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IN-SITU RAMAN SPECTROSCOPIC STUDIES ON COADSORPTION OF THIOUREA WITH ANIONS AT SILVER ELECTRODES

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Abstract—Thiourea (TU) adsorbed at Ag electrodes both in neutral and acidic solutions has been studied using surface enhanced Raman (SER) spectroscopy and differential capacitance measurements. The coadsorption of TU with anions may be through the NH_2 group in neutral solutions, and the NH_3^+ group in acidic solutions respectively. Replacement of ClO_4^- ions coadsorbed with TU by Cl^- ions can only take place at more negative potentials as TU changes orientation at the surface. The different orientations of adsorbed TU have substantial effects on the H_2 evolution at Ag electrodes. In neutral solutions the H_2 evolution is catalysed by the TU adsorbed parallelly to the surface, however, in acid media the H_2 evolution is inhibited considerably by the TU adsorbed perpendicularly.

INTRODUCTION

Thiourea (TU) is widely used in the electrodeposition of metals as an additive for promoting lustre and smoothness and also as a complexing agent[1]. The catalytic effect of TU on H_2 evolution at various electrodes has also been reported[2, 3]. Therefore, the adsorption of TU, both from aqueous and non-aqueous solutions onto the surface of different metallic electrodes represents an interesting topic over many years[4–7]. Recently, adsorption of TU on passivated Fe has been studied using *in-situ* FTIR spectroscopy[8]. Several papers of SER studies on TU adsorbed to Ag and Cu electrodes have been published[9–12]. The authors have reported coadsorption of TU with supporting electrolyte anions by observing the SER signals of these species simultaneously in acid solutions[10–12]. Surface enhanced Raman Studies has advantages over conventional electrochemical techniques for investigating coadsorption as the latter inevitably measures the sum of all the processes at the electrode/solution interface[13, 14]. By analysing relations of the SER spectra and the electrochemical parameters, it is possible to study coadsorption at molecular level. In this paper more extensive stuides on the adsorption behavior of TU, particulary the coadsorption with anions, and its effect on H_2 evolution from Ag electrodes both in acidic and neutral solutions are presented.

EXPERIMENT

The Raman spectra were recorded either with a Spex 1403 double monochromator spectrometer or with a modified Coderg T800 spectrometer having an additive triple monochromator using Argon ion 514.5 nm radiation (about 60 mW at the sample) with a bandpass of 5 cm^{-1}. Unfocused radiation was used to minimise any possible photolysis. The spectroelectrochemical cell was similar to that which has been described elsewhere[13]. The working electrode consisted of a 5 mm diameter rod of 99.99% silver (Johnson Matthey Chemical Ltd.) sheathed in Kel–F from Tring Engineering. The polished electrodes were subjected to one oxidation–reduction cycle (ORC) in 1 M KCl solution[15] then transferred to TU solutions studied. The differential capacitance measurements were carried out using a potentiostat (Hi–Tek instruments Type DT2101) and a waveform generator (Hi–Tek instruments PPRI) and a phase sensitive detector (ORTEC Brookdeal 9501 lock–in amplifier). The AC voltammograms (4 mV AC signal superimposed on a linear ramp at 4 mV s^{-1}) were recorded using a Farnell *x–y* recorder. All potentials are referred to the saturated calomel electrode scale (SCE).

RESULTS AND DISCUSSION

Coadsorption of TU with anions in acidic and neutral media

Figure 1 demonstrates that the SER spectra showing the coadsorption of TU with anions are strongly dependent on the nature of the supporting electrolyte including the concentration and composition. The intense band at 934 cm^{-1} is from the totally symmetric stretching mode of ClO_4^-, indicating coadsorption of this anion with TU. Figure 1(a) and (b) presents the effect of the increase of the molar ratio of ClO_4^- to TU from 1 about to 10 in the solution at a constant pH value and potential (− 1.0 V). All of the SER bands rise in intensity distinctly with increase of the anion concentration, indicating increase in the activity of coadsorption for TU and ClO_4^-. In order to confirm that the increase in intensity of the band at 934 cm^{-1} is due to increase of the surface species rather than the concentration in the bulk phase, 0.01 M H_2SO_4 was added to this system. The intense band at 934 cm^{-1}

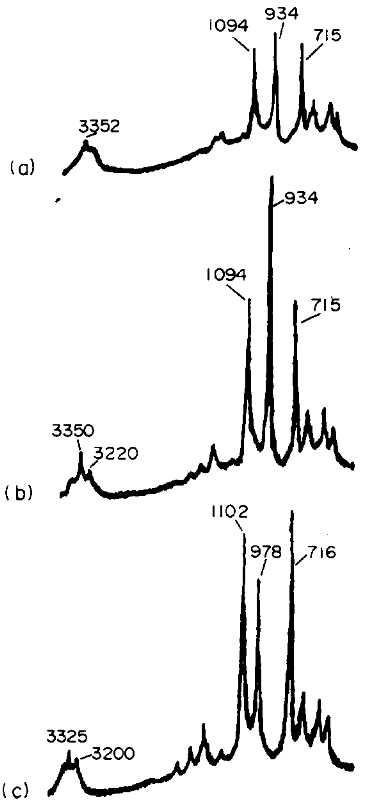

Fig. 1. SER spectra ($\Delta\upsilon$/cm^{-1}) of TU and ClO_4^- and SO_4^{2-} for the region 400–3600 cm^{-1} from Ag electrodes at − 1.0 V in 0.1 M TU (a) + 0.01M $HClO_4$ + 0.01 M $NaClO_4$, (b) + 0.09 M $NaClO_4$ and (c) + 0.01 M H_2SO_4

