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EFFECT OF ADSORPTION OF TETRABUTYLAMMONIUM CHLORIDE IN POLAROGRAPHY

By

ABDULGHANI HAMZA, TAWFIQ A. AMIREH AND SAEED H. AL-DOUDAM
Chemistry Department, Faculty of Science, King Abdul Aziz University, P. O. Box 9028
Jeddah 21413, Saudi Arabia

تأثير إدمصاص رباعي بيوتيل كلوريد الأمونيوم في التحليل البولاروجرافي

عبد الغني حمزة و توفيق عميره و سعيد القحطاني

لقد تم دراسة السلوك البولاروجرافي لأيونات الكرومات واليودات والخارصين في وجود تركيزات مختلفة من رباعي بيوتيل كلوريد الأمونيوم في محاليل كبريتات الصوديوم وحمض الكبرتيك تركيزها ار . مولار . وقد درس تأثير هذه المادة العضوية على جهد نصف الموجه وعلى تيار الانتشار للموجات البولاروجرافية . وفسرت النتائج على ضوء إحلال دقائق المادة العضوية محل الأيونات الموجودة على سطح القطب وكذلك على أساس إعاقة عملية إنتقال الشحنة من سطح القطب إلى المحلول . وأظهرت النتائج القدرة الكبيرة لإدمصاص رباعي بيوتيل كلوريد الأمونيوم على سطح قطرات الزئبق والذي لوحظ من النقص الكبير في تيار الانتشار ومن الازاحة في جهد نصف الموجه .

Key Words: Polarography, Tetrabutyl ammonium chloride, Chromate, Iodate, Zinc

ABSTRACT

The polarographic behaviour of chromate, iodate and zinc has been investigated in the presence of different concentrations of tetrabutylammonium chloride in 0.1 M Na_2SO_4 and 0.1 M H_2SO_4. The effect of organic compound on the half-wave potential and on the limiting current of the polarographic wave was investigated. The results are discussed in terms of displacement of these species from the electrode surface by the adsorbed organic species and the retardation of the charge-transfer process. The results indicated the high tendency of tetrabutylammonium chloride adsorption on the mercury drops as revealed from the decrease in the limiting current and the shift in $E_{1/2}$ potential.

INTRODUCTION

In polarography the adsorption of surface active agents at the electrode surface may decrease the limiting current, shift the half-wave potential ($E_{1/2}$) or change the shape and the number of polarographic waves[1,2]. Recently, a study was made on the effect of adsorption of propiononitrile and ethylamine on the polarographic behaviour of chromate and iodate ions[3].

The present work was devoted to study the effect of tetrabutylammonium chloride adsorption on the polarographic behaviour of chromate, iodate and zinc ions as examples of negative and positive ions. Tetrabutylammonium chloride was chosen because it is used as supporting electrolyte in many systems before, especially in alkaline media and at the most negative potentials if necessary[4]. In this study it cannot be considered as supporting electrolyte, since its concentration is comparable with the depolarizer ions (i. e. CrO_4^{2-}, IO_3^-) and Na_2SO_4 and H_2SO_4 are present in major concentrations.

EXPERIMENTAL

Reagents and Materials

All reagents were of analytical grade. 0.02 M of tetrabutylammonium chloride was prepared by taking 2.6 ml of tetrabutylammonium hydroxide solution (40% w/w) in water and 0.35 ml of concentrated HCl and diluted with distilled water to 100 ml.

0.01 M K_2CrO_4 and 0.002 M KIO_3 were prepared by dissolving the appropriate amounts of solid reagents in distilled water. 1 M Na_2SO_4 and 1 M H_2SO_4 were used as supporting electrolytes.

Instrumentation

Polarograms were recorded using Brucker type-310 polarograph. The drop time of mercury is 4.0 seconds and its flow rate is 1.24 mg s^{-1}. A saturated calomel electrode (SCE) was used as a reference electrode in the electrolysis cell.

RESULTS AND DISCUSSION

Effect of adsorption of tetrabutylammonium chloride on the polarographic behaviour of chromate

The polarography of chromate has been the subject of several works[5, 6]. The first wave-followed by a large minimum corresponds to reduction of adsorbed CrO_4^{2-} into Cr(III). Figure 1 shows the polarograms of 0.1 mM K_2CrO_4 in 0.1 M Na_2SO_4 with different concentrations of tetrabutylammonium chloride. It is evident from the figure that the first wave occurs at ~ -0.4 V *vs.* SCE. By the addition of the organic compound, the wave height decreases gradually and disappears almost completely when the concentration of the organic compound reaches 1.6 x 10^{-4} M. This behaviour is due to the replacement of the adsorbed chromate by tetrabutylammonium chloride species which leads to the current decrease.

