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The Investigation Of Chromate Reduction On Platinum Electrode In Basic Media

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The current-potential curves obtained by potentiostatic methods revealed that bichromate reduction in NaOH solution with oxidized and reduced platinum electrodes took place at the reduction potantial of the electrode metal oxide. It was found that the chromate reduction was restricted to a narrow concentration and potential range when using an oxidised platinum electrode,where as the range was considerably extended when the reduced electrodes were used.

According to the magnitude of the slopes of the lines that show the dependence of the limiting current to the bichromate concentration, the same reduction processes take place in a definite potential region in acidic and basic media. In this study, a new potential step at around 0.6 V that corresponds to theequilibrium potential of $Cr_2O_7^{=}$/ Cr^{3+} is found

INTRODUCTION

Although it is well accepted by various investigaters who work on the same topic that a film is formed on the electrode surface during cathodic reduction of bichromate, the sturucture, composition and formation potential of the film is still debatable.

The composition, the proporties of the film [1–4] and the dependence of pH[5–7] were investigated by various investigaters.

Some investigaters state that, film is solved in acids [8] and according to others it is transformed into a more permeable

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form against chromate ion[9]. According to Kolthoff[10] this film shows an amphoteric character. To investigate the proporties of the film closely cathodic reduction of bichromate and the proporties of the film was investigated by the author[2] in sulphuric acid solution containing radioactive H_2SO_4 (S_{16}^{35}) by obtaining current-potential curves. This study has demonstrated that the film formed on the electrode surface from the second step and contains $SO_4^=$ ion. These $SO_4^=$ ions are exchangeable to other anions and this film is dissolved in acid media as well as in basic media. It is proved that the solubility of the film or ion exchange in N NaOH is faster in N H_2SO_4 and $HClO_4$. So the film which dissolved both in acidic and basic media has an amphoteric character and chromate reduction can take place in basic media as well as in acidic media. This study was made to investigate whether chromate reduction is possible on platinum electrode in basic media and to find out if it is possible, whether reduction potential of chromate corresponds to the reduction potential of platinum oxide.

In our previous studies, it was pointed out that chromate reduction with platinum, palladium, gold[7], rhodium and iridium[11] electrodes in acidic solutions are produced in the same potentials where their oxides are reduced. Aside from this, in this study the influence of the buffer solutions on chromate reduction was investigated.

Experiments

In these experiments, great care was taken to see that all chemicals were chemically pure and solutions were prepared with double distilled water and glass ware was made of pyrex glass.

Current-potential curves obtained in NaOH solutions showed that NaOH contains impurities. For this reason, concentrated NaOH solutions were prepared, preelectrolyze[12] throughout a day then suitable solutions were prepared.

Current-potential curves were obtained with Wenking-Breitband potentiostat Model 61 RS. Nitrogen gas was passed

through the solution for one hour prior to each experiment. Hgl Hg_2SO_4, $SO_4^=$ electrode was used as a reference electrode.

The solution in the cell was continuously kept at the same level and mixed with a magnetic stirrer during the experiment.

Platinum wire in 3 cm lenght and 0.5 mm diameter was used as cathode.

Reducing the electrode: The electrode was dipped into 1 N H_2SO_4 solution as anode and a current of 200 mA was passed for five minutes. Then it was inserted in a cell which contained 1 N H_2SO_4 solution through which nitrogen gas was passed continously; the potential of the electrode held stable at 400 mV and waited until the current fell to zero μ A. In this text the elecrode prepared in the above manner is called 'reduced electrode'.

Oxidizing the electrode: The reduced electrode prepared with the above procedure was again oxidized, anodically, for five minutes under a current of 200 mA. This electrode is called oxidized electrode.

Conclusions

Current-potential curves obtained with oxidized platinum electrode in 1 N NaOH and 1 N NaOH with various concentration of bichromate solutions are shown in Fig. 1. The reduction potentials of platinum oxides obtained in 1 N NaOH are in good agreement with the potential steps obtained with platinum electrode in KOH by Kozowa[13] and Giner[14] and in NaOH by Kolthoff and Tanaka[15]. The potential step seen around 0.6 V when bichromate is added in the solution is particularly interesting. Considering the pH of the solution, this step corresponds to the equilibrium potential of $Cr_2O_7^=/Cr^{3+}$, that is 1.36 V. In acidic medium this step is not found out through platinum electrode.

