MECHANISM OF THE REDUCTION OF SOME OXYGEN-CONTAINING ANIONS

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For a number of years we have investigated the mechanism of the reduction of oxygen-containing anions on a dropping mercury cathode. The data obtained by one of us on the reduction of NO_3^- ions in the presence of singly, doubly and triply charged cations have already been published [1–4]. The present communication is devoted to the reduction of NO_3^- ions in the presence of $ThCl_4$ and the effect of the nature and concentration of the base electrolyte's cations and also the temperature on the reduction of BrO_3^- ions.

1. REDUCTION OF THE NO_3^- ION IN THE PRESENCE OF $ThCl_4$

An analogy was observed between the reduction of NO_3^- in the presence of $ThCl_4$ and $LaCl_3$. The polarization curves of $ThCl_4$ solutions containing KNO_3 showed jumps (Fig. 1) and hysteresis loops, but these were much narrower than in the case of $LaCl_3$ solutions. On acidification of the $ThCl_4$ solution, the NO_3^- wave was displaced toward more negative potentials (Fig. 2) and, as is known, this indicates the autocatalytic nature of this reaction. This gives grounds for considering that the mechanism whereby the current jumps and hysteresis arise, developed for the reduction of NO_3^- with $LaCl_3$ as the base electrolyte [2], is also true in principle for the case examined.

The distinguishing characteristic of the reduction of the NO_3^- ion in the presence of $ThCl_4$ was the growth of the wave with acidification of the solution. In the initial solution of $ThCl_4$, which was slightly acid due to hydrolysis, the limiting current (i_l) was considerably less than the diffusion current (Curve 1, Figs. 1 and 2). As the concentration of $ThCl_4$ (Fig. 1) or acid (Fig. 2) increased, the NO_3^- wave grew [in proportion to the amount of acid added in the latter case (Fig. 3)] and reached a limiting height. Under all conditions studied, i_l was proportional to $h^{1/2}$ (h is the height of the mercury column), which indicates its diffusion nature.

The reduction potentials of NO_3^- in the presence of $LaCl_3$ and $ThCl_4$ practically coincided; this indicates that in the presence of $ThCl_4$ the process is caused by the presence in solution of at least triply charged thorium cations. The difference in the polarographic behavior of NO_3^- in $LaCl_3$ and $ThCl_4$ solutions examined is explained by the great tendency of $ThCl_4$ to be hydrolyzed. In the reduction of NO_3^-, the pH at the electrode surface (pH_S) actually increased due to the consumption of H^+ ions, for example, by the reaction

$$NO_3^- + 8e + 10H^+ \rightarrow NH_4^+ + 3H_2O \qquad (1)$$

The rise in pH_S with an increase in cathode potential must lead to slowing and then cessation of NO_3^- reduction as a result of a fall in the charge of the thorium ions close to the electrode. The higher the acid or $ThCl_4$ concentration, the greater the current strengths which may be reached before the reduction of NO_3^- ceases. Under the given conditions, i_l must be determined by the rate of diffusion of H^+ ions to the electrode and its increase with acidification of the solution according to (1) must be 0.8 of i_d of H^+ ions, which was confirmed by experiment.

The effect of the charge of the thorium cations on the kinetics of the process in which H^+ ions do not participate was demonstrated from the reduction of the anion $S_2O_8^{2-}$ (Figs. 4 and 5). The acceleration of the process in this case is indicated by the disappearance of the specific minimum from the polarization curve. As Fig. 4 shows, acidification of the $ThCl_4$ solution led to appreciable acceleration of the process, while in the presence of $LaCl_3$ similar acidification of the solution hardly changed the polarization curve.

