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Double-Layer Effect in the Polarographic Reduction of Vanadate

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The effect of inert electrolytes on the polarographic reduction of metavanadate ions is studied in neutral solutions, buffered and unbuffered. The effect of the nature of the cation and anion of the supporting electrolyte, as well as the effect of the ionic and buffer strength on the shape of the polarographic wave is in accordance with modern theories of the mechanism of the reduction of negative ions at the dropping mercury electrode. An accelerating action in the series $Li^+ < Na^+ < Cs^+$, and $Na^+ < Ca^{2+}$, and of anions: I^-, $SCN^- < Cl^- < NO_3^- < ClO_4^- < SO_4^{2-} < F^-$ is found. A combined influence of the cation and anion is established as well. The inhibition, occurring at the beginning of the electrode reaction and observed in the form of a small prewave on the polarographic wave is described.

Investigations of the polarographic behaviour of ammonium metavanadate in buffer solutions[1-3] have shown that in the range of *p*H from about 3 to 9 the current-voltage curves display a decrease of the current, causing a dip or a minimum in the polarogram[1] (Fig. 1). Filipović and co-workers[1] have found that foreign salts influence the height and the shape of the current-voltage curves of metavanadate in phosphate and borate buffers. Subbaraman and Shetty[3], investigating polarographic minima in metal-triphosphate complexes, have shown that large cations such as caesium and tetrabutyl ammonium tend to suppress the minima of vanadium in the order of their adsorbability on the dropping mercury cathode. The formation of similar polarographic minima on the current-voltage curves of certain polarographically reducible cationic and anionic species have been reported and many theories have been proposed to explain these minima[4,5]. The theory advanced by Frumkin[6] has found general acceptance. According to this theory, the double-layer at the electrolyte-electrode interface influences the kinetics of the electrochemical reactions. A very detailed study of the double-layer effects in the polarographic reduction of chromate ion and other depolarizers was published by Gierst and coworkers[7-9]. Žutić and Branica[10] recently reported on the results of investigations of the double-layer effect on the polarographic reduction of uranyl peroxodicarbonato ion. D. Elliott[11] studied the effect of the double-layer structure on the electrode kinetics of the vanadium perchlorate system.

Results obtained up to now[1] in investigations of the polarographic behaviour of vanadate in phosphate buffers and the similarity of behaviour of other anions justify the conclusion that the peculiar shape of the current-voltage curves of ammonium metavanadate is a consequence of the double-layer effect. Therefore, systematic investigations of the influence of the concentration and composition of the supporting electrolyte on the polarographic reduction of vanadate in buffer solutions of constant *p*H have been performed. A neutral solution of *p*H 7 was chosen because previous results of investigations have shown[1] that polarographic minima and peaks on the current-voltage curves are very well expressed near this *p*H. The following reactions are probably proceeding at the dropping mercury electrode (Fig. 1):

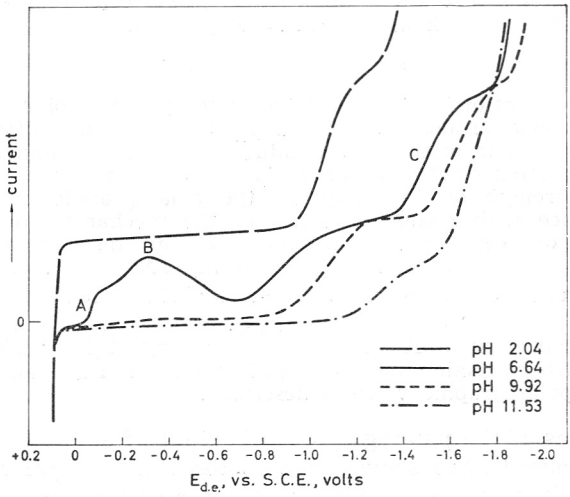

Fig. 1. Polarographic waves of 1 m*M* ammonium metavanadate in 0.2 *M* phosphate buffers: *p*H, 2.04, 6.64, 9.92, and 11.53[1].

wave (A): adsorption wave

wave (B): unbuffered solution:

$$VO_3^- + 2\,H_2O + e^- \rightarrow VO^{2+} + 4\,OH^-$$

buffered solution:

$$VO_3^- + 2\,H_2PO_4^- + e^- \rightarrow VO^{2+} + 2\,H_2O + 2\,PO_4^{3-}$$

wave (C): $VO^{2+} + H_2O + 2\,e^- \rightarrow V^{2+} + 2\,OH^-$

EXPERIMENTAL

The polarographic curves were recorded with the polarographs Polariter PO—4 (Radiometer) and Radelkis OH—102. Polarographic current-time curves were measured by means of a Hewlett-Packard Oscilloscope Model 130C and photographically recorded by an Exacta Varex IIA camera with a Flektogon wide-angle lens. Additionally, the equipment consisted of a »first drop« timer, described by Nemec and Smoler[12]. Capillary characteristics in 0.02 *N* phosphate buffer (*p*H 7), at 35 cm mercury column height and measured at open circuit, were: $m = 2.16$ mg/sec, $t_1 = 4.32$ sec and $m = 1.51$ mg/sec, $t_1 = 5.10$ sec. All potentials are given with

respect to the calomel electrode with a saturated solution of sodium chloride. All measurements were carried out at a constant temperature of 25 ± 0.1° C.