Although this step was not found out through metal electrodes by other investigaters, it was demonstrated with palladium electrode by the author[2,6] of this article and Kabasakaloğlu found out the same step through rhodium and iridium electrodes in low current densities in acidic solutions.[16,17]

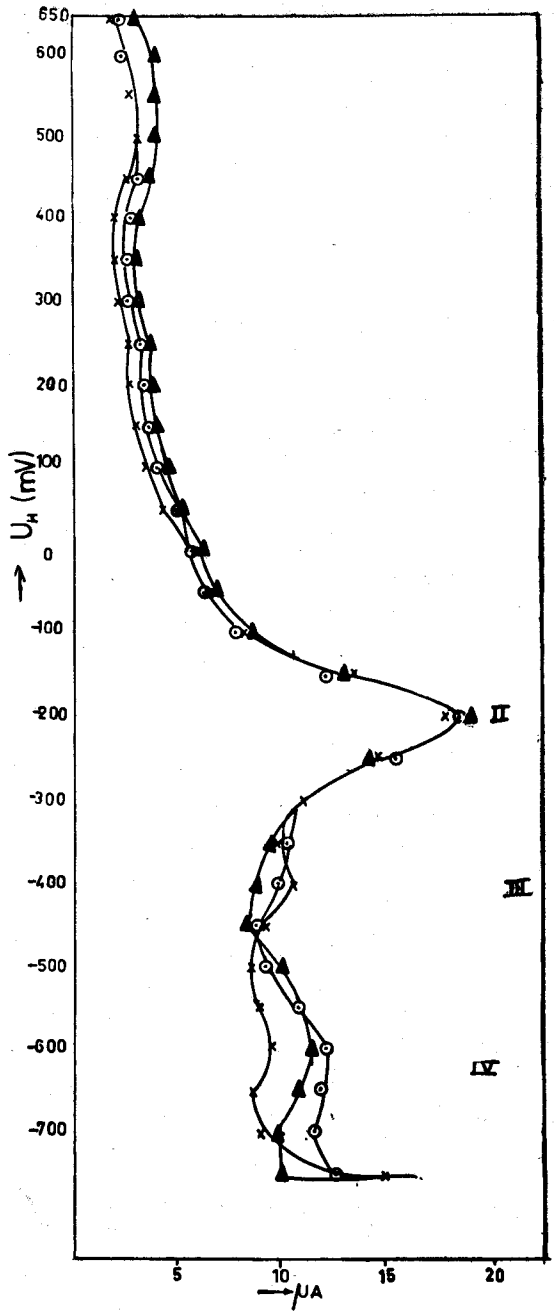

Fig. 1. Current-potential curves with oxidized platinum electrode in × 1 N NaOH, ⊙ 1 N NaOH+10^{-5}M $K_2Cr_2O_7$, ▲ 1 N NaOH+10^{-4}M $K_2Cr_2O_7$

If we consider the difference of pH between acidic and basic solutions and potential drift of 59 mV with each pH, second step around –0.2 V correspond to the reduction potential of platinum oxide in acidic solution.[7,11] The increase of bichromate concentration is not parallel to the increase of the current intensity in this step and the limiting current is not observed. It was established that current intensity was proportional with bichromate to a definite bichromate concentration region in acidic bichromate solutions.[7,11] In basic medium, it is observed that also current intensity decreased at the third step, it increased a little at the forth step with bichromate concentration as the case of oxidized platinum electrode.

The potential steps in the current-potential curves that were obtained from our previous studies[7,17,19] in acidic bichromate solution with oxidized platinum electrode is given in table 1 with the potential steps in the current-potential curves obtained in basic bichromate solutions in order to compare to each other. It is seen that these steps are in good agreement if we consider the difference of pH.

