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Effect of Adsorption of Tetraalkaylammonium Chloride in Polarography

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ABSTRACT. The polarographic behaviour of chromate, iodate and paranitroaniline has been investigated in the presence of different concentrations of tetramethyl, tetraethyl and tetrabutylammonium chloride in 0.1M Na_2SO_4 and 0.1M H_2SO_4. The change in wave height and (E½) was explained on the basis of adsorption of tetraalkylammonium species on the surface of Hg drop. Results are discussed in terms of displacement process and hindrance of charge transfer.

The results show that the adsorption strength depends on the molecular weight of tetraalkylammonium salts. Very weak adsorption was observed in case of tetramethyl, while relatively strong adsorption was observed for tetrabutylammonium species.

Introduction

The adsorption of surface active agents at the electrode surface may decrease the limiting current, shift the halfwave potential (E½) or change the shape and the number of polarographic waves[1,2].

The effect of adsorption of propionitrile and ethylamine on the polarographic behaviour of chromate and iodate has been studied[3]. Also, the effect of adsorption of tetrabutylammonium chloride on the polarographic behaviour of CrO_4^{2-}, IO^{3-} and Zn^{2+} ions has been studied[4].

The present work is devoted to study the effect of adsorption of tetraalkylammonium species, including tetramethyl, tetraethyl and tetrabutylammonium ions on the polarographic behaviour of chromate, iodate and paranitroaniline to compare the adsorption strength of these compounds on the Hg surface.

Experimental

Reagents and materials

All reagents were of analytical grade.

Aqueous 0.01 M tetramethylammonium chloride solution (TMA) was prepared from tetramethylammonium hydroxide and HCl. Aqueous 0.01 M and 0.02 M tetraethyl and tetrabutylammonium chloride solutions (TEA, TBA) were prepared in a similar way.

Aqueous 0.01 M K_2CrO_4, 0.002 M KIO_3 and 0.0025 M paranitroaniline solutions were prepared. Na_2SO_4(0.1 M) and H_2SO_4(0.1 M) were used as supporting electrolytes.

Instrumentation

Polarograms were recorded using Brucker type-310 polarograph. The drop time is ~ 4S and the flow rate is ~ 1.24 mgs^{-1}. A saturated calomel electrode was used as reference electrode and a Pt wire as an auxiliary electrode.

Results and Discussion

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

The polarographic behaviour of chromate has been the subject of several works[5,6]. The first wave followed by a minimum corresponds to the reduction of adsorbed chromate[6].

Figure 1 shows the polarograms of 0.1 mM CrO_4^{2-} in 0.1 M Na_2SO_4 with different concentrations of tetramethylammonium TMA^+ species. The wave splits into two waves as the concentration of TMA^+ increases and there is a slight decrease in the total current even if the concentration of TMA^+ is four times that of CrO_4^{2-}. This indicates a weak adsorption of TMA^+ ions on the Hg surface. As shown in the figure there is a slight shift in E½ as concentration increases.

Figure 2 shows the polarograms of CrO_4^{2-} in the presence of TEA^+ species. The wave splits into two waves and the decrease of current indicates the increasing tendency of TEA^+ to be adsorbed as compared to TMA^+ species. Also there is more shift in E½ compared to TMA^+ species.

Figure 3 shows polarograms of CrO_4^{2-} in the presence of TBA^+ species. The wave height decreases gradually and disappears almost completely when the concentration of TBA^+ species reaches 0.16 mM. This behaviour is due to the