For the preparation of solutions analytical-grade chemicals were used, except in the case of caesium nitrate (*purissimum*-grade), caesium fluoride (*purum*-grade), and tetrabutylammonium hydroxide (*purum*-grade). The buffered solutions of vanadate were prepared from a 0.01 *M* stock solution of ammonium metavanadate. Phosphate buffers were prepared by dissolving the calculated amounts of Na_2HPO_4, adding appropriate amounts of the other chemicals, adjusting the *p*H to 7 (± 0.05) by the addition of phosphoric acid, and making up the volume to the mark in a volumetric flask. Acetate buffers were prepared from sodium or calcium acetates and acetic acid. The borate buffer was prepared by neutralization of boric acid with sodium hydroxide, and the ammonia buffer by addition of the corresponding acid to the ammonia solution. At least two days were allowed for the equilibrium to be established in solutions between orange coloured polyvanadates and colourless metavanadates and orthovanadates.[1,2,13-23] The solutions were prepared with redistilled water. Triply-distilled mercury was used throughout.

RESULTS

The observed[1] altering of potential range for polarographic waves as well as the altering of current intensity can be explained by the structure of the electrolyte-electrode interface according to the theory of Frumkin[6]. By altering the concentration and composition of the supporting electrolyte, the structure of the double-layer is changed and the ψ-potential also undergoes a change. The rate of electrode reaction on positively charged mercury is altered by electrostatic attraction of anions, whereas on negatively charged mercury the attraction of cations affects the rate of electrode reaction. An additional specific adsorption of ions produces stronger effects.

However, variations of the apparent rate constant may arise also of a prior charge-decreasing process involving ion-pairing.[9]

The electroreduction of vanadate ions is *p*H dependent[1] and, consequently, the electroreduction is preceded by a protonation step. If this prior chemical step is sufficiently slow, it causes a decrease in the limiting current[7]. Such a protonation reaction is also influenced by the structure of the interface[5].

All these effects have been systematically investigated in this work. By the change of the concentration and the kind of the supporting electrolyte, *i. e.* the nature of the supporting anion and cation, a systematic variation of the double-layer structure was performed. Besides, the influence of the ionic strength, and of the concentration and the kind of the buffer solution, *i. e.* of the protondonating substance, was investigated as well.

Effect of the nature of the supporting anion. — Polarographic waves of 1 m*M* ammonium metavanadate in 0.2 *N* phosphate buffer at neutral *p*H, containing 0.78 *N* sodium salt of the corresponding anion are shown on Fig. 2. Thus at constant buffer strength and constant concentration and nature of the supporting cation the effect of the nature of the foreign anions can distinctly be observed. Strong surface-active anions I^- and SCN^- completely eliminate the peak current at such a high concentration, and the reduction occurs at considerably negative potentials (— 0.7 to — 0.9 v. *vs.* S. C. E.). The polarographic wave is resembling the wave resulting from the reduction of VO_4^{3-} ion in basic solution. SCN^- inhibits the electrode reaction more intensively than I^-. Other investigated anions display a different effect when the electrode reaction procedes on a positively or negatively charged mercury surface, *i. e.* in the range of the rising portion of the polarographic wave or

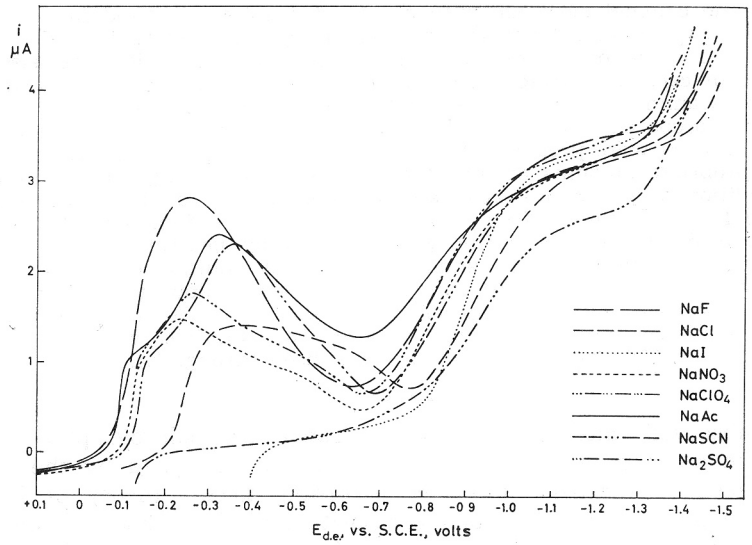

Fig. 2. Effect of the nature of the anion. 0.2 *N* phosphate buffer (*p*H 7) + 0.78 *N* sodium salt + + 1 m*M* ammonium metavanadate.