The curves obtained with reduced platinum electrode in 1 N NaOH solution and with addition of bichromate was shown in figure 2. In these curves it was seen that limiting current is obtained in the fourth step as the bichromate concentration is increased to the 10^{-5} M $K_2Cr_2O_7$, as bichromate increased further, current decreased after it reached to a maximum. At the third step current began to increase in low bichromate solutions and at the forth step, it increased proportionally with bichromate concentration. As bichromate concentration is increased further, it was seen that bichromate reduction was possible at the second step.

If the curves obtained with oxidized and reduced electrodes compared with each other (Fig. 1 and 2) it was seen that they were similar. Only, limiting current was proportional with the bichromate concentration at the forth step as the case of reduced platinum electrode and current intensity was smaller at the first and the second step in figure 2 than in the same step in figure 1. These steps were not observed in low bichromate solution but

they existed when bichromate concentration was increased; the explanation of this process is that electrode surface is oxidized when bichromate concentration is increased.

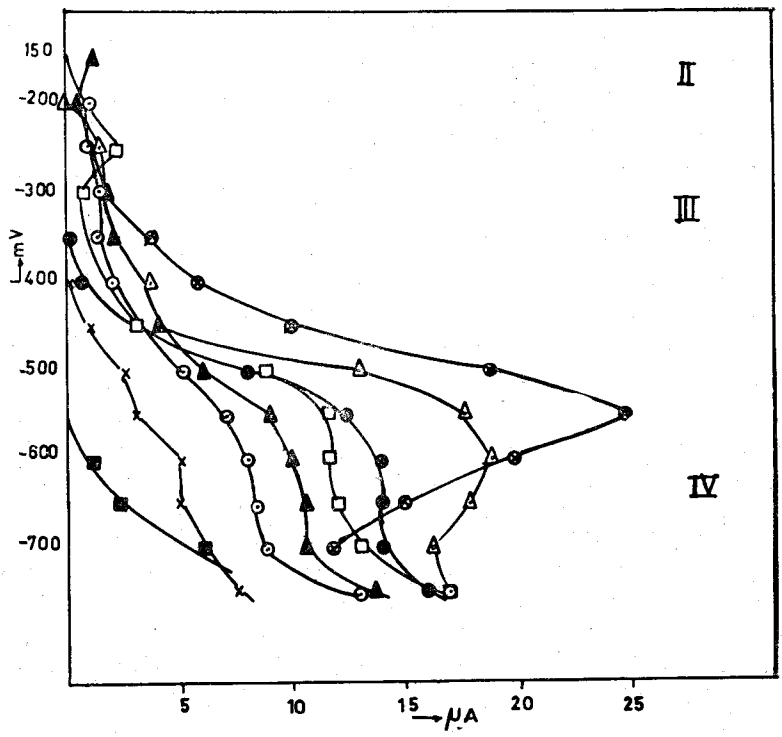

Fig. 2. Current-potential curves with reduced platinum electrode in ■ 1 N NaOH and in 1 N NaOH with addition of × 4×10^{-6}, ⊙ 6×10^{-6}, ▲ 8×10^{-6}, □ 10^{-5}, ● 1. 5 $\times10^{-5}$ △ 2×10^{-5}, ⊕ 4×10^{-5}M $K_2Cr_2O_7$.

In the previous sttudies[11,16] it was shown that electrode surface was oxidized by bichromate in basic media. The reason why the current intensities at the first and the second steps in figure 2 are smaller then the current intensities in figure 1 is that the oxide film formed by the oxidation of electrode surface by bichromate gets thinner than the one which is formed by the anodic oxidation[15].

Current potential curves obtained in ammonia-ammonium chloride buffer with reduced platinum electrode are shown in figure 3. The curves a and b are obtained in 0.005 N and 0.05 N buffer solutions respectively. As it is seen, limiting current can be obtained as the buffer capacity is increased. That is, after reaching maximum, the return of the current is decreased. Further increase of buffer capacity does not effect the curve. The ostensible effect of buffer is that the current increased after second step and three steps are almost the same.

