

The value thus found for the concentration is substituted in Eqn. (4):

$$V = -\Delta\varphi_c - A \int_0^l \frac{dy}{L_1 + (c_0 - L_1)/\sqrt{\pi D\tau} \int_0^y \exp(-u^2/4D\tau) du} + \\ + B \int_0^l \frac{\text{grad} \{L_1 + (c_0 - L_1)/\sqrt{\pi D\tau} \int_0^y \exp(-u^2/4D\tau) du\} dy}{L_1 + (c_0 - L_1)/\sqrt{\pi D\tau} \int_0^y \exp(-u^2/4D\tau) du} \quad (10)$$

We divide the integration range into two parts: $0 \leq y \leq \delta$, the region of variable concentration, and $\delta \leq y \leq \infty$, the region of constant concentration. Since y varies between limits which are far smaller than unity, the integral with respect to u in the denominator of Eqn. (10) can be approximated to a linear relation, so that Eqn. (10) becomes

$$V = -\Delta\varphi_c - A \left[\int_0^\delta \frac{dy}{L_1 + (c_0 - L_1)y/\sqrt{\pi D\tau}} + \int_\delta^l \frac{dy}{L_1} \right] + B \ln \frac{c_0}{L_1} \quad (11)$$

We replace $-Al/c_0$ by $\Delta\varphi_{ohm}^2$, the ohmic resistance of a column of liquid electrolyte equal in height to the distance between the electrodes. After integration of Eqn. (11) with respect to y we then obtain

$$V = -\Delta\varphi_c + \Delta\varphi_{ohm}^2 - \frac{A\sqrt{\pi D\tau}}{c_0 - L_1} \ln \frac{c_0}{L_1} + B \ln \frac{c_0}{L_1} \quad (12)$$

This relation is of interest on its own account. It can be utilised to find the concentration at the electrode surface of the substance undergoing discharge. In order to obtain an explicit relation, Eqn. (12) must be solved for L_1 , which, however, is difficult with the form in which the equation is given. It can readily be done after the logarithm has been expanded in a series.

On the other hand, if the polarisation accompanying electrolysis is due to concentration effects, the concentration at the electrode surface can be determined from the Nernst equation:

$$c_{y=0} = L_1 = c_0 \exp \left(-\frac{\Delta\varphi F z_c}{RT} \right) \quad (13)$$

Eqn. (12) together with (13) becomes after simple rearrangement

$$V = -\Delta\varphi_c + \Delta\varphi_{ohm}^2 - \Delta\varphi \left\{ \frac{i\sqrt{\pi D\tau}}{F z_c c_0 (z_c D_c + z_a D_a) [1 - \exp(-\Delta\varphi F z_c / RT)]} - \frac{(D_c - D_a) z_c}{z_c D_c + z_a D_a} \right\} \quad (14)$$

Eqn. (14) can be simplified by assuming that at high polarisation potentials limiting-current conditions ensue.

As the polarisation potential in Eqn. (14) tends to infinity, i.e. as $\Delta\varphi \rightarrow \infty$, Eqn. (14) acquires, with the transformations carried out in Ref. 9, a form which is very simple for practical applications:

$$\frac{i}{i_{lim}} = \left[1 - \exp \left(-\frac{\Delta\varphi F z_c}{RT} \right) \right] \left[1 - \frac{V + \Delta\varphi_c - \Delta\varphi_{ohm}^2}{\Delta\varphi} \right] \quad (15)$$

Bearing in mind Eqn. (3), we obtain

$$i/i_{lim} = \left[1 - \exp \left(-\frac{\Delta\varphi F z_c}{RT} \right) \right] \left[1 - \frac{\Delta\varphi_{ohm}^2}{\Delta\varphi} \right] \quad (16)$$

If the expression $i/i_{lim} [1 - \exp(-\Delta\varphi F z_c / RT)]$ is plotted against $1/\Delta\varphi$, the value of $\Delta\varphi_{ohm}$ can be estimated from the slope.

The form of Eqn. (16) is identical with that obtained in Ref. 9 for electrolysis with a rotating disc electrode.

I express my gratitude to Professor S. V. Gorbachev for his interest in this work.