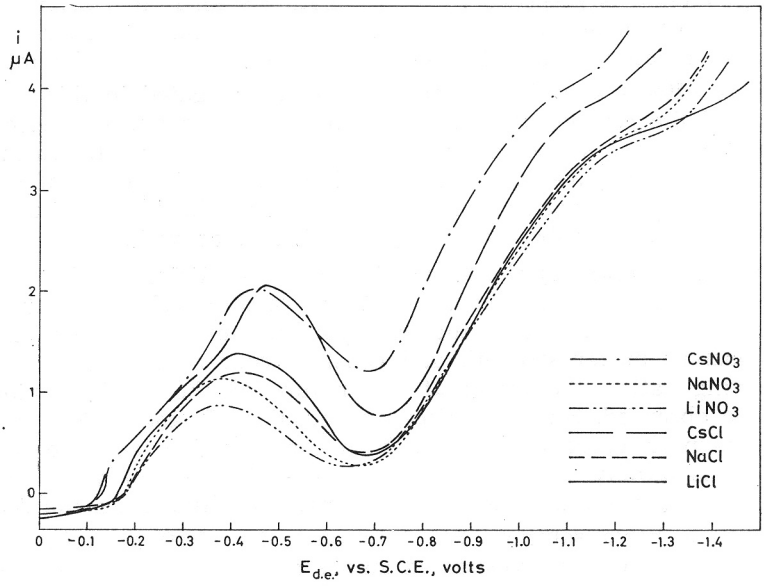

Fig. 3. Effect of the nature of the cation. 0.02 *N* phosphate buffer (*p*H 7) + 1 *M* sodium salt + + 1 m*M* ammonium metavanadate.

in the range of minima. The beginning of the electroreduction of metavanadate is facilitated on addition of anions in the order; $Cl^- < SO_4^{2-} < NO_3$, $ClO_4^- < Ac^- < F^-$, while the peak current is increased in the order: $Cl^- < NO_3^- < ClO_4^- < SO_4^{2-} < Ac^- < F^-$. The rate of electrode reaction on a negatively charged mercury surface, *i. e.* in the region of the minimum, is increased by anions in the order: $NO_3^- < ClO_4^-$, $SO_4^{2-} < Cl^-$, $F^- < Ac^-$. The shape of the wave is changed a little in the presence of Cl^-, the peak current is flattened and the minimum is shallow.

Effect of the nature of the supporting cation. — The influence of the nature of the supporting cation was investigated at a low buffer strength of 0.02 *N* and at a high (1 *M*) concentration of the salt, with the aim of excluding the influence of the buffer cation. Lithium, sodium and caesium nitrate and chloride were used for comparison of the simultaneous effect of supporting cation and anion. Fig. 3 gives the results of investigations. Cs^+ accelarates the reaction in relation to Li^+ and Na^+ in the form of nitrate and chloride. The effect is better expressed at NO_3^- than at Cl^-. There is no difference in the effect on the minimum for Li^+ and Na^+, but these ions, contrary to Cs^+, suppress the minima more considerably with Cl^- than with NO_3. The peak current is increased by the alkali nitrates in the order $Li^+ < Na^+ < Cs^+$, while for alkali chlorides it is $Na^+ < Li^+ < Cs^+$.

The effect of tetrabutyl ammonium cation, $(Bu)_4N^+$, was also investigated in 0.02 *N* phosphate buffer (Fig. 4). With the increasing concentration of $(Bu)_4N^+$ the peak current occurs at more positive potentials, it is diminished and the wave flattens.

Effect of the buffer strength and the ionic strength. — The investigation was performed in buffer solutions in the absence of capillary-active ions. Consequently, the ionic strength in the buffer was varied by adding sodium fluoride. Fig. 5 shows the influence of the buffer strength (capacity) at a constant ionic strength. In the region of the peak current the reaction rate increases with the increase of the buffer strength, *i. e.* the wave and the

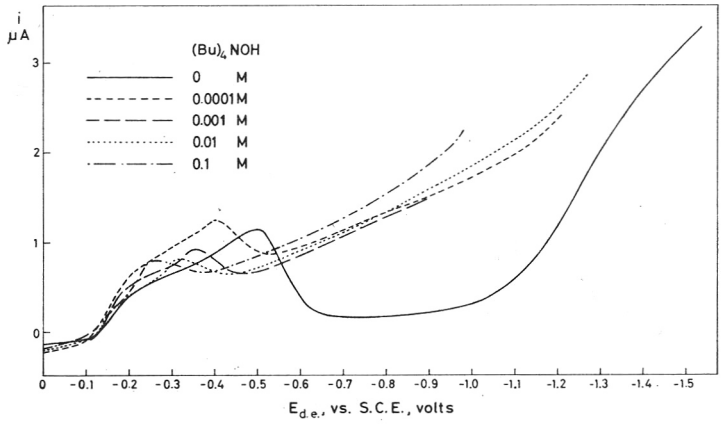

Fig. 4. Effect of the tetrabutylammonium ion on the polarographic wave for 1 m*M* ammonium metavanadate in 0.02 *N* phosphate buffer (pH 7).