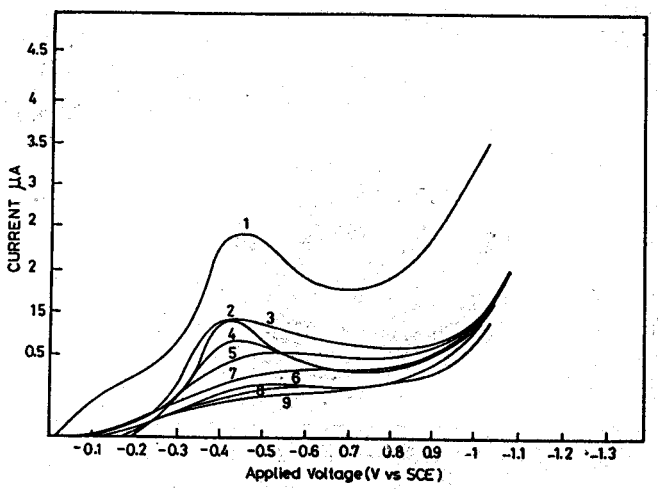

Figure 1: Polarograms of 0.1 mM K_2Cr0_4 in 0.1 M Na_2SO_4 with different concentrations of tetrabutylammonium chloride
(1) 0.00 (2) 2 x 10^{-5} (3) 4 x 10^{-5}
(4) 6 x 10^{-5} (5) 8 x 10^{-5} (6) 1.6 x 10^{-4}
(7) 2.4 x 10^{-4} (8) 3.2 x 10^{-4} (9) 8.0 x 10^{-4} M.

Figure 2 shows the plot of the surface coverage (θ) *vs.* the concentration of the organic substance $\theta = \frac{(i_o - i)}{i_o}$, where i_o is the current of the first wave in the absence of the organic substance and i, is the current in the presence of a ceratin amount of the organic substance. It is evident from this figure that about 80% of the Hg surface is covered when the concentration of the organic compound is about 1.6 x 10^{-4} M.

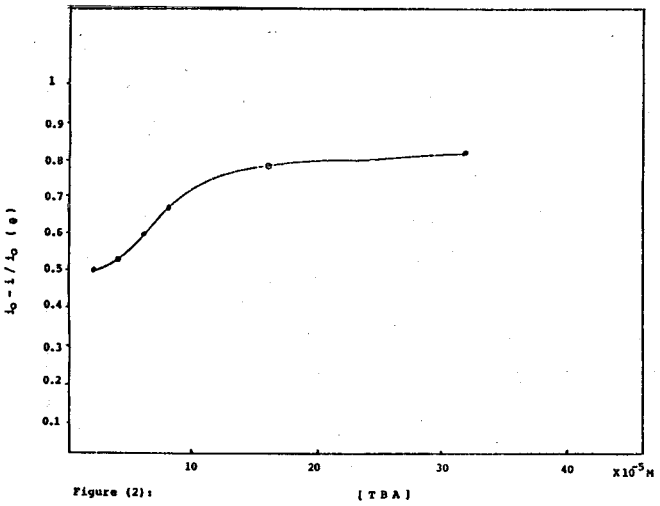

Figure 2: Plot of θ *vs.* concentration of tetrabutylammonium chloride from the polarograms of 0.1 mM K_2CrO_4 in 0.1 M Na_2SO_4.

Effect of adsorption of tetrabutylammonium chloride on the polarographic behaviour of iodate

It has been reported that the reduction of iodate at Hg electrode goes through a 6-electron wave[2]. Figure 3 shows the polarograms of 0.2 mM KIO_3 in 0.1 M H_2SO_4 with different concentrations of tetrabutylammonium chloride. It is clear that the $E_{1/2}$ shifts to more negative potentials by increasing the organic substance concentration. This phenomenon is attributed to the adsorption of the organic substances on the electrode surface which hinders the charge transfer and makes the reduction process more difficult. Figure 4 shows a plot of $E_{1/2}$ *vs.* concentration of the organic substance. It is clear from this figure that the amount of $E_{1/2}$ shift is about 200 mV when the concentration of the organic substance changes from 6.0 x 10^{-5} M to 1.8 x 10^{-4} M. At higher concentrations the amount of $E_{1/2}$ shift is very slight due to the surface saturation of the Hg drop.