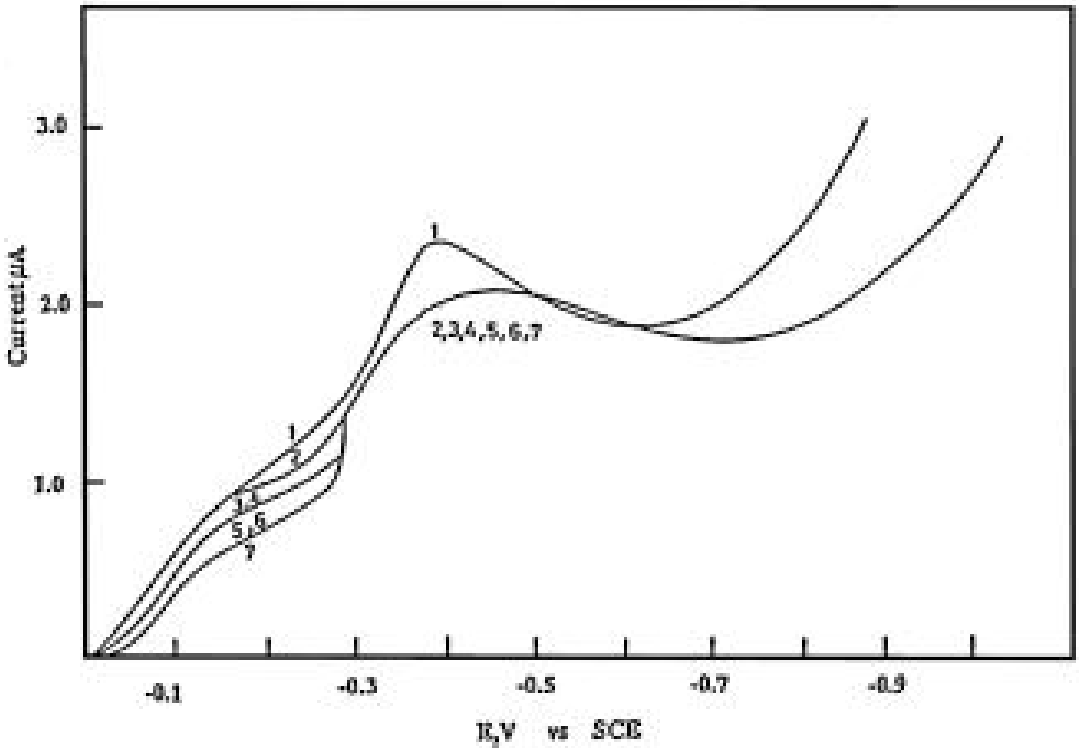

FIG. 1. Polarograms of aqueous 0.1 mM K_2CrO_4 in 0.1 M Na_2SO_4 with different concentrations of tetramethylammonium chloride (1) 0.0, (2) 8.0×10^{-5}, (3) 1.6×10^{-5}, (4) 3.4×10^{-5}, (5) 8.0×10^{-4}, (6) 2.0×10^{-3} and (7) 4.0×10^{-3} M.

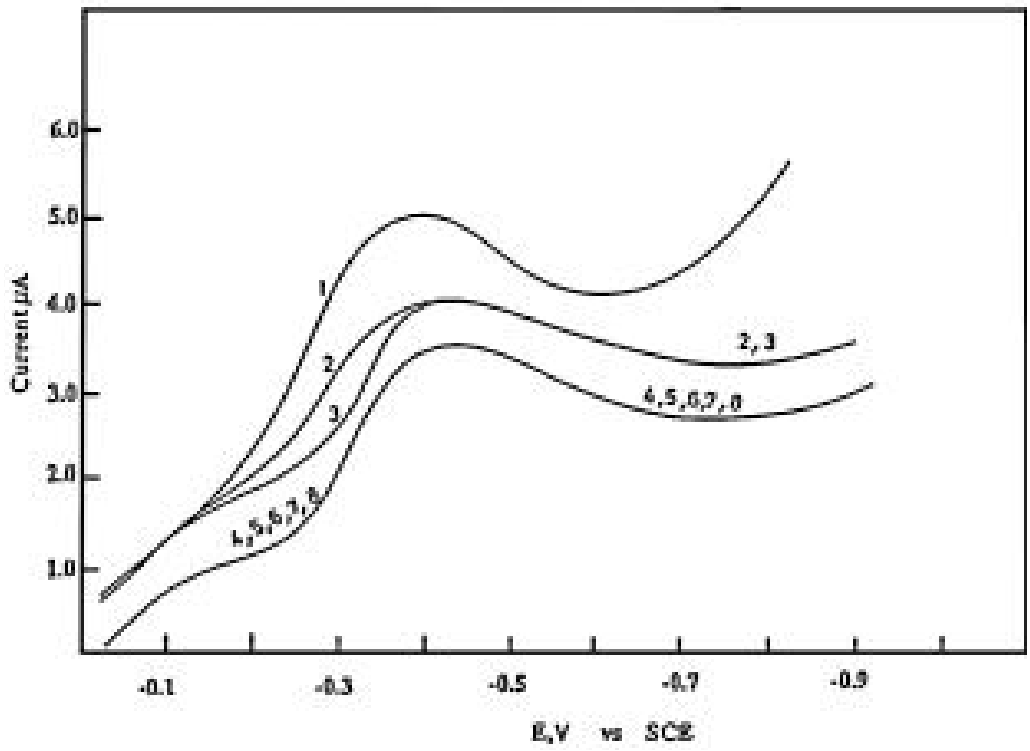

FIG. 2. Polarograms of aqueous 0.1 mM K_2CrO_4 in 0.1 M Na_2SO_4 with different concentrations of tetramethylammonium chloride (1) 0.0, (2) 8.0×10^{-5},(3) 1.2×10^{-4}, (4) 2.4×10^{-4}, (5) 4.0×10^{-4}, (6) 8.0×10^{-3}, (7) 1.6×10^{-3} and (8) 7.4×10^{-2} M.

replacement of the adsorbed chromate by adsorbed TBA^+ species. In this case 80% of Hg surface is covered with TBA^+ species when its concentration is about 0.16 mM. This indicates a strong adsorption of the TBA^+ species on Hg surface. Also the E½ shifts to more negative potentials as the concentration of TBA^+ species increases.