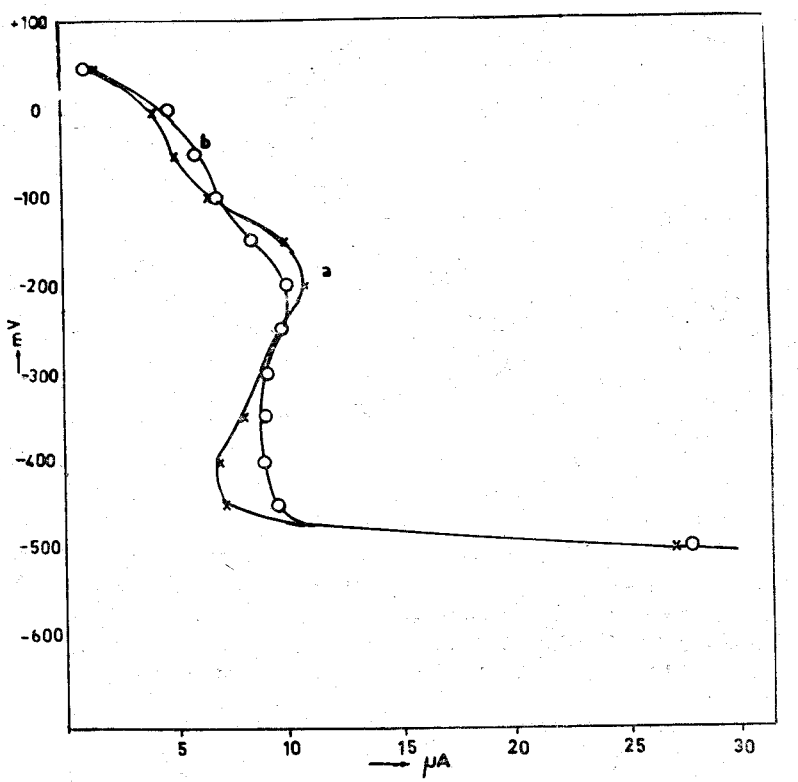

Fig. 3. Current-potential curves with reduced platinum electrode in ×0.1 N KCl+0.005 N NH_4Cl + 0.005 N NH_3+4×10^{-6} M $K_2Cr_2O_7$ and ⊙ in 0.1 N KCl+ 0.05 N NH_4Cl + 0.05 N NH_3+4×10^{-6} M $K_2Cr_2O_7$.

The curves obtained in 0.05 N buffer solution and addition of bichromate are shown in figure 4. Current intensity and bichromate concentration is proportional around–0.2 V. If we consider the difference of pH, this step corresponds to the third step. At the forth step, current intensity is proportional with bichromate up to the 6×10^{-6}M $K_2Cr_2O_7$.

