent mercury forms an unstable hydroxide, which decomposes according to the equation

$$Hg_2(OH)_2 \rightleftarrows Hg^0 + HgO + H_2O ,$$
$$HgO + H_2O \rightleftarrows Hg(OH)_2 .$$

Therefore in alkaline solutions in the presence of mercurous ions the mercury electrode behaves as a metal | metal oxide electrode and its potential must be a function of the pH of the solution:

$$\varphi = \varphi^0 + \frac{0.058}{2}\lg K_1[H^+]^2 ,$$

where $K_1 = SP[Hg(OH)_2]/K_w^2$ and SP is the solubility product: $SP[Hg(OH)_2] = 1.4 \times 10^{-26}$ (see Bagotskaya[15]). Therefore

$$\varphi = \varphi_0^1 - 0.058\,pH .$$

Using the above relation, it is possible to calculate φ at different pH. The measurements have been made[10,16] with the aid of a glass electrode. As the pH increases,

the potential is displaced towards more negative values (see Table).

The variation of the potential of the $Hg-Hg^{2+}$ system with the pH is plotted in Fig. 1.[17] In the region of pH 7 in the presence of complex-forming anions (Cl^-, Br^-, I^-, SCN^-), the potential is almost independent of the pH, because these are the anions of strong acids. However, in the presence of the anion of a weak acid (CN^-), the concentration of which decreases as the pH is reduced, the potential of mercury shifts towards more positive values in the acid region, with a corresponding decrease of the reducing activity of mercury.

Variation of the mercury electrode potential* with the pH in 0.01 M mercurous nitrate solution at 20°C.

pH	Potential, V		pH	Potential, V	
	calc.	expt.		calc.	expt.
1.93	0.75	0.75	4.23	0.67	0.68
2.40	0.75	0.75	5.27	0.60	0.63
3.25	0.72	0.70	6.80	0.51	0.58

* Saturated calomel electrode.

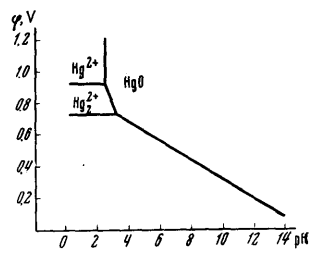


Figure 1. Effect of acidity on the oxidation-reduction potential of mercury.

Thus the equilibrium and steady-state potentials of mercury and hence its reducing properties depend to a high degree on the nature of the anion present in the solution. The effect of the anion is due to its capacity for adsorption, which is closely related to the phenomenon of complex-formation and the formation of sparingly soluble salts. The anion can influence significantly the mechanism of the oxidation of mercury. In particular, when the solution contains readily adsorbable anions (Cl^-, Br^-, I^-, etc.), the process takes place at a higher local concentration of the anions and is described by the equation

$$Hg^0 - 2e \rightleftarrows Hg^{2+}.$$

Data confirming this mechanism were obtained with the aid of non-steady-state techniques (anodic oxidation of mercury in the presence of applied constant and alternating potentials).

It has been noted[18-20] that ions adsorbed directly on the surface of mercury form mercury halides. On the other hand, in the presence of weakly adsorbed anions (NO_3^-, SO_4^{2-}) the process may be different, namely

$$2Hg^0 - 2e \rightleftarrows Hg_2^{2+}.$$

III. KINETICS AND MECHANISM OF THE ELECTROCHEMICAL OXIDATION OF MERCURY

1. Mechanism of the Anodic Oxidation of Mercury

The anodic oxidation of mercury has still been relatively little investigated. Among studies dealing with this problem, those of Ives and coworkers[21-28] and Bewick et al.[29] should first be mentioned.

The anodic oxidation of mercury has been investigated in the following ways[21-23]: (a) by studying the dependence of the potential of the mercury electrode on the amount of electricity passed through the system; (b) by recording $\varphi - t$ curves after switching off the current; (c) by recording micropolarisation curves in the intervals between current pulses in order to establish the degree of reversibility of the process; (d) by recording oscillographic $E-t$ curves with simultaneous application of alternating and constant potentials.