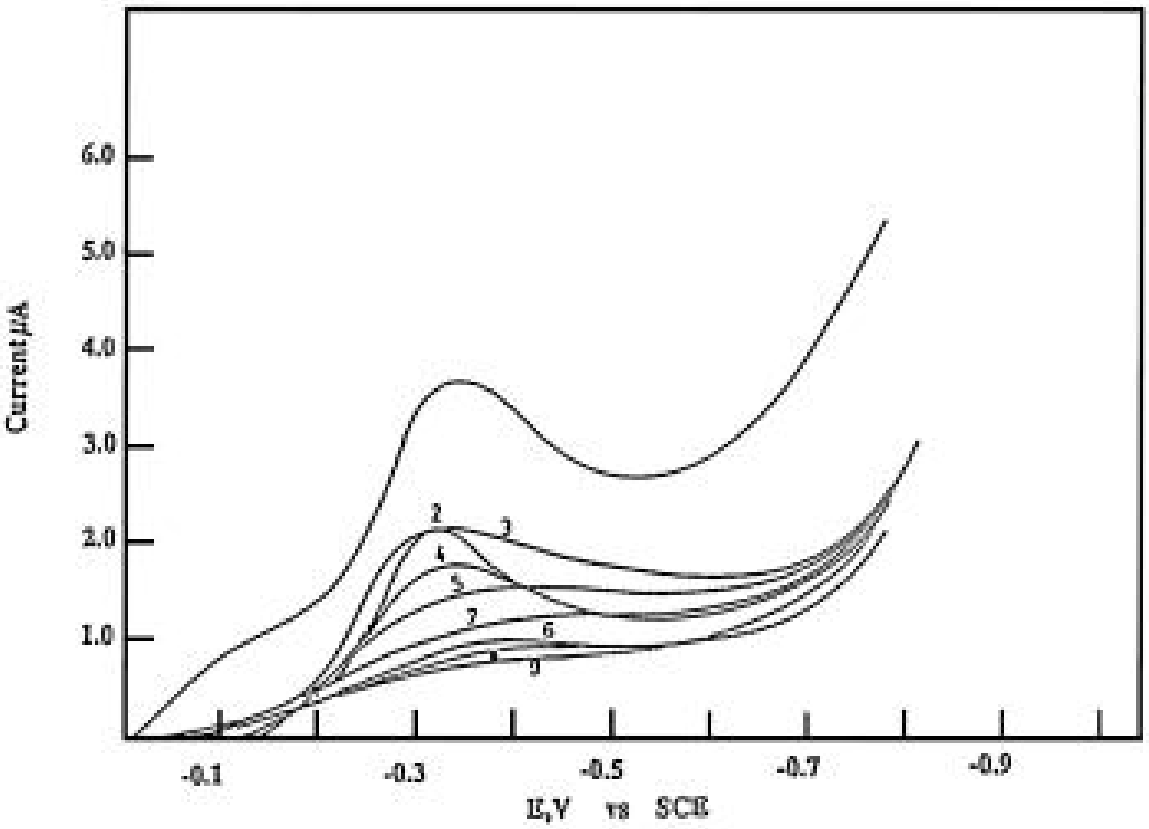

FIG. 3. Polarograms of aqueous 0.1 mM K_2CrO_4 in 0.1 M Na_2SO_4 with different concentrations of tetrabutylammonium chloride (1) 0.0, (2) 2.0×10^{-5}, (3) 4.00×10^{-5}, (4) 6.0×10^{-5}, (5) 8.0×10^{-5}, (6) 1.6×10^{-4}, (7) 2.4×10^{-4}, (8) 3.4×10^{-4} and (9) 8.0×10^{-4} M.

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

It has been reported that the reduction of iodate goes through a single 6-electron wave[2]. It was observed that the addition of either TMA^+ or TEA^+ species has no effects on the IO_3^- electroreduction wave, while TBA^+ species only shift the value of E½ to more negative potentials as shown in Fig. (4).

This effect is attributed to the adsorption of TBA^+ species on the Hg surface.