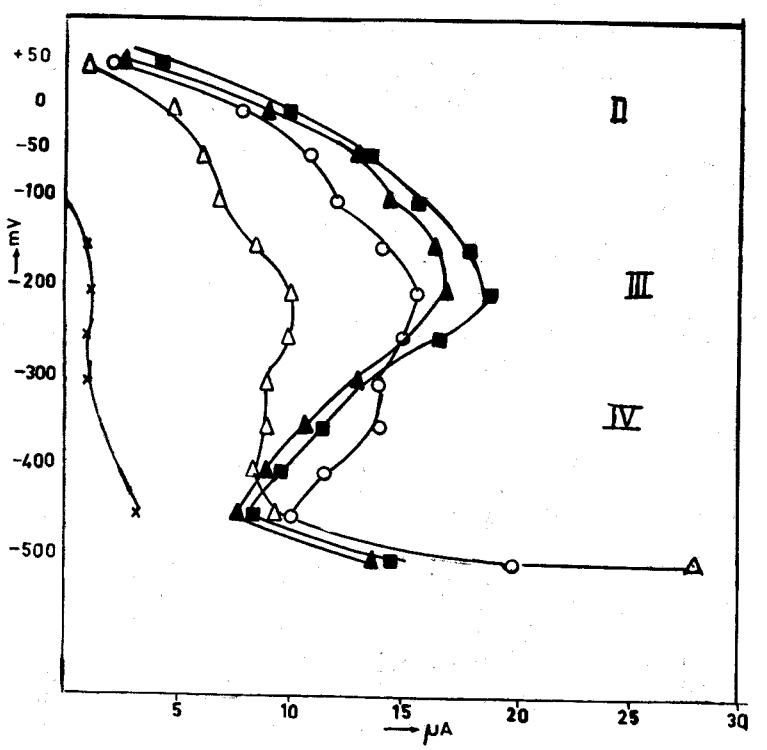

Fig. 4. Current-potential curves with reduced platinum electrode in × 0.1 N KCI+ 0.05 NH_3+ 0.05 N NH_4CI and in 0.1 N KCI + 0.05 N NH_3 +0.05 N NH_4CI with addition of △ 4×10^{-6}M ⊙ 6×10^{-6}, ▲ 8×10^{-6}, ■ 10^{-5} M $K_2Cr_2O_7$.

DISCUSSION

The comparision of the curves which are seen in figures 2, 3 and 4 with figure 1 show that the reduction of bichromate on reduced platinum electrode occurs more positive potential. Bi-

chromate reduction does not take place at the second and the third step in fig. 1 are shown clearly that oxide layer entirely prevent the diffusion of bichromate ion; in another words, bichromate reduction is prevented on passive electrode surface[7,17,19]. With reduced electrode in basic medium limiting current can be obtained at the forth step in low bichromate concentration. As the bichromate concentration increases, current decreases quickly after reaching to a maximum. The same case is established in the buffer solutions (fig. 4). The return of the curves like this can be explained as changing the sturucture of the film. As bichromate concentration is increased, when the oxidation rate of bichromate to the electrode surface is passing over the cathodic reduction rate, the thickness of the film is increased. So, reduction of bichromate demands over voltage and reduction takes place over a more negative potential[7,17,19].

However, it is seen clearly that bichromate is reduced in basic and in buffer solutions from that limiting current increased proportional with bichromate concentration (fig. 5 and 6). As is seen from fig. 5, particularly limiting current goes proportional with bichromate concentration between 0.55 and 0.65 V to 1.5×10^{-5} M $K_2Cr_2O_7$ The calculated slope of the line 2.5 mA/milimole cm^2 (Table III) is in good agreement with K value (Table II) that calculated in acidic bichromate solution. So, the same reductions occur in acidic and basic bichromate solution in this potential region.

The established dependence of limiting current to bichromate concentration in NH_3+NH_4Cl buffer solutions for bichromate reduction was shown in fig. 6. At the third step, the slope of the line table (IV) is nearly two-times of the basic medium (IV step). In table II how limiting current is dependent to bichromate concentration is shown[19]. As is seen, as the potential decreases K values increases for the electrode surface become suitable to bichromate reduction in acidic medium. As is seen from fig.3 and 4, the K values in basic and basic buffer solutions are not different from the K values in acidic solutions. But K values in basic and basic buffer solutions decrease once more. So, the magnitude of the K mean a measure of bichromate reduction; repeated