The anodic oxidation of mercury has been carried out[21-23] in acid (hydrochloric acid) and in neutral solutions (potassium chloride, potassium bromide, and potassium iodide) freed from atmospheric oxygen. In the study of acid solutions the polarising current density was 0.25 mA cm^{-2}. The current was interrupted after 5000 μC of electricity had been passed through. After a certain time interval the passage of current was restarted. Following the interruption of current, the variation of the potential with time was observed. Micropolarisation experiments consisted in the measurement of $I-\varphi$ curves at increasing and decreasing current densities.

The degree of reversibility was determined from the hysteresis between the ascending and descending branches of the polarisation curve or from the average slope dI/dt, which should approach infinity for ideally reversible processes.

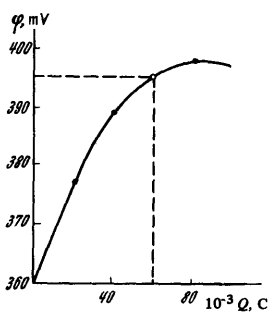


Figure 2. Variation of the mercury potential with the amount of electricity passed through the system.

The study of the dependence of the mercury electrode potential on the total amount of electricity passed through the system is of primary interest. The experimental relation[21-23] (in 0.1 N hydrochloric acid) is represented by the curve shown in Fig. 2. The measurements have shown that 6×10^{-2} C of electricity is required for the attainment of the potential of the calomel electrode (396.8 mV, 0.1 N HCl). However, if calomel were the only anodic reaction, then an incomparably smaller amount of

electricity (about 10^{-12} C) would be sufficient to saturate the entire solution (100 ml) with calomel.

Fig. 2 shows that the variation of the mercury potential with the amount of electricity passed is represented by a curve with a maximum. The potential of the maximum is more positive by 2.2 mV than that of the calomel electrode in 0.1 *N* hydrochloric acid. It has been shown[21-23] that, after the attainment of the maximum, calomel crystals are precipitated. The formation of calomel crystals is accompanied by a decrease of the potential to the value corresponding to the reversible calomel electrode. This led the authors of the above investigations to conclude that the primary product of the anodic reaction is not monovalent but divalent mercury.

The micropolarisation tests and the time variation of the mercury potential after the interruption of current confirm this view[21-23]. The observed hysteresis in the $I-\varphi$ curves disappears after a time, which suggests that the electrode attains a state of equilibrium.

$\varphi-I$ curves have two characteristic features: in the first place the potential falls slowly after the interruption of current, which suggests a slow diffusion of the potential-determining substance from the surface of the electrode; in the second place the potential is displaced towards positive values relative to that of the calomel electrode, passes through a maximum, and then falls to the potential of the calomel electrode. The authors have explained the form of the curve by the occurrence of two consecutive processes: (a) an electrochemical process—anodic generation of Hg^{2+} and (b) a non-electrical (slow but autocatalytic) process—the formation of calomel by the reaction

$$Hg^{2+} + Hg^0 \rightleftarrows Hg_2^{2+}.$$

Thus, according to these data, the product of the anodic reaction at low current densities (0.25 mA cm^{-2}) is divalent mercury; calomel forms as a result of a secondary reaction. After the attainment of equilibrium by the electrode, the reaction takes place according to the equation

$$Hg_2^{2+} + 2e \rightleftarrows 2Hg^0.$$

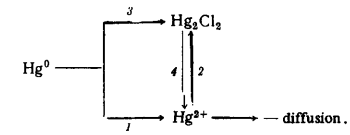
This contradicts the established view[15] concerning the nature of potential-determining processes at the equilibrium potential.

At extremely low current densities the generation of Hg_2^{2+} and Hg^{2+} ions at the equilibrium concentrations is to be expected, since the departure of the electrode from the state of equilibrium is only slight. Hg^{2+} ions arise within the double layer at a high local concentration of chloride ions, with formation of $HgCl_4^{2-}$. As a result of the formation of the complex $HgCl_4^{2-}$, prolonged cathodic polarisation following the anodic polarisation does not restore the electrode to the state of equilibrium.

Oscillographic data for this system confirm the above conclusion[21-23] concerning the mechanism of the anodic oxidation of mercury. $E-t$ curves have two peaks. The first peak is believed to correspond to the formation of Hg^{2+} ions. The rising branch of the peak comes to an end as soon as the calomel film begins to form on the surface of mercury. The horizontal section of the $E-t$ curve corresponds to the gradual coverage of the surface of mercury by the calomel film. When the coverage of the surface by calomel is complete, the discharge of chloride ions begins: the $E-t$ curve shows the corresponding rise. The chlorine liberated oxidises the calomel film, forming $HgCl^+$ ions which diffuse into the bulk of the solution. After a time the film is exhausted and the electrode returns to the non-passive state, this being accompanied by a decrease in the curve.