The adsorbate hinders the charge transfer and makes the electroreduction process more difficult.

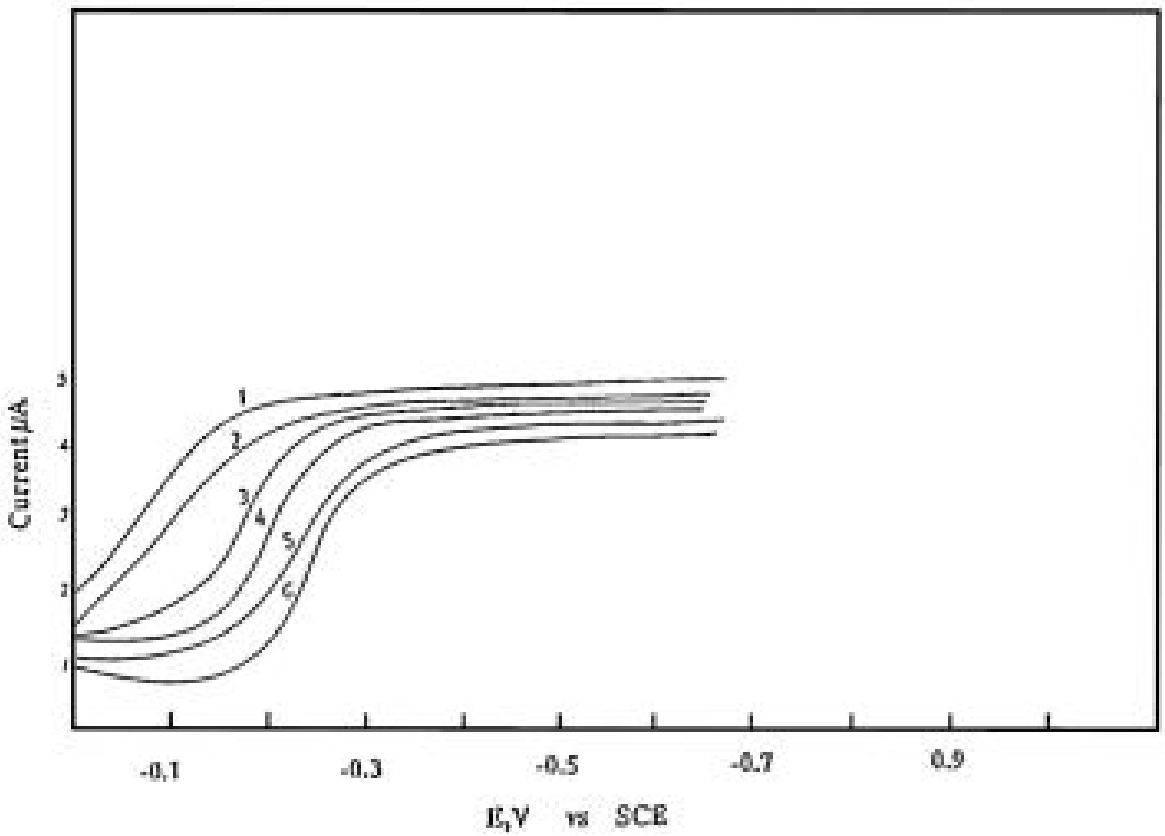

FIG. 4. Polarograms of aqueous 0.2 mM KIO_3 in 0.1 M H_2SO_4 with different concentrations of tetrabutylammonium chloride (1) 0.0, (2) 4.0×10^{-5}, (3) 8.0×10^{-5}, (4) 1.2×10^{-4}, (5) 1.6×10^{-4} and (6) 2.4×10^{-4} M.

Effect of adsorption of tetraalkylammonium chloride on the polarographic behaviour of paranitroaniline

In acidic solutions, paranitroaniline molecules first are preprotonated, and then their electroreduction goes through a single 6-electron irreversible wave[7]. The polarograms of 0.25 mM paranitroaniline shows a maximum which can not be removed by the addition of TMACl solution up to 6.4 mM.

This fact indicates that TMACl species are not adsorbed on the Hg surface. One-fourth of the maximum height only was eliminated by adding 6.4 mM TEACl solution. Therefore, it can be concluded that the adsorption of TEA^+ species on the Hg surface is very weak.

On the other hand, by increasing the concentration of TBACl to 1.6 mM, the maximum is removed completely, and by further increasing the TBACl concentration, the wave splits into two waves as it is shown in Fig. 5. The inhibition effect produces the splitting of the original wave into two waves. This result indicates that TBACl can be used as a polarographic maximum suppressor. However, the addition of TBACl has to be made carefully, to avoid any effect on the limiting current of the electroactive species.