SUMMARY

1. The theoretical method suggested previously for calculating concentration polarisation with allowance for the ohmic factor has been applied to the case of a plane electrode operating under non-stationary conditions of electrolysis.
2. The ohmic potential in the region of variable concentration can be estimated [Eqn. (16)].

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Received 10th July 1961

EFFECT OF THE ADSORPTION OF SURFACE-ACTIVE IONS ON THE REDUCTION OF IRON-GROUP METALS AT A DROPPING MERCURY ELECTRODE

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It has been shown¹ that the rate of reduction of iron-group metals at a dropping mercury electrode with inert salts as supporting electrolyte and the degree of reversibility of the process depend on the nature and concentration of the supporting electrolyte, the pH of the solution, and the concentration of ions of the reducible metal. It has also been shown that the reduction becomes more reversible in the presence of concentrated CaCl_2 solution. It was suggested that the cause of this decrease in polarisation was the formation of readily deformable complexes with the Cl^- ions. Investigation of the reduction products of these metals revealed that they form microcrystals on the mercury surface, the wettability of which by the mercury depends on the electrode potential, the pH of the solution, and the nature and concentration of the supporting electrolyte. The aim of the present work was to study the effect of the specific adsorption of surface-active ions and

of the magnitude of the ψ_1 potential on the kinetics of the discharge of iron-group metals and the nature of the products formed by their reduction at the dropping mercury electrode.

Fig. 1 (curve 1) illustrates the variation of $\varphi_{1/2}$ for the reduction of ferrous ions with the concentration of CaCl_2 : between 0.01 *N* and 2.0 *N* the values of $\varphi_{1/2}$ become more negative, but at 2–10 *N* a considerable shift to more positive potentials is observed. Similar curves occur with Ni^{2+} and Co^{2+} . The half-wave potentials $\varphi_{1/2}$ for Fe^{2+} , Co^{2+} , and Ni^{2+} in 10 *N* CaCl_2 are respectively -1.125, 0.9, and -0.48 V (relative to the saturated calomel electrode).

The same diagram shows for comparison the variation with CaCl_2 concentration of $\varphi_{1/2}$ for the reduction of hydrogen ions (curve 2). Experiments show that the shift in $\varphi_{1/2}$ for Fe^{2+} and H^+ towards positive potentials increases in concentrated solutions in the sequence CaCl_2 , CaBr_2 , CaI_2 . With both these cations in 9 *N* CaCl_2 , $\varphi_{1/2} = -0.8$ V relative to the saturated calomel electrode. The limiting current falls considerably with increasing concentration of the supporting electrolyte, because of the increased viscosity of the latter. In order to determine the effect of the concentration of the supporting electrolyte on the degree of reversibility of the reduction, $i-t$ curves were obtained covering the life of a mercury drop at different potentials (along the polarographic wave). These curves were determined for the dropping mercury electrode by means of a TsLA-01 oscillographic polarograph. If the rate of the electrode process is determined by its kinetics, the current at the dropping mercury electrode is directly proportional to the drop time raised to the power 2/3, whereas a diffusion-controlled process would give a corresponding exponent of 1/6. The values obtained in 1 *N* KCl varied from 0.625 in the lower part of the wave to 0.26 at potentials corresponding to the limiting current. In 10 *N* CaCl_2 the exponent was 0.345 at the start of the wave, indicating a considerably greater reversibility of the electrochemical stage of the process. At the half-wave potential the exponent of t has already become 0.2.

The occurrence of these processes accompanied by the adsorption of halide anions and a surface-active cation, for example tetrabutylammonium (TBA), is of interest. From Fig. 2 (curves 1 and 2) it is seen that the presence of TBA in 1 *N* KCl appreciably retards the reduction of Fe^{2+} ions.

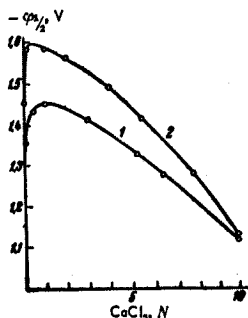


Fig. 1. Effect of calcium chloride concentration on the reduction of (1) Fe^{2+} ions (2×10^{-3} *N*) and 2) hydrogen ions (10^{-3} *N*).