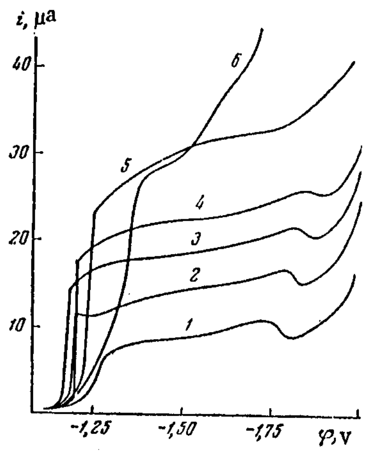

Fig. 1. Effect of $ThCl_4$ concentration on the reduction of the NO_3^- ion $[NO_3^-] = 10^{-3}$M; [KCl] = 0.1 M; $[ThCl_4]$: 1) $6.56 \cdot 10^{-4}$ M; 2) $1.3 \cdot 10^{-3}$ M; 3) $1.94 \cdot 10^{-3}$ M; 4) $2.58 \cdot 10^{-3}$ M; 5) $3.82 \cdot 10^{-3}$ M; 6) $7.35 \cdot 10^{-3}$ M. In curves 2–5 observed current jump. Hysteresis loop not shown.

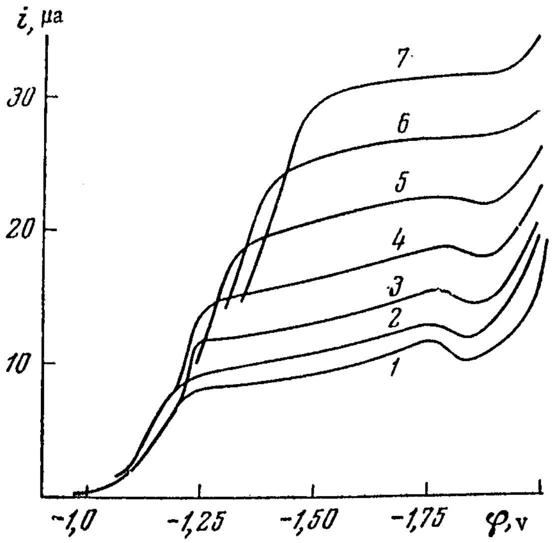

Fig. 2. Effect of HCl addition on the reduction of NO_3^- ion in the presence of 10^{-3} M $ThCl_4$. [KCl] = 0.1 M; $[KNO_3] = 10^{-3}$ M. HCl was added to give the concentrations: 1) 0; 2) $3.26 \cdot 10^{-4}$ M; 3) $9.7 \cdot 10^{-4}$ M; 4) $1.6 \cdot 10^{-3}$ M; 5) $2.24 \cdot 10^{-3}$ M; 6) $2.86 \cdot 10^{-3}$ M; 7) $3.48 \cdot 10^{-3}$M.

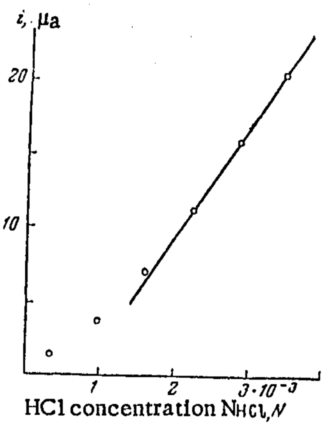

Fig. 3. Relation between the increase in i_l of NO_3^- in the presence of 10^{-3} M $ThCl_4$ and the amount of HCl added (from data in Fig. 2). The disturbance of proportionality with the addition of the first portions of acid was produced by the displacement of the hydrolytic equilibria of thorium.

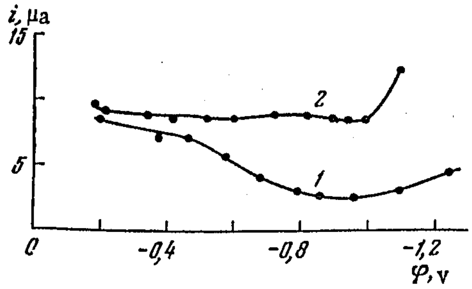

Fig. 4. Effect of pH on the reduction of 10^{-4} M $S_2O_8^{2-}$ in the presence of $1.6 \cdot 10^{-4}$ M $ThCl_4$. 1) 10^{-3} N KCl; 2) 10^{-3} N HCl.