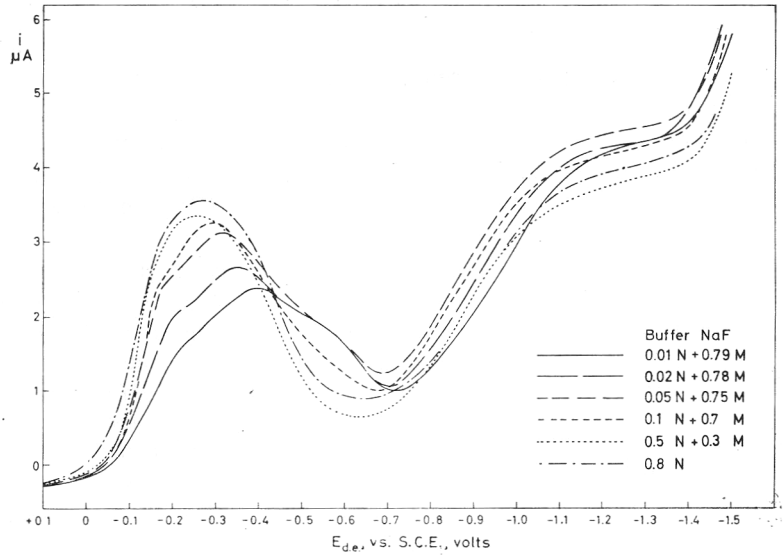

Fig. 5. Effect of buffer strength at constant supporting cation concentration (*p*H 7). 1 m*M* ammonium metavanadate.

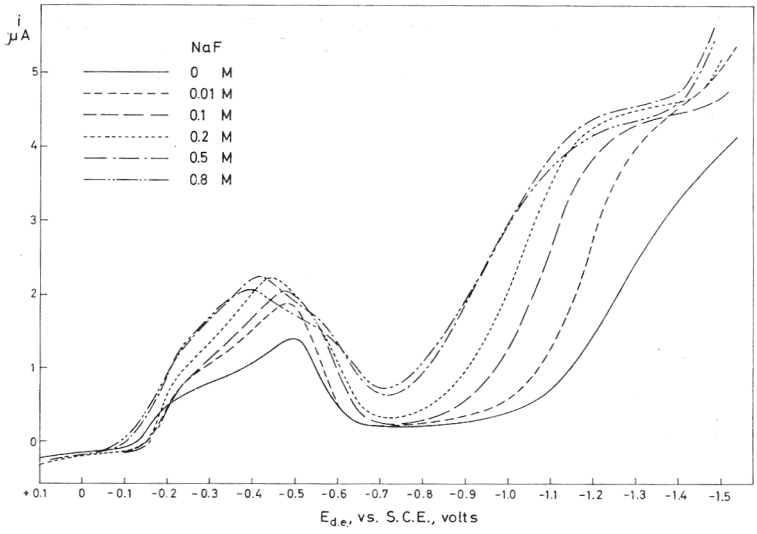

Fig. 6. Effect of the supporting electrolyte concentration. 1 m*M* ammonium metavanadate in 0.02 *N* phosphate buffer (*p*H 7).

peak current rise and they are formed at more positive potentials. In the region of minima the effects of buffer strength and the ionic composition seem to be reverse. When the ionic composition is slightly changed (low buffer strength) the accelerating effect of the increasing buffer strength becomes evident.

The effect of the supporting electrolyte concentration or the ionic strength of the buffer solution (0.02 *N* phosphate buffer) is shown in Fig. 6. The electroreduction rate of metavanadate increases with the increasing ionic strength in the whole investigated potential range.

The accelerating action of cations from Na^+ to Cs^+ becomes distinctly visible at low buffer strengths (Fig. 7). The effect of Cs^+ is especially pronounced, causing the reduction of vanadate to begin at considerably more positive potentials (2 N CsF).

Effect of the charge of the supporting cation. — Na^+ and Ca^{2+} were chosen for comparison, being of similar ionic size. Because calcium phosphate is insoluble the measurement was performed in acetate buffer. A special effectiveness of Ac^- in eliminating minima was observed in the systematic investigation of anions in the phosphate buffer (Fig. 2). The effect of concentration of sodium and calcium acetate in the acetate buffer at *p*H 7 is shown on Fig. 8. At the beginning of the wave the electrode process is inhibited less in the presence of Na^+ than of Ca^{2+}, but the wave height increases with the increasing concentration of Na^+ and Ca^{2+}. A concentration increase results in a decrease of minima, particularly with Ca^{2+}. At 2 *N* sodium and calcium acetate minima are completely eliminated and the normal diffusion plateau is restored.

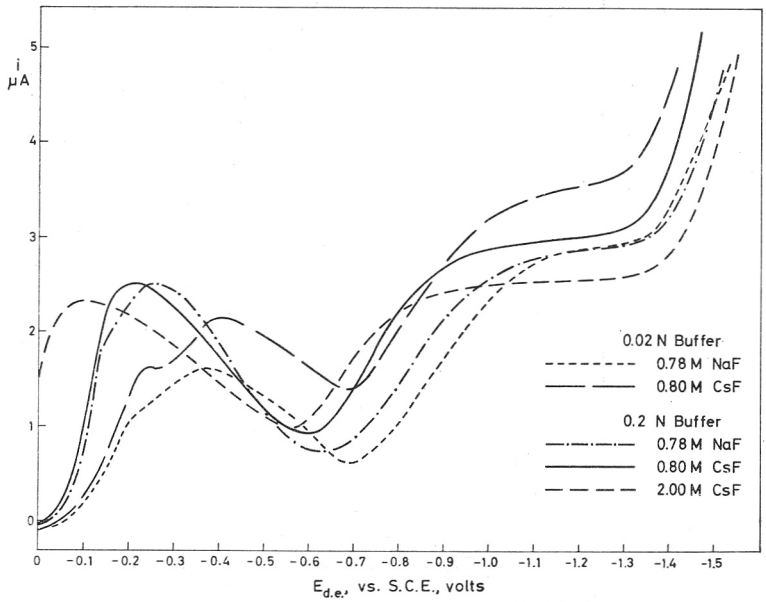

Fig. 7. Accelerating action of cations in 0.02 *N* and 0.2 *N* phosphate buffer (*p*H 7). 1 m*M* ammonium metavanadate.