At the desorption potential of TBA (-1.54 V²) the current increases suddenly to values corresponding to the limiting diffusion current. In 10 *N* CaCl_2 the retardation by the TBA of reduction has a different character (Fig. 2, curves 3 and 4), the limiting Fe^{2+} reduction current being almost completely suppressed; a sharp maximum arises on the $i-\varphi$ curve in the region of the desorption potentials of TBA. With 0.002 *N* Fe^{2+} and 0.001 *N* TBA in 10 *N* CaCl_2 the height of the peak reaches almost 100 μA , whereas the diffusion current for the reduction of iron in the absence of TBA is 2 μA : *i.e.* the current has increased by a factor of about 50. The broken parts of curves 4 and 5 (Fig. 2) indicate the region in which the current drops from the maximum, where measurements of current and potential are difficult. The fall from the peak terminates at potentials of -1.6 to -1.7 V depending on the TBA concentration. The height of the maximum is also proportional to the latter concentration. On acidification of the solution (to pH 3) the peak is somewhat lowered (Fig. 2, curve 5). A current maximum appears on the $i-\varphi$ curves in the reduction of Ni^{2+} too, but it begins at somewhat more positive potentials than in the case of Fe^{2+} , the drop which follows the maximum terminating at the same potentials as with iron. In the case of the reduction of hydrogen ions in the presence of TBA in 10 *N* CaCl_2 as supporting electrolyte, the wave has the normal form, but $\varphi_{1/2}$ is displaced by the addition of TBA about 100 mV towards more negative potentials. No maximum current then arises.

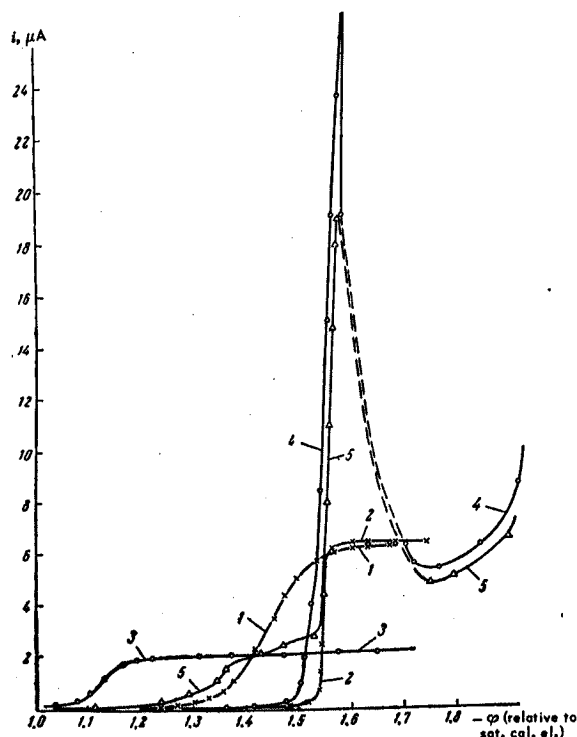


Fig. 2. Effect of tetrabutylammonium (TBA) bromide on the kinetics of the reduction of Fe^{2+} ions (2×10^{-3} *N* in all cases): 1) 1.0 *N* KCl , pH = 5.5; 2) 1.0 *N* KCl , 10^{-3} *N* TBA; 3) 10 *N* CaCl_2 , pH ~ 5; 4) 10 *N* CaCl_2 , 0.3×10^{-3} *N* TBA; 5) 10 *N* CaCl_2 , 0.3×10^{-3} *N* TBA, pH ~ 3.

In order to investigate the reasons for the occurrence of a current maximum, $i-t$ curves for the dropping mercury electrode were obtained at potentials in the neighbourhood of the maximum. Figs. 3a and 3b illustrate such curves for the discharge of Fe^{2+} and Ni^{2+} ions respectively in the presence of TBA. The difference in the form of the curves for the two metals can be explained by a difference in TBA concentration. The $i-t$ curves have roughly the same shape at equal concentrations of TBA and identical concentrations of Fe^{2+} and Ni^{2+} . It can be seen from the curves that two successive processes are occurring: inhibition of reduction of the metal with the appearance of a maximum current due to hydrogen and the transition of the curves into their usual form following the fall after the maximum. A photomicrograph of a hanging mercury drop taken at the peak potential shows copious hydrogen evolution. At more negative potentials the evolution of hydrogen gradually ceases. No decrease in the drop time or acceleration in the movement of the drop surface and the layer adjacent to the electrode is observed with a dropping mercury electrode at the peak potential.