Experiment showed that the nature of the polarization curves of NO_3^- in the presence of $ThCl_4$ depended on the previous treatment of the $ThCl_4$ solution. The data presented were obtained with a solution of $ThCl_4$, which was prepared from $Th(NO_3)_4$ by 2 to 3 evaporations to dryness with hydrochloric acid. Fig. 6 shows polarization curves of NO_3^- in $ThCl_4$ solutions prepared by solution of a sample of $ThCl_4 \cdot 8H_2O$. This case showed the following peculiarities: 1) current jumps and hysteresis were absent; 2) the wave was at more positive potentials; 3) on acidification of the solution,

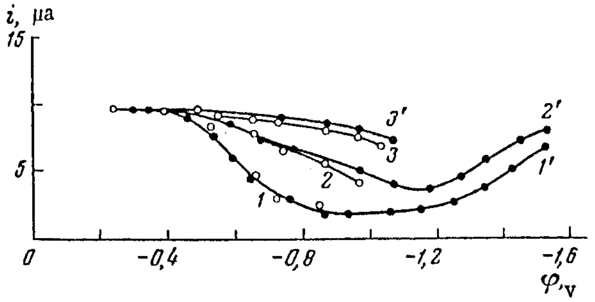

Fig. 5. Effect of pH on the reduction of 10^{-4} M $S_2O_8^{2-}$ in the presence of $LaCl_3$. 1) 10^{-5} N $LaCl_3$ + 10^{-3}N HCl; 1') 10^{-5} N $LaCl_3$ + 10^{-3} N KCl; 2) $2 \cdot 10^{-5}$ N $LaCl_3$ + + N HCl; 2') $2 \cdot 10^{-5}$ N $LaCl_3$ + 10^{-3} N KCl; 3) $3 \cdot 10^{-5}$ N $LaCl_3$ + 10^{-3} N HCl; 3') $3 \cdot 10^{-5}$ N $LaCl_3$ + 10^{-3}N KCl.

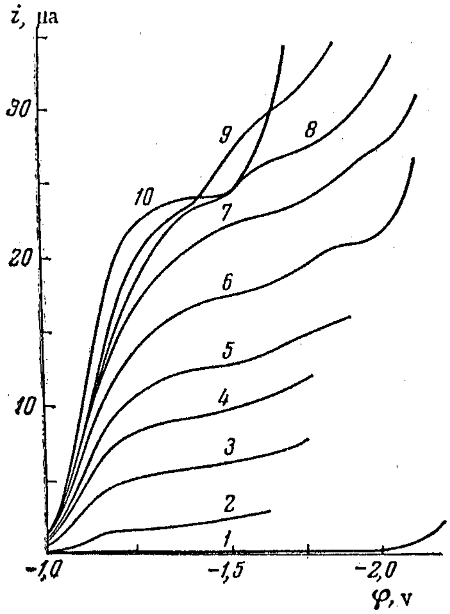

Fig. 6. Effect of the concentration of $ThCl_4$, prepared by solution of $ThCl_4 \cdot 8H_2O$, on the reduction of 10^{-3} M NO_3^-. [KCl] = 0.1 M; [$ThCl_4$]: 1) 0; 2) $3.28 \cdot 10^{-4}$ M; 3) $1.3 \cdot 10^{-3}$ M; 4) $2.25 \cdot 10^{-3}$ M; 5) $3.19 \cdot 10^{-3}$M; 6) $4.7 \cdot 10^{-3}$ M; 7) $6.2 \cdot 10^{-3}$ M; 8) $7.6 \cdot 10^{-3}$ M; 9) $1.03 \cdot 10^{-2}$ M; 10) the same + + 10^{-2} M HCl.

the position of the wave remained practically unchanged up to 10^{-2} N HCl. A displacement of the NO_3^- wave in a negative direction was observed only at higher acid concentrations. The reasons for the different behavior of the NO_3^- ion in $ThCl_4$ solutions of different origin deserve further study. It seems to us that available data indicates that the reason for this lies in the higher charge of thorium cations in solutions prepared by solution of $ThCl_4 \cdot 8H_2O$.