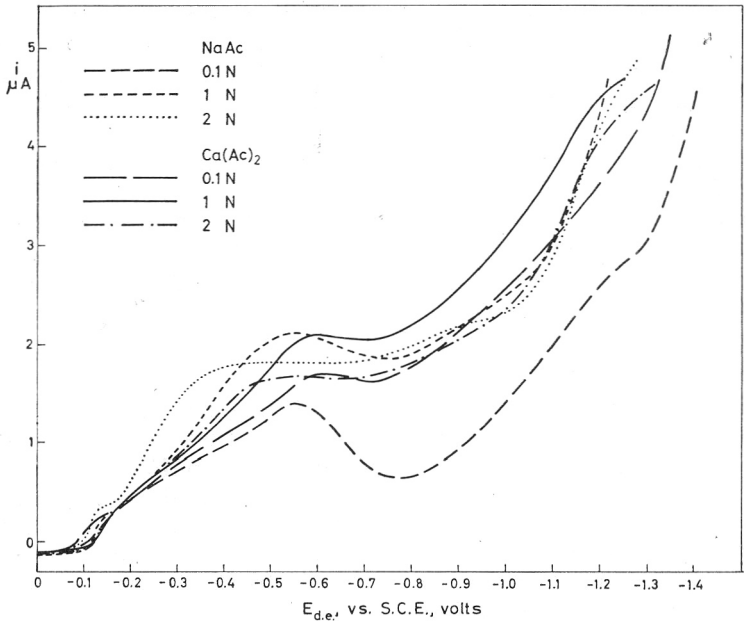

Fig. 8. Effect of the charge of the supporting cation. 1 m*M* ammonium metavanadate in acetate buffer (pH 7).

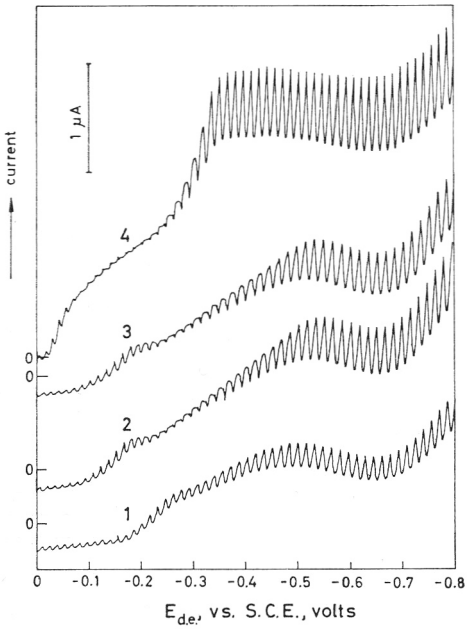

Fig. 9. Effect of the buffer kind (pH 7): 1 1 *M* $CsNO_3$, 2 1 *M* $CsNO_3$ in 0.02 *N* ammonia buffer, 3 1 *M* $CsNO_3$ in 0.02 *N* borate buffer, 4 1 *M* $CsNO_3$ in 0.02 *N* phosphate buffer. 1 m*M* ammonium metavanadate.

Effect of the buffer kind. — Neutral 0.02 *N* buffer solutions of phosphate, borate, and ammonia were used, containing 1 *M* $CsNO_3$ and 1 m*M* ammonium metavanadate (Fig. 9). For comparison the solution of the same *p*H and composition with respect to caesium and vanadate was also used but without buffer. From Fig. 9 it can be seen that the nature of the buffer influences the rate of the electrode reaction, on the positive as well as on the negative side of the electrocapillary maximum. Phosphate is more effective than borate and ammonium ion, which are approximately equally effective. The formation of a »prewave« occurs in the range of about —0.2 v. *vs.* S. C. E. due to a certain adsorption process indicated by typical irregularities in current oscillations. The increase in current following the »prewave« may correspond to the reduction with a higher overvoltage at the covered electrode surface or it can be due to a desorption process.

Unbuffered solutions. — In unbuffered solutions the electro-reduction of metavanadate is proceeding at a lower rate (Fig. 10). The inhibition of the electrode process is pronounced at more positive potentials, while at negative potentials the current in minimum is approximately the same as in buffered solutions. However, the addition of Cs^+ accelerates considerably the electrode reaction rate.