The results can be completely explained by taking into account the effect of the supporting electrolyte and TBA ions on the structure of the double layer, the kinetics of the process, and the nature of the reduction products of the metals. The observed variation in $\varphi_{1/2}$ with the concentration of the supporting electrolyte (see Fig. 1) can be explained by the fact that the growth of polarisation with increase in concentration in dilute solutions of the latter up to 2 N is caused by a decrease in the negative value of the ψ_1 potential due to a decrease in diffuseness of the

double layer; with further increase in the concentration of the supporting electrolyte, increased specific adsorption of halide ions becomes effective, leading to an increase in the negative values of the ψ_1 potential and hence a considerable diminution in polarisation³. These ideas are confirmed by the similarity between curves 1 and 2 for the reduction of iron and hydrogen, since in the latter case the decrease in polarisation under the given conditions can be caused only by the factors indicated above. In addition to these, the formation of easily deformable complex ions may, as mentioned above, play some part in the diminution of polarisation, which is indirectly supported by the increase in the transfer coefficient α from 0.33 in 1 N KCl to 0.56 in 10 N CaCl_2 in the case of iron, whereas α remains practically unchanged (0.5–0.48) for the reduction of hydrogen ions.

The effect of the TBA cation in dilute solutions of inert salts on the retardation of the electrode reaction can be explained on the basis of views put forward in Ref. 4. In very concentrated solutions of inorganic salts the adsorption of TBA cations is substantially increased with the formation on the electrode surface of a dense film which is practically impervious to bivalent cations, in agreement with the conclusions in Ref. 5. At fairly negative potentials (–1.5 V) the compact TBA film is partly desorbed, which makes it possible for the metal ions to penetrate to the electrode, leading to some increase in their reduction current. The further growth of the current and the occurrence of a maximum can be explained by supposing that, under the conditions of partial desorption of TBA, practically no wetting of the microcrystals of the deposited metal by the

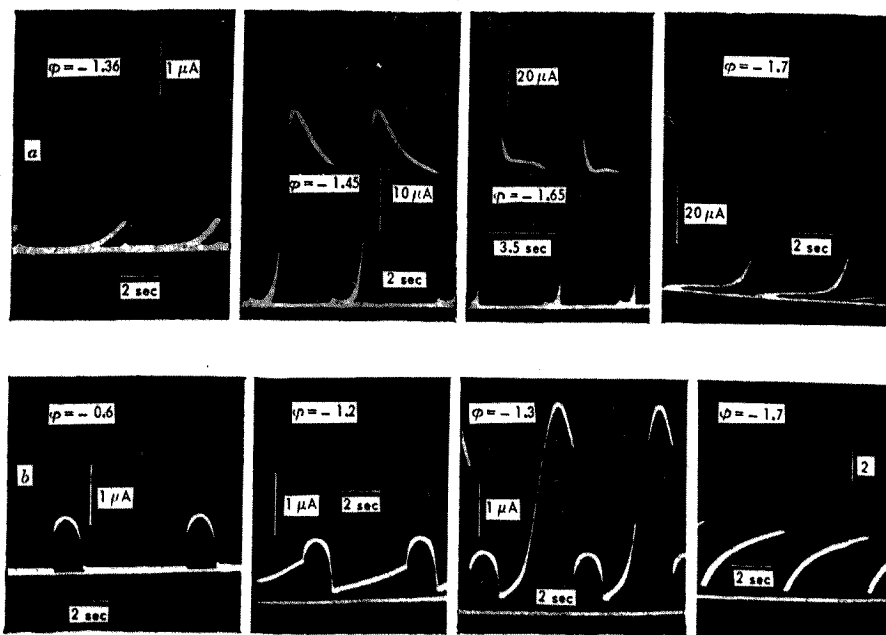


Fig. 3. Change in the shape of $i-t$ curves with variation in potential along the polarographic wave for the reduction of Fe^{2+} and Ni^{2+} in the presence of the tetrabutylammonium (TBA) ion in 10 N CaCl_2 : a) 2×10^{-3} N Fe^{2+} + 10^{-3} N TBA; b) 2×10^{-3} N Ni^{2+} + 0.3×10^{-3} N TBA.

mercury takes place. The lower hydrogen overpotential for the dispersed iron compared with its value for mercury results in the flow of a catalytic hydrogen reduction current at potentials between -1.5 and -1.7 V and the development of a maximum on the $i-\varphi$ and $i-t$ curves. The water molecules act as proton donors in this process, since the diffusion of hydrogen ions in a solution of pH 5 cannot provide the currents observed at the peaks.