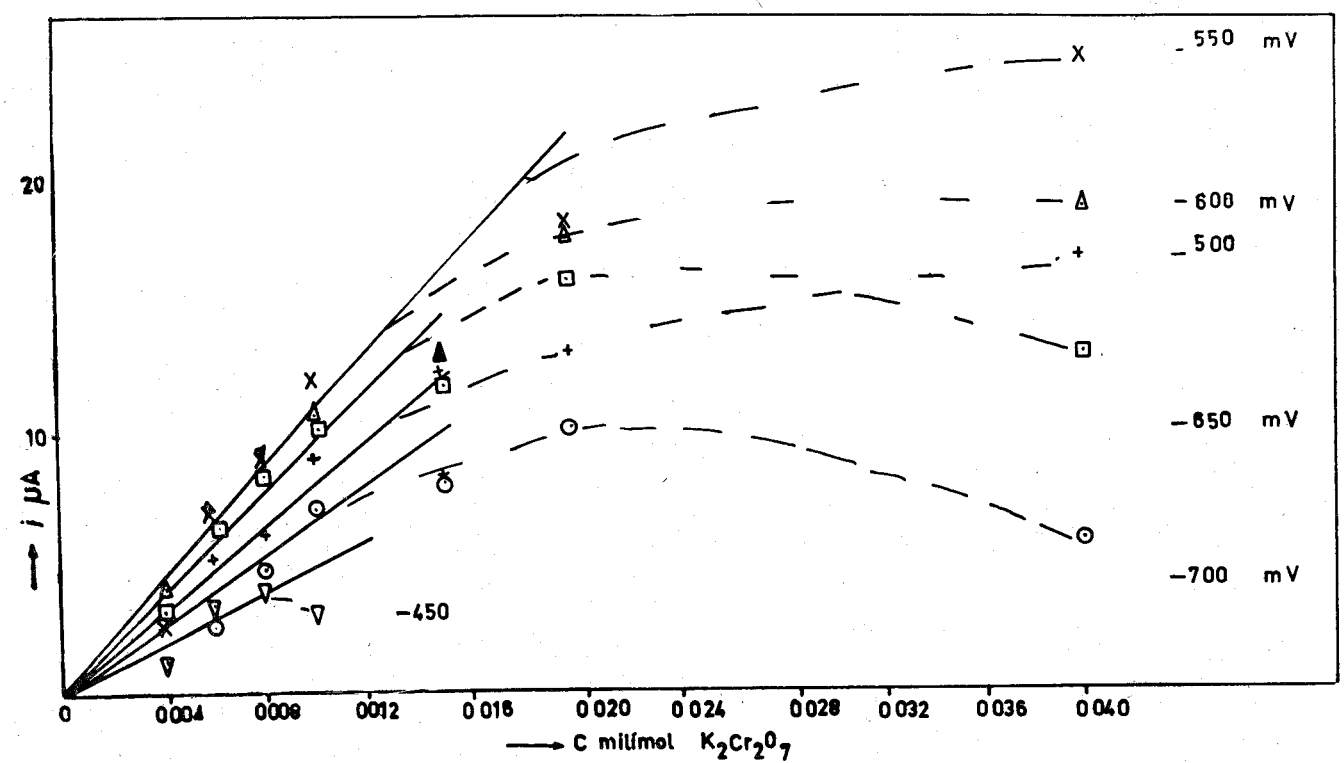

Fig. 5. The variation of limiting current with bichromate concentration in 1 N NaOH with reduced platinum electrode.

decrease can be attributed to the changing of the film to a less suitable form to bichromate reduction.

It was shown that film changes its sturucture along the current-potential curves by Gerischer and Kappel([20]). author([2]) and Weiner and Schiele([21–24]).

According to Gerischer and Käppel film has an oxidic sturucture. As the potential decreases low valency ([5], [4], [3]) oxides of chromium is produced on the electrode surface (Cr_5O_{13}, Cr_2O_5 CrO and Cr_2O_3). Where as after that Weiner and Schiele([23]) established that, by the aid of differaction lines that are obtained by them, after heating the film with electron rays, film is composed by only three valency chromium oxide or a mixed oxide that is composed electrode metal oxide and chromium oxide but only three valency oxide. They did not establish other chromium oxides. So, the idea of the Gerischer and Käppel that bichromate reduction can take place over the chromium oxide does not admit. Metal oxide and chromium oxide established by Weiner and Schiele([24]) experimentally in the composition of the film are more suitable to the reduction scheme that is given previously (Üneri 25, 31 march 1960). That is, at least in the positive potential region, chromate reduction occurs over the electrode metal oxide.

According to a pH or the existance of the foreign ion concentration, two kinds of films can be formed on the electrode surface, It was shown that first film was formed at the reduction potential of the metal oxide and changes its structure according to potential and it exsists to the metal deposition potential by using radioactive sulphuric acid by author([2]).