Curve 9 (see Fig. 6) shows two NO_3^- waves of which the second disappeared with sufficiently strong acidification of the solution. The value of i_d of the sum of the two NO_3^- waves was approximately equal to i_d of NO_3^- with $LaCl_3$ as base electrolyte. Since the ratio of the heights of the NO_3^- waves in the presence of $ThCl_4$ and $LaCl_3$ also coincided approximately, the first NO_3^- wave should be ascribed to the reduction of NO_3^- to hydroxylamine and the second, to the reduction of hydroxylamine to ammonia. Apparently, in the presence of $ThCl_4$, undissociated NH_3O molecules are reduced to ammonia more readily than NH_3OH^+ cations and, due to this, the second NO_3^- wave disappears on acidification of the solution. Hydroxylamine was detected in an acid solution of $ThCl_4$, containing NO_3^-, after prolonged electrolysis at potentials at which NO_3^- is reduced [6].

Data analogous to those presented in Fig. 6 were obtained by A. M. Vasil'ev and V. I. Gorokhovskaya-Proukhina in acid solutions of $ZrO(NO_3)_2$ [5]. The authors considered the NO_3^- wave as a catalytic hydrogen wave because it increased in proportion to the concentration of H^+ ions and it was not observed in the absence of NO_3^- ions.

2. REDUCTION OF THE BrO_3^- ION*

At pH > 5 in the presence of singly and doubly charged cations, BrO_3^- gave one wave corresponding, as microcoulometric measurements showed, to the irreversible reaction

$$BrO_3^- + 6e + 3H_2O \rightarrow Br^- + 6OH^-. \tag{2}$$

The nature and concentration of the base electrolyte had a considerable effect on the kinetics of this process.

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* These data were presented in detail in two articles sent to the Journal of Physical Chemistry, Academy of Sciences USSR.

When the concentration of the base electrolyte (c) was increased and also on going from LiCl to CsCl at a given concentration, $\varphi_{1/2}$ became less negative. A linear relation was found between $\varphi_{1/2}$ and lg c.

The rate of BrO_3^- reduction was independent of pH at pH > 5.

In acid solutions, together with the wave already described, another one was observed at much less negative potentials. With a large excess of H^+ ions, i_l of this wave was proportional to the BrO_3^- concentration. The value of $\varphi_{1/2}$ was independent of the BrO_3^- concentration, indicating that the reaction was first order with respect to the BrO_3^- ion. With an increase in the acid concentration, $\varphi_{1/2}$ became more positive according to a semilogarithmic law. With excess BrO_3^-, the wave height was proportional to the concentration of H^+ ions. In this case $\varphi_{1/2}$ was independent of acid concentration (indicating that the reaction was first order with respect to H^+ ions), but became more positive with an increase in the BrO_3^- concentration.

All these phenomena may be explained satisfactorily according to the theory of slow discharge, taking into account the structure of the electrical double layer, with the assumption of equiponderant formation of electrically active ion pairs:

$$Me^+ + BrO_3^- = [Me^+ \ldots BrO_3^-] \tag{3}$$

or equiponderant formation of undissociated acid molecules, capable of ready reduction at the cathode:

$$H^+ + BrO_3^- = HBrO_3. \tag{4}$$

It can be shown that the semilogarithmic relation between $\varphi_{1/2}$ and the base electrolyte concentration at pH > 5 or on the H^+ ion concentration at pH < 5 agrees with this theory. The equations from the theory of slow discharge, applied to this case, give the number of cations incorporated into the ion pairs. It was found that over the range of base electrolyte concentrations investigated, the ion pairs had the simplest composition (3).