The »prewave« and the influence of vanadate concentration. — In phosphate buffer of *p*H 7, and ammonium metavanadate concentrations greater than 0.5 m*M* a »prewave«[1] (Fig. 1) is formed at potentials about —0,2 v. *vs.* S. C. E., having a tendency to level off as the vanadate concentration increases

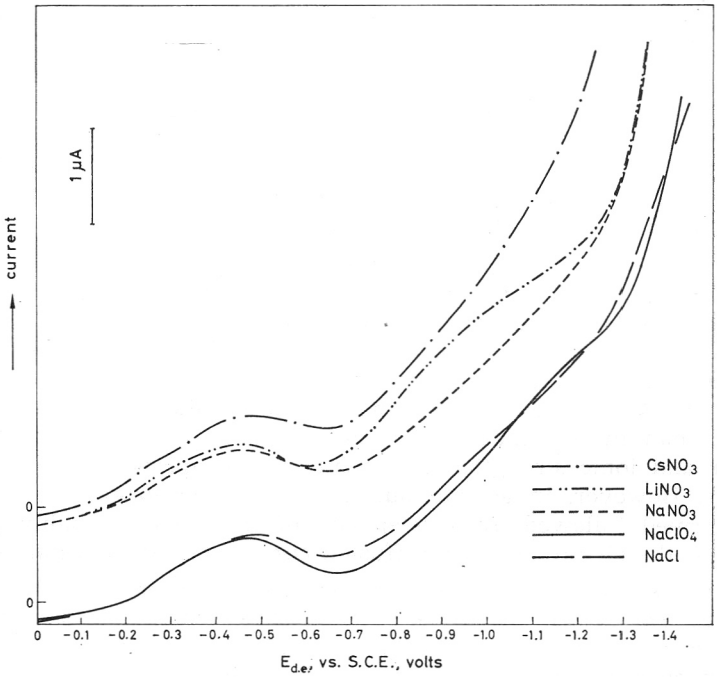

Fig. 10. Effect of the nature of the cation and of the anion in unbuffered solution. 1 m*M* ammonium metavanadate + 1 *M* sodium salt.

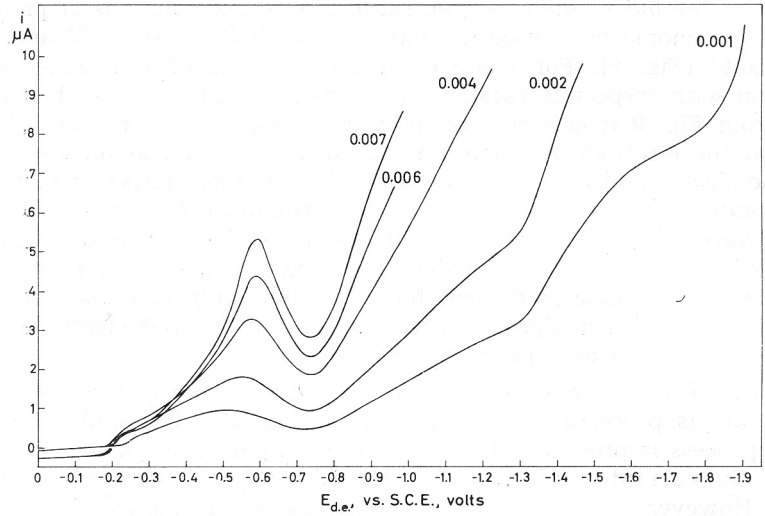

Fig. 11. Polarographic waves of ammonium metavanadate in 1 *M* sodium acetate buffer (*p*H 7): 1, 2, 4, 6 and 7 m*M* ammonium metavanadate.

and becoming independent on the vanadate concentration at concentrations greater than 2 m*M* (Fig. 11). As may be concluded from the above reported results of investigations, a »prewave« is formed in other buffer solutions as well (Figs. 8 and 9) and it is due to the inhibition of the electrode process by adsorption. The structure and porosity of the adsorbed layer does not depend on the ionic strength only (Figs. 6 and 9), but also on the nature of supporting anions (Fig. 2) and cations (Fig. 3) as well as on the buffer strength (Fig. 5). The following effects can be discerned: with increasing concentration of F^- the »prewave« increases, at greater buffer strength, *i. e.* higher concentrations of phosphate, the »prewave« disappears (Fig. 5). In the presence of F^-, at a high buffer strength and ionic strength, there is no inhibition of electrode reduction of metavanadate ion (Fig. 7).

Effect of p*H and buffer kind.* — The polarographic behaviour of vanadate in phosphate and acetate buffers at *p*H 6, 7, and 8 was investigated (Fig. 12). The increase of *p*H slows down the rate of electrode reaction and the polarographic wave is formed at more negative potentials[1]. In phosphate buffers minima are pronounced and become deeper with increasing *p*H[1]. In acetate buffers at *p*H $\leqslant 7$ there are no minima, but at *p*H > 7 a minimum less pronounced than in phosphate buffer can be seen. In phosphate buffers of high buffer and ionic strengths (2 *N* solutions) no »prewave« occurs on the polarograms. However, in acetate buffers of the mentioned acidity a »prewave« is formed followed by a steep rise of the wave, probably due to a desorption on the electrode and a diffusion current plateau is established.

Polarographic current-time measurements. — In order to be able to interpret the kinetics of the electrode reaction, the instantaneous current-time curves (*i*—*t* curves) were recorded at potentials in the region of the »prewave«, of the peak current, and of the minima. Investigations were performed in systems with pronounced inhibition effects.