The film that is formed in acidic media with foreing ion have a structure that can not hinder the bichromate reduction, on the contrary, if the concentration of acid is low and in the absence of foreign ion, the formed film is thick and hinders the chromate reduction. As the case of pure chromic acid, while Cr^{3+} ion that is formed from the reduction of Cr^{6+} shows a tendency to form a complex; there is no anion except $CrO_4^{=}$; it sediments on the electrode surface as a thick layer hinders the chromate reduction. If there is a foreign anion Cr^{3+} which

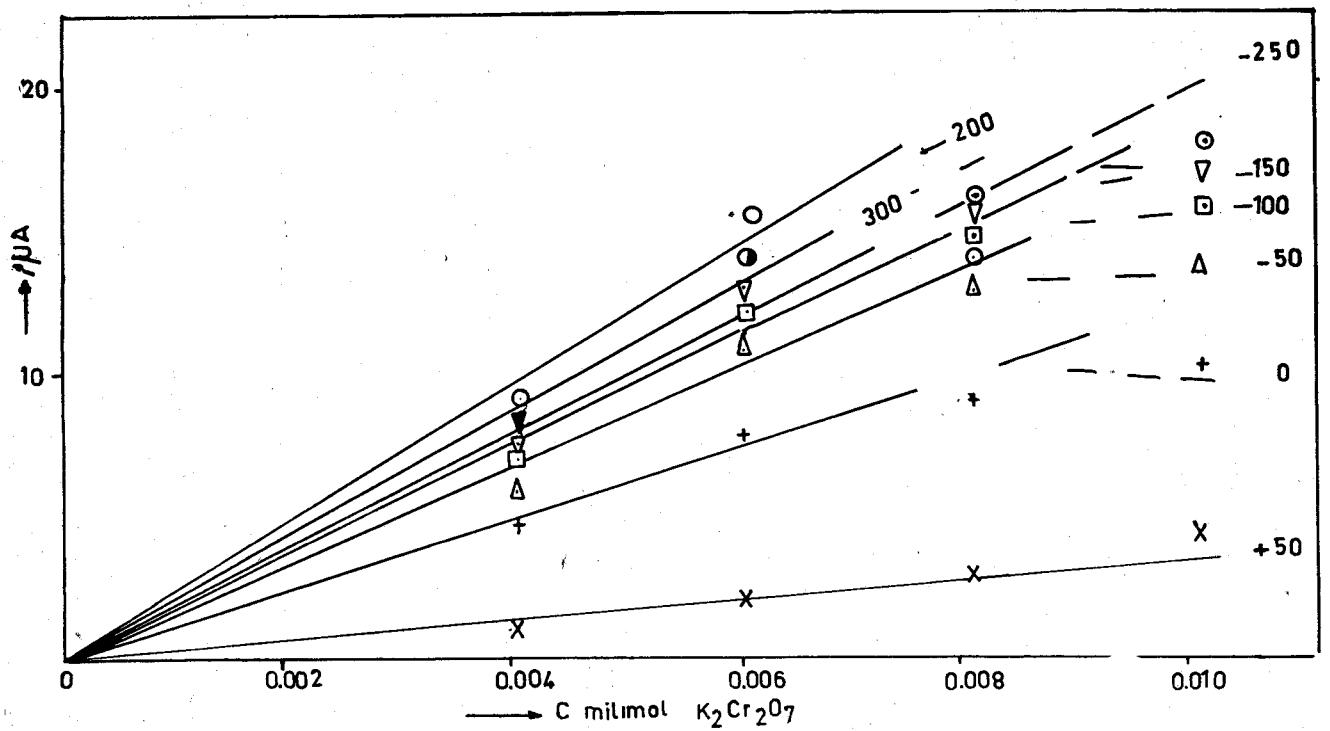

Fig. 6. The variation of limiting current with bichormate concentration in 0.1 N KCI+ 0.05 NH_3+0.05 N NH_4CI buffer solution with reduced platinum electrode.

is in the film structure transforms into solution as forming a complex or with ion exchange with these anions and after that as forming a hidroxso complex in the solution. Some of the foreign ions are again given to the solution. It gives possibility to continue the bichromate reduction. If it is accepted that the film has an amphoteric character, bichromate reduction in basic medium can occur over the CrO_2^- anion to a scheme given by Lingane and Kolthoff ([26]).

Like the proposals of some investigaters, if reduction of Cr^{6+} to Cr^{3+} takes place at only the first step, the reduction of bichromate on noble metals such as platinum, rhodium, iridium, palladium and gold take place on the same potential. The changing of reduction potential in accordance with the electrode metal makes us consider that electrode metal must have on effect on the electrode reaction. The investigation of the reduction of metal oxide with oxidized and reduced noble metal electrodes in basic or in acidic bichromate solutions or only in H_2SO_4 or $HClO_4$([7]) showed that chromate reduction advanced over the reduction of metal oxide at least at the first and the second step [2,7,17,19]).