The large difference between the kinetics of BrO_3^- ion reduction in neutral and acid solutions also indicates that in the first case there is discharge of ion pairs and in the second, of undissociated acid molecules.

The acceleration of the process at pH > 5 in going from LiCl to CsCl, noted above, agrees with the data of Grahame [7], according to which the differential capacity of a mercury electrode with a negative charge on the surface increases in the series $Li^+ \rightarrow Cs^+$. This indicates that Cs^+ is closer to the electrode surface than Li^+ or, in other words, there is a displacement of the φ_1-potential in a positive direction on going from Li^+ to Cs^+.

At pH >5, a rise in temperature produced an increase in i_l of BrO_3^- and a displacement of the wave toward more negative potentials. The current strength at a given potential decreased in the presence of singly charged cations and increased in the presence of doubly charged cations. These data apparently cannot be interpreted unequivocally since the potentials cannot be referred to the reversible oxidation-reduction potential of BrO_3^-/Br^- as the latter is not known with sufficient accuracy and were measured relative to a normal calomel electrode at the same temperature as the polarizable electrode. Only certain conjectures may be made on the basis of these data. Since BrO_3^- ions are reduced with a high overvoltage (η) in the presence of singly charged cations, then the activation energy of the process according to

$$A = A^0 - \eta\alpha F \tag{5}$$

is considerably reduced. In this case, the fall in concentration of the ion pairs due to their dissociation probably has a determining effect when temperature is raised. It is possible that in the presence of doubly charged cations, the importance of the change in activation energy prevails since the process proceeds with a lower overvoltage in this case.

APPENDIX

If the hypothesis that the accelerating action of the OH^- ion on the reduction of NO_3^- in the presence of La^{3+} is explained by a displacement of the equilibrium $NO_3^- + OH^- \rightleftharpoons HNO^{2}{}_{4}^{-}$ to the right under the action of La^{3+} [1] is correct, then one would expect that the addition of lanthanum nitrate to an aqueous solution would accelerate the exchange of O^{18} between water and nitrate.

Some data on isotope exchange between H_2O^{18} and KNO_3, which were obtained in cooperation with V. N. Vasil'ev, are presented in the table. The exchange was carried out in sealed quartz ampoules for 3 days at 150°. 2 g of H_2O^{18} and 1 g of KNO_3 was used for each experiment. The degree of exchange was calculated from the results of mass spectral analysis of the oxygen liberated by thermal decomposition of the salt after the experiment.

As can be seen from the table, the addition of $LaCl_3$ produced considerable exchange of O^{18} between H_2O^{18} and KNO_3. With acidification in the presence of $LaCl_3$, the degree of exchange increased strongly and reached almost 100%, while with the addition of alkali, it decreased.

Data on the Exchange of O^{18} Between H_2O^{18} and KNO_3 in the Presence of $LaCl_3$

Concentration, M			Degree of exchange, %
$LaCl_3$	HCl	KOH	
—	—	—	0
0,816	—	—	31
0,780	$3{,}6 \cdot 10^{-3}$	—	90
0,625	$1{,}8 \cdot 10^{-2}$	—	96
0,780	—	$2{,}8 \cdot 10^{-3}$ *	29
0,625	—	$1{,}4 \cdot 10^{-2}$ *	26

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* Precipitates were formed.

The acceleration of exchange on the addition of $LaCl_3$ seemed to confirm the hypothesis at first. However the results of experiments with the addition of acid and alkali contradicted this. It is most likely that the action of acid consists of the formation of free HNO_3 and the more rapid exchange of the latter with water. The effect of the addition of alkali may be explained by a reduction in the charge of the lanthanum ions [1]. However, it is possible that the hydrolysis of $LaCl_3$ proceeded so far at 150° that the alkali added was actually consumed in neutralization of the free acid.

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