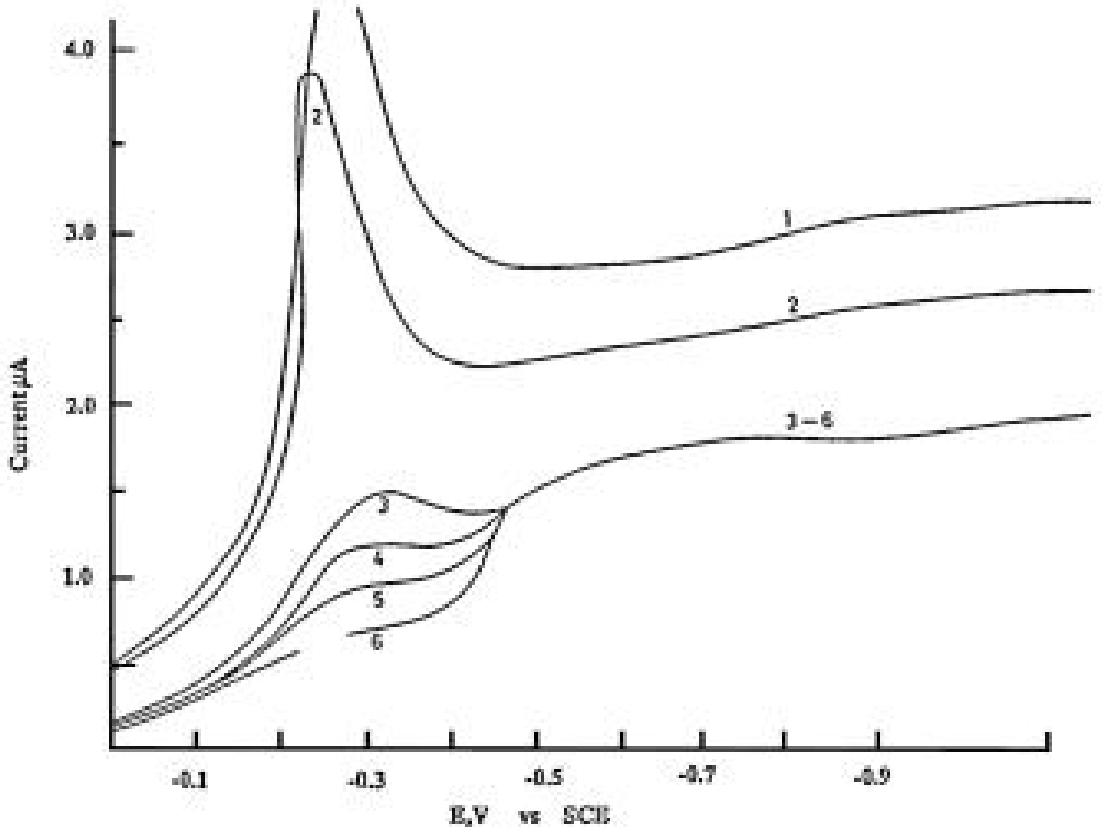

FIG. 5. Polarograms of aqueous 0.25 mM paranitroaniline in 0.1 M H_2SO_4 with different concentrations of tetrabutylammonium chloride (1) 0.0, (2) 3.2×10^{-4}, (3) 1.6×10^{-3}, (4) 3.2×10^{-3}, (5) 4.8×10^{-3} and (6) 6.4×10^{-3} M.

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تأثيـر إدمصـاص رباعي ألكيـل كلوريد الأمونيـوم في الطرق البولاروجرافية

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جـــدة – المملكة العربية السعودية

المستخلص. تمت دراسة السلوك البولاروجرافي للكرومات واليودات والبارانيتروأنيلين في تركيزات مختلفة من رباعي ميثيل ورباعي إيثيل ورباعي بيوتيل كلوريد الأمونيوم في محلول كبريتات الصوديوم ومحلول حامض الكبريتيك . ولقد لوحظ تغير في طول الموجة وجهد نصف الموجة .

وقد فسر ذلك على أساس ادمصاص رباعي ألكيل كلوريد الأمونيوم على سطح قطرة الزئبق . وعولجت النتائج على أساس الإحلال وإعاقة انتقال الشحنة .

وأوضحت النتائج أن درجة الادمصاص تعتمد على الوزن الجزيئي لأملاح رباعي ألكيل كلوريد الأمونيوم . وقد لوحظ ادمصاص ضعيف في حالة رباعي ميثيل بينما لوحظ ادمصاص قوي في حالة رباعي بيوتيل كلوريد الأمونيوم .