According to Müller([18]) the reason why the reduction can take place at the equilibrium potential of Cr^{6+} to Cr^{3+} at 1.36 V at none of metals, only can take place at carbon electrode is that the surface of the graphite is porous and the film formation is hindered to high current density, then the reduction drifts to negative potential and at this negative potential (forth step) hdyrogen discharge occurs with the reduction of a little Cr^{3+}. As is seen in the upper section, the bichromate reduction is hindered because of a thick oxide film on the surface of the electrode and the idea that electrode metal oxide is responsible of reduction potential of the bichromate, it is possible to explain the reason of the potential step at 1.36 V at graphite electrode up to a high current density. Therefore carbon has no solid oxide; an oxide layer that covers the surface of the electrode can not be formed on the electrode and at the first step reduction takes place at the equilibrium potential of $Cr_2O_7^{=}/Cr^{3+}$. As has previously been stated that second and the third step are not found

at the carbon electrode, explained that these steps probably related to the low valency oxide of metal electrodes. The first step which corresponds to the equilibrium potential of $Cr_2O_7^{=}/Cr^{3+}$ system in basic medium in the present article about 0.6 V is attributed that platinum oxide or hidroxide dissolves less in basic media than in acidic media. This step is not found in acidic media because of the platinum hidroxide which corresponds to this step must dissolve easily in acid solution.

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TABLE I.

The potential steps that found in acidic and basic media

acidic media (from literature 7 and 20) step pot. (mV) steps		Basic media (from figure 4) step pot. (mV)
I	.....	650–600
II	800–600	100–(–200)
III	400–300	–350–(–400)
IV	100	–550–(–600)

TABLE II.

The dependence of bichromate concentration to the limiting current in 1 N H_2SO_4

platinum electrode			
Oxidized		Reduced	
mV	K (mA/cm^2 milimole $K_2Cr_2O_7$)		K (mA/cm^2 milimole $K_2Cr_2O_7$)
600	—		0.7
550	2.2		—
500	2.7		1.2
400	3.2		1.4
300	3.5		1.9
200	4.2		2.5
150	4.2		2.5
100	4.5		2.8

TABLE III.

The dependence of bichromate concentration to the limiting current in 1 N NaOH with reduced platinum electrode, (i=KC).

mV	K (mA /cm² milimole $K_2Cr_2O_7$
–450	1.1
–500	1.7
–550	2.5
–600	2.5
–650	2.5
–700	1.5

TABLE IV.

The dependence of bichromate concentration to the limiting current in 0.1 N KCI+0.05 N NH_3+0.05 N NH_4CI with reduced platinum electrode, (i = KC).

mV	K (mA /cm² milimole $K_2Cr_2O_7$)
+50	0.72
0	2.48
–50	3.32
–100	3.84
–150	4.8
–200	4.8
–300	4.2

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ÖZET

Potansiyostatik metotla NaOH li ortamlarda bikromat çözeltilerinin oksitli ve redüklenmiş platin elektrotlarla redüksiyonu için elde edilen akım-potansiyel eğrileri, bikromat redüksiyonunun metal oksidinin redüklendiği potansiyelde cereyan ettiğini göstermiştir. Oksitlenmiş platin elektrot kullanıldığı zaman bikromat redüksiyonunun dar bir potansiyel ve konsantrasyon aralığında ereyan ettiği halde, redüklenmiş elektrotla bu alanın genişlediği tespit edilmiştir.

Sınır akımının bikromat konsantrasyonuna bağlılığını gösteren eğrilerin eğimlerinin büyüklüklerine göre, asidik ve bazik ortamlarda belirli potansiyel bölgelerinde aynı redüksiyon olayları cereyan etmektedir.

Bu araştırmada $Cr_2O_7^{=}$ / Cr^{3+} denge potansiyeline tekabül eden 0,6 V civarında yeni bir potansiyel basamağı bulunmuştur.

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