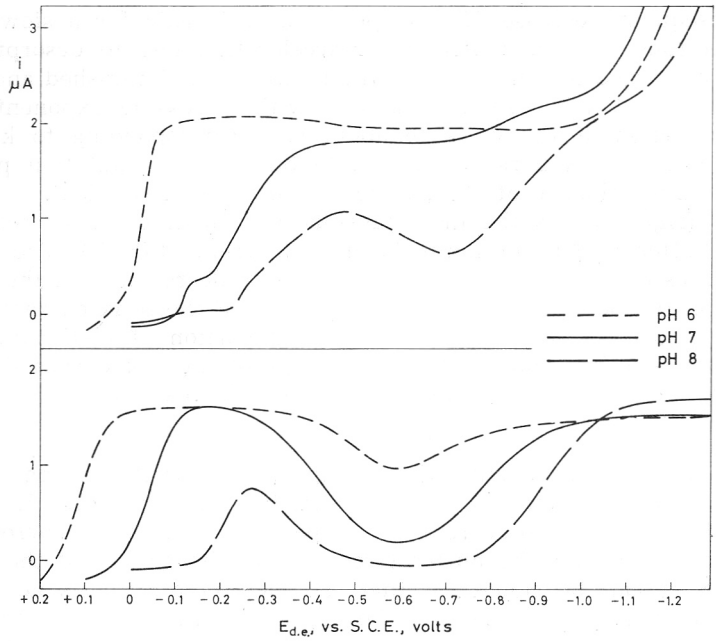

Fig. 12. Polarographic waves of 1 m*M* ammonium metavanadate in 2 *N* phosphate buffer (lower part) and in 2 *M* sodium acetate buffer (upper part): *pH*, 6, 7 and 8.

Fig. 13 (left) gives the instantaneous current-time curves at potentials of the »prewave« and of the minimum in 0.02 *N* phosphate buffer in the presence of 1 *M* $CsNO_3$. At the beginning of the »prewave« (— 0.1 v *vs.* S. C. E.) the shape of the *i*—*t* curve is indicating an adsorption-equilibrium controlled electrode process. In the region of the plateau of the »prewave« the *i*—*t* curves show an initial steep current rise, resulting in a maximum

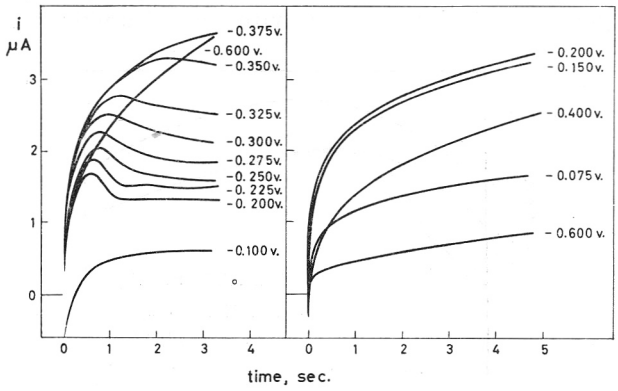

Fig. 13. Current-time curves of reduction of vanadate at different potentials. Left: 1 m*M* ammonium metavanadate + 1 *M* $CsNO_3$ in 0.02 *N* phosphate buffer (*p*H 7). Right: 1 m*M* ammonium metavanadate + 0.78 *M* NaF in 1 *N* phosphate buffer (*p*H 7).

with a subsequent decrease. The shape is characteristic for a slow transfer rate of electrons, with a subsequent reacceleration due to desorption[24]. At a negatively charged mercury surface the inhibition is diminished and, finally, the *i*—*t* curves become regular parabolas, with increasing exponents on the descending portion of the wave to about 0.45, corresponding to kinetically controlled currents. In borate and acetate buffers the inhibition process is similar, but the influence of the nature of the buffer is evident.

Fig. 13 (right) shows the instantaneous current-time curves recorded in phosphate buffer (1 *N*), containing sodium fluoride (0.78 *M*). The shape of the *i*—*t* curves corresponds to a reversible electrode reaction in the presence of fluoride at the potentials of the rising portion of the peak current (— 0.075 to — 0.200 v. *vs.* S. C. E.). On the descending portion of *i*—*E* curve before the minimum (— 0.4 v. and — 0.6 v.) the shape of the *i*—*t* curves shows that the current is limited by the rate of the electrode reaction.

DISCUSSION

On the base of the results of these investigations it may be concluded that the process of electroreduction of vanadate at a neutral *p*H is rather complex. The value of the current in the peak as well as the current in the minima depend on both the buffer strength and the acidity of the solution, consequently it can be concluded that the electroreduction is accompanied by a protonation step. The values of the exponent x in the relationship $i \sim h^x$ are considerably smaller than 0.5 in the region of the peak current, and in the minimum the current is practically independent of the height of the mercury column *(h), i. e.* the electroreduction is kinetically controlled. The kinetics of the protonation reaction, its velocity and, consequently, the current intensity depend on the nature of the proton donor (H_2O, HPO_4^{2-}, NH_4^+, HAc, HBO_2), as well as on its concentration, *i. e.* on the buffer strength.

When treating the double-layer effect in the polarographic reduction of metavanadate at neutral *p*H its surface activity[1] should be also considered. Recorded electrocapillary curves (drop time as a function of the electrode potential) show its surface activity (Fig. 14).