It has also been stated[24] that an amount of electricity greater by a factor of 10^{10} than the amount required for the saturation of the entire solution (dilute hydrochloric acid) with calomel must be passed through the mercury electrode. Under these conditions (low current density, hydrochloric acid), Hg^{2+} ions are generated. However, at a fairly high current density a small fraction of the above amount of electricity is sufficient for the attainment of equilibrium. Calomel is then generated. Such an electrode is unstable and ceases to be reversible after a short time. This spontaneous decrease of reversibility results from the disproportionation of calomel.

Thus Dibbs et al.[24] conclude that the mercury electrode can attain thermodynamic equilibrium in two different ways according to the scheme



Pathways *1* and *2* operate exclusively at low current densities, becoming superseded by pathways *3* and *4* at high current densities. An increase of the concentration of hydrochloric acid favours reactions *1* and *4*.

The problem of the kinetics and mechanism of the anodic oxidation of mercury was developed further in later investigations[25-28], where solutions containing potassium chloride, potassium bromide, and potassium iodide were studied together with hydrochloric acid. The effect of anions on the kinetics of anodic oxidation of mercury in acid and alkaline solutions has been investigated in detail[15,30,31]. Chloride, bromide, iodide, cyanide, etc. ions displace the steady-state potentials of mercury towards negative values, which must influence the rate of the anodic oxidation of mercury. Bagotskaya[15] notes that the anodic oxidation of mercury is reversible. Accordingly, the polarisation arising under these conditions is of a purely concentration type. Therefore the relation between the anodic mercury dissolution current and the potential must be represented by the equation

$$\varphi = \varphi_0 = \frac{RT}{nF} \ln \frac{I_{Hg}}{(Id)_{Hg}},$$

where φ is the standard potential of the mercury electrode at unit concentration of mercuric ions and Id is the anodic diffusion current of mercury.

Bagotskaya calculated the potential shift in the presence of various anions from the above formula having measured the anodic currents for mercury under these conditions.

The limiting mercury oxidation current depends not only on the nature of the anion but also on its concentration, which serves as a basis for its quantitative determination[32].

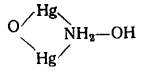
The polarisation phenomena at the dropping mercury electrode have also been investigated by Micka[33].

The kinetics of the anodic oxidation of mercury have been investigated by Elwakkad et al.[34], who demonstrated the validity of the kinetic equation

$$\partial n = AK \times \exp \frac{\alpha \varphi z F}{RT}$$

for low anodic current densities (∂n is the number of mercury atoms dissolving during time t).

The anodic oxidation of mercury in alkaline solutions has also been described[35-38]. The general conclusion that the primary product of the electrode reaction is mercuric oxide was reached. This hypothesis is supported by the finding that the mercury potential found by extrapolating the $E-t$ curves to $t = 0$ is +0.31 V and corresponds to the equilibrium potential of the Hg–HgO system. It is also interesting to note that the potentials of mercury in alkaline solutions containing suspensions of Hg_2O, HgO, and $Hg_2O.NH_2OH$ are similar. This suggests that here the potential-determining system is Hg–HgO. Then mercurous oxide and the amino-compound can be regarded as consisting of mercuric oxide and metallic mercury. Indeed X-ray diffraction analysis of "mercurous oxide" shows that this compound consists of mercuric oxide and finely dispersed metallic mercury. The amino-compounds formed when ammonia reacts with mercuric nitrate and mercurous nitrate do not have the cyclic structure



but are represented by the formula $HgO.Hg.NH_2OH$ and therefore they include mercuric oxide in their composition.

2. Kinetics of Exchange Reactions at the Mercury Electrode at Equilibrium Potentials

Measurements of the rate exchange in the system

$$Hg_2^{2+} + 2e \rightleftarrows 2Hg^0$$

at the equilibrium potential have been made by means of various non-steady-state methods[39-41]. The measurements have shown that the exchange current density for this process is high (0.4 A cm^{-2}). The authors of the investigation disregarded the ψ_1 potential because the measurements were made at a high concentration of an indifferent electrolyte. In the absence of such an electrolyte the ψ_1 potential cannot be neglected. Losev took the ψ_1 potential into account in his investigations[42-44].