Effect of adsorption of tetrabutylammonium chloride on the polarographic behaviour of zinc ions

It is known that Zn^{2+} is reduced at -1.0 V *Vs* SCE in Na2SO4 solutions. Fig. 5 shows that $E_{1/2}$ shifts as the concentration of tetrabutylammonium chloride increases. The amount of $E_{1/2}$ shift is ~200 mv as the concentration

reaches 1.0 x 10^{-5} M. At higher concentrations the shift is very slight due to surface saturation.

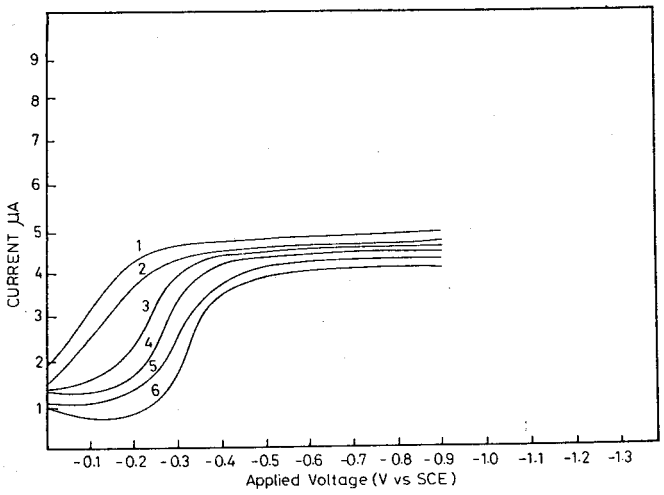

Figure 3: Polargrams of 0.2 mM KIO_3 in 0.1 M H_2SO_4 with different concentrations of tetrabutylammouium chloride (1) 0.00, (2) 4.0 x 10^{-5} (3) 8.0 x 10^{-5} (4) 1.2 x 10^{-4}, (5) 1.6 x 10^{-4} (6) 2.4 x 10^{-4} M.

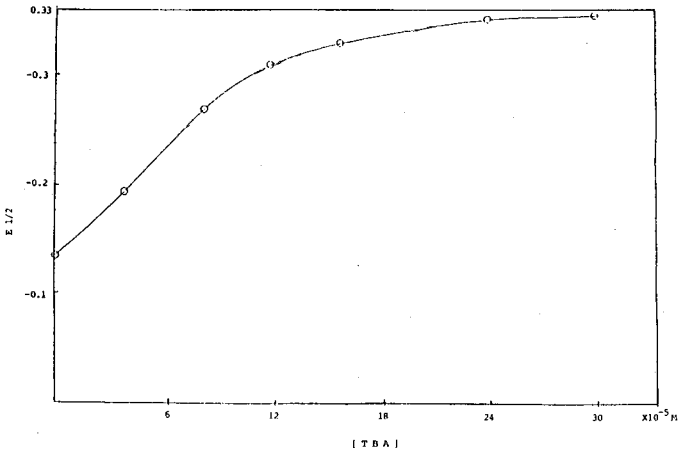

Figure 4: Plot of $E_{1/2}$ *vs* tetrabutylammonium chloride concentration for polarograms of 0.2 m M KIO_3 in 0.1 M H_2SO_4.

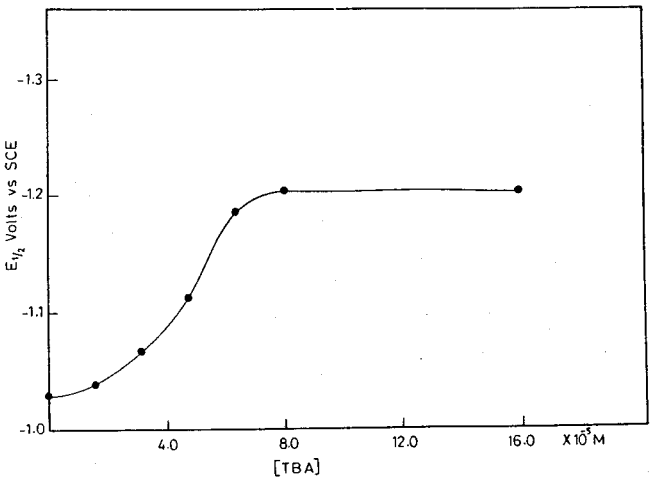

Figure 5: Plot of $E_{1/2}$ *vs.* tetrabutylammonium chloride concentration for polarograms of 0.1 mM $ZnSO_4$ in 0.1 M Na_2SO_4.

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