The slight decrease in the height of the peak on acidification of the solution (Fig. 2, curve 5) is apparently associated with an increase in polarisation on reduction of the metal and with better wetting of the metal microcrystals by the mercury¹.

After the potential has reached -1.65 V, the TBA film is completely removed, and it becomes possible for the metal microcrystals to be amalgamated. The catalytic-current maximum disappears. In dilute solutions of supporting electrolyte no catalytic current of the above type is observed, since the microcrystals of the metal are readily amalgamated at high polarisation. If reduction of the metal at the dropping mercury electrode is carried out in the absence of TBA and at low polarisations, the deposited microcrystals are apparently readily passivated¹. This on the one hand prevents their amalgamation, and on the other considerably diminishes their catalytic activity with respect to hydrogen evolution.

The authors express their gratitude to Academician A. N. Frumkin for constant interest in the work and for valuable advice.

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Received 11th July 1961

HEATS OF COMBUSTION OF SOME ANHYDRIDES†

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The heats of combustion of the following anhydrides have been determined in a massive isothermal microcalorimeter of our own design¹: seryl seryl, valyl alanyl, glycyl phenylalanyl, glycyl tyrosyl, valyl leucyl, alanyl phenylalanyl,

† The Russian nomenclature in naming these compounds has been retained although they are in fact 2,5-dioxopiperazine derivatives of the amino-acids (Ed. of Translation).

TABLE 1.

Anhydride	N content		M.p., °C		References
	calc.	found	found	published value	
Seryl seryl	10.34	10.19	—	—	2
Valyl alanyl	16.18	16.27	246	245	3
Glycyl phenylalanyl	13.66	13.71	280	281	4
Glycyl tyrosyl	—	—	—	—	2
Valyl leucyl	13.20	13.30	274	271—273	5
Alanyl phenylalanyl	—	—	—	—	6
Valyl phenylalanyl	11.39	11.50	247—248	246—247	7

TABLE 2.

Anhydride	$-\Delta H_c$, kcal mole ⁻¹	Anhydride	$-\Delta H_c$, kcal mole ⁻¹
Seryl seryl	698.6 ± 0.2	Valyl leucyl	1568.1 ± 0.1
Valyl alanyl	1107.7 ± 0.2	Alanyl phenylalanyl	1517.9 ± 0.6
Glycyl phenylalanyl	1361.9 ± 0.4	Valyl phenylalanyl	1837.7 ± 0.9
Glycyl tyrosyl	1322.0 ± 0.1		

and valyl phenylalanyl¹. The weight of material used in a calorimetric experiment was ~20 mg. The amount of water in the bomb was 0.1 g, the oxygen pressure 30 atm, and the volume of the bomb 8.2 ml. The heat of combustion of the benzoic acid which we used to calibrate the calorimeter was taken as 6319.0 cal g⁻¹ (1 cal = 4.1840 J). Data on the anhydrides are listed in Table 1.

All the anhydrides were recrystallised from alcohol and water, and chromatographed in the butanol-water-acetic acid (4:5:1) solvent system. They were developed on the chromatogram with benzidine. All the anhydrides were chromatographically pure.

The results of the determinations (repeated three times) of the heats of combustion of the anhydrides are given in Table 2.

SUMMARY

The heats of combustion have been determined of seven anhydrides — seryl seryl, valyl alanyl, glycyl phenylalanyl, glycyl tyrosyl, valyl leucyl, alanyl phenylalanyl, and valyl phenylalanyl.

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† The seryl seryl and glycyl tyrosyl preparations were kindly provided by A. A. Akimova, a member of the scientific staff of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.