According to present views, the electrochemical oxidation of a metal can take place in stages with comparable or different rates in the individual stages. It is believed that the slow stage in the oxidation of metallic mercury is $Hg_2^{2+} - 2e \rightarrow 2Hg^{2+}$, whose rate in fact determines the rate of the entire process.

The exchange currents in the system $Hg–Hg_2^{2+}$ in solutions of mercurous perchlorate, mercurous nitrate, and mercurous fluoride have been measured by the radioactive tracer method[42-44]. The exchange current was found to be 0.1 A cm^{-2}. The linear relation between the exchange current and the concentration of mercury ions in solution is thought to be evidence that the rate of the overall process is limited by diffusion. Therefore the observed exchange currents do not characterise the true rate of the electrochemical stage but the rate of diffusion of mercury ions in solution.

Losev's data are inconsistent with the results of French investigators[45-47]. The latter found that the rate of exchange is almost independent of the concentration of mercurous ions in solution and suggested that the rate of exchange is influenced by the rate of migration of mercury ions through the interface with their subsequent rapid hydration in solution and exchange by the reaction

$$Hg(aq) + Hg^{2+} \rightleftarrows Hg_2^{2+}.$$

It is believed that Hg_2^{2+} ions undergo disproportionation and the exchange takes place between hydrated atoms of metallic mercury and mercuric ions in solution.

IV. REDUCING PROPERTIES OF MERCURY

It has been established in practice that mercury has a reducing effect on a relatively large number of ions. As early as 1842, Schaffhäutel[48] showed that mercury is oxidised in the reaction with iron(III) in hydrochloric acid solution with formation of ferrous chloride and calomel. Later Borar[49] investigated the effect of mercury on certain oxidising agents and observed that their reduction is accelerated with increasing concentration of hydrochloric acid and on heating.

MacCay and Anderson[50] investigated the reduction of iron(II) with mercury and established that the reaction is quantitative. Later they studied the reduction of vanadic acid with mercury. Subsequently MacCay[51,52] discovered the conditions for the quantitative reduction of pentavalent antimony to the trivalent state. Furman and Murray[53] investigated the reduction of oxygen with mercury in hydrochloric acid solution and observed the evolution of hydrogen peroxide in this process. They also studied the reduction of molybdenum(VI) and established that the reaction leads to the formation of tri- or penta-valent molybdenum (depending on the concentration of hydrochloric acid) and calomel. Holtje and Geier[54] confirmed the above data concerning the effect of the concentration of hydrochloric acid on the extent of reduction of molybdenum(VI).

On the basis of these results, Syrokomskii and Klimenko[55] proposed a method for the determination of molybdenum in the presence of vanadium involving the reduction of molybdenum(VI) with metallic mercury.

Burriel-Marti et al.[56] studied the effect of ions forming complexes with mercury on the reducing properties of the latter and established that the presence of such ions leads to an enhancement of the reducing capacity of mercury.

According to Suranova[57], mercury reduces tungsten(VI) quantitatively to the pentavalent state.

Speranskaya and Kozlovskii[58] made a quantitative study of the reduction of a number of ions [copper(II), iron(III), selenium(IV), tellurium(IV), molybdenum(VI) etc.] with metallic mercury in different media. The experiments showed that in non-acidified solutions mercury is capable of reducing persulphate and molybdate. Other ions are reduced only in acid solutions (hydrochloric or sulphuric acid) containing added chloride.

The above data suggest that mercury is reactive with respect to many ions. In this connection, one may expect that ions interact with mercury during their electrochemical reduction at a mercury cathode.

The degree of participation of cathodic mercury in reactions of the above type can be assessed on the basis of kinetic characteristics. However, it should be noted that the kinetics and mechanism of these reactions have not been investigated. Nevertheless, having at their disposal empirical data concerning the possibility of the interaction of metallic mercury with ions undergoing polarography, some investigators have incorrectly interpreted the nature of polarographic waves[59-61]. A correct understanding of these questions requires a detailed study of the kinetics and mechanism of the reactions of metallic mercury with various ions.

The problems of the kinetics of the reactions of mercury with certain ions have been discussed[62-65].

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Kazakh State University, Alma-Ata