The observed effect of the nature of the anion and cation of the supporting electrolyte is generally in accordance with the Frumkin theory[6], *i. e.* the

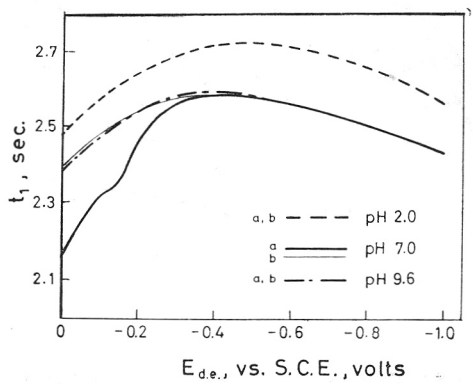

Fig. 14. Electrocapillary curves of: *a* 1 m*M* ammonium metavanadate in 0.2 *N* phosphate buffer at *p*H: 2.0, 7.0 and 9.6, and *b* 0.2 *N* phosphate buffer at *p*H 2.0, 7.0 and 9.6.

current increases and the wave is formed at more positive potentials with the positivation of the ψ-potential. The following effectiveness of anions was found for the increace of the peak current: I^-, $SCN^- < Cl^- < NO_3^- < ClO_4^- < SO_4^{2-} < Ac^- < F^-$. This order is in parallel with the decreasing specific adsorption of anions on mercury[8]. The following order was found for the positivation of electrode reaction potentials: $Cl^- < SO_4^{2-} < NO_3^-$, $ClO_4^- < Ac^- < F^-$.

At potentials corresponding to the minimum current of the polarographic wave the reaction rate increases on addition of anions in the order: $NO_3^- < ClO_4^-$, $SO_4^{2-} < Cl^- < F^- < Ac^-$. The reaction rate of the wave (C) is increased similarly.

The accelerating action in the series $Li^+ < Na^+ < Cs^+$ is in accordance with their specific adsorption to the mercury surface[4,5], as well as with their increasing tendency for ion-pairing.[9] Li^+ inversion was observed in the presence of chloride, this being also found in other systems[9]. All cations are more effective with Cl^- than with NO_3^-, this being certainly, in connection with the competing effect of anions. This anionic effect is less pronounced with Cs^+, probably due to its stronger surface-activity. The divalent cation, Ca^{2+}, is slightly more effective than Na^+ in the region of polarographic minima, as could be expected. A more detailed study of the influence of divalent ions is in course.

The strong specifically adsorbed $(Bu)_4N^+$ ion shows a normal effect, reducing minima even at small concentrations. However, the increase of coverage with concentration of $(Bu)_4N^+$ ions inhibits charge transfer causing a slower electrode rate.

The increase of the electroreduction rate with the ionic strength at potentials corresponding to positively, neutral, and negatively charged mercury surface is in accordance with the corresponding diminishing of the double-layer effect enabling the increase of the local concentration of the specifically adsorbed vanadate ion.

The inhibition of the electrode process on the rising portion of the wave and the formation of the »prewave« is, presumably, due to the adsorbed layer of vanadate (Fig. 14). The effect of the adsorbed layer is a function of its structure and thickness, which depend on the *p*H of the solution, on the concentration of vanadate, on the nature and concentration of the supporting cation and anion, and on the ionic strength of the solution. The charge of the double layer, has also, probably, its role, and on it depends also the possibility of the penetration of vanadate ions through the layer to the electrode surface[25]. Investigations of *i-t* curves have shown that the inhibition is greater at beginning voltages, and that by negativation of the voltage it diminishes and disappears. It can be concluded that the inhibition of the electrode reaction causes the adsorption of metavanadate, which is subsequently prevented presumably by a product of the electrode reaction (Fig. 14). The effect of the F^- ion to accelerate the electrode reaction is in accordance with such a theory, because electrocapillary measurements have shown that a desorption of vanadate occurs at potentials more negative than — 0.1 v. *vs.* S. C. E. in the presence of the F^- ion.

CONCLUSION

From the results of polarographic measurements in neutral solutions of metavanadate it may be concluded that the specific influence of investigated foreign ions on the electrode reaction can be explained:

(1) with regard to the effect on the electron layer on the mercury surface or on the ψ-potential,
(2) from the standpoint of the supporting of the buffer effect,
(3) with regard to the effect with other reaction participants (VO_3^-, VO^{2+}, PO_4^{3-}, etc.)
(4) with regard to the possibility of combination with foreign ions.

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IZVOD

Utjecaj elektrokemijskoga dvostrukog sloja na polarografsku redukciju vanadata

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Studiran je utjecaj osnovnog elektrolita na polarografsku redukciju vanadata u puferiranim i nepuferiranim otopinama kod neutralnog *p*H. Pokazano je da postoji slaganje s postojećim teorijama o mehanizmu redukcije aniona na kapajućoj živinoj elektrodi. To se moglo zaključiti ne samo na temelju utjecaja prirode kationa i aniona osnovnog elektrolita, nego i na temelju utjecaja ionske jakosti i puferske jakosti na maksimume i minimume polarografskog vala vanadija. Nađeno je da brzina elektrodne reakcije raste u nizu $Li^+ < Na^+ < Cs^+$, zatim $Na^+ < Ca^{2+}$, kao i u nizu: J^-, $SCN^- < Cl^- < NO_3^- < ClO_4^- < SO_4^{2-} < Ac^- < F^-$. Međutim, otkrivene su i stanovite inverzije u nizu kationa i aniona. Osim toga, ustanovljen je i međusobni utjecaj kationa i aniona. Nadalje je proučen i proces inhibiranja elektrodne reakcije, koji se javlja kod potencijala pozitivnijih od elektrokapilarnog maksimuma. Inhibiranje potpomažu ioni Cs^+ i Ac^-, a ion F^- priječi.

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