was replaced by 978 cm^{-1} (see Fig.1(c)), which means that SO_4^{2-} replaced ClO_4^- on the surface. In addition, the main N–H stretching bands at about 3220 and 3350 cm^{-1} were shifted down to about 3200 and 3325 cm^{-1}, and the N–C–N stretching band was shifted in frequency from 1094 to 1102 cm^{-1} while the C–S stretching band at 715 cm^{-1} remained unchanged (vibrational mode assignments of TU in this paper are based on a paper by Ishiguro *et al.*[16]). This phenomenon reveals that the replacement of the anions can affect the N–C–N and N–H stretching bonds more strongly than the other bonds, which could be an evidence that the coadsorption of TU with anions is through the amine groups.

In the present study, the SER spectra of TU and anions had been also recorded simultaneously from neutral solutions (*eg* 0.01 M TU + 1.0 M $NaClO_4$[17]). In this case, however, the band intensity of the anion is relatively weak. The ratio of the SER intensity of the 934 cm^{-1} band from ClO_4^- to the 1094 cm^{-1} band from TU in the acidic medium (pH < 2) is twice as high as that in the neutral solution, which implies that the nature of the surface species in the coadsorption may not be the same in the acidic and neutral solution. As the TU is adsorbed at the Ag electrode via its sulphur[9–11], one could assume that in the acid solution H^+ has been protonating to the NH_2 group of TU and the protonated TU can induce anions to be coadsorbed at the surface more effectively than the neutral TU. There are three possibilities about the way the anions may be bonded to the NH_2 (or NH_3^+) group in the coadsorption: (a) the anion forms a bond directly with the N atom; (b) with the H atom; (c) with H^+ protonating the N atom. Assumption (a) is most likely since this would cause the frequency of the N–C–N stretching band to decrease and the N–H band increase, which is in contrast to the experimental data. Assumption (b) and (c) may correspond to the case of the coadsorption in neutral and acidic solutions respectively.

The change in orientation for adsorbed TU

In the previous SER studies, Fleischmann *et al.* have reported that the band at 612 cm^{-1} designated as SCNN out of plane bending mode rose in intensity with increasingly negative potential, which means that TU changes its orientation from essentially perpendicular to parallel to the surface[11]. In order to have a deeper insight on it, the differential capacitance and SER measurements were carried out. Figure 2 presents the differential capacitance curves of 0.01 M TU at Ag electrodes in 0.5 M $NaClO_4$ with various pH values. The curve (d) was recorded only at less negative potentials because of the interference of high faradaic current of H_2 evolution. Since TU can be adsorbed on the electrode surface in a wide potential region[10–11], peak I in the curves is probably due to desorption of TU at very negative potentials. Particular attention should be paid to peak II at around − 0.6 V because it is in this potential region that the band at 610 cm^{-1} becomes visible and increases in intensity considerably with increasingly negative potentials[17]. With decrease of concentration of TU the peak II shifts to more positive potentials, which is in satisfactory agreement with the SER data. In the SER studies, the 610 cm^{-1} band emerges at more positive potentials in the system with lower concentration of TU[17]. A set of SER spectra with various

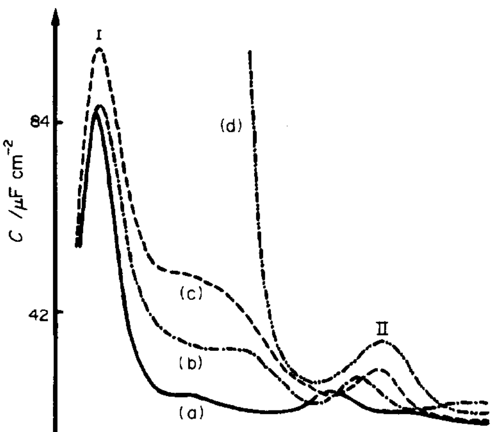

Fig. 2. Differential capacitance curves for Ag electrodes in 0.01 M TU and 0.5 M $NaClO_4$ with various concentration of $HClO_4$ (a) 0 M, (b) 0.001 M, (c) 0.01 M and (d) 0.1 M.

concentration of TU at a constant potential of − 0.8V is shown in Fig. 3. With decrease of the concentration of TU, all the bands decrease in intensity due to decrease of the surface coverage[11]. However, the relative intensity of the 612 cm^{-1} band in the spectrum increases considerably (*eg* the ratio of the intensity of the 612 cm^{-1} band to the 1096 cm^{-1} band is about 0.2 in Fig. 3(a), but 0.7 in Fig. 3(d)). This is presumably because the change in orientation becomes easier at the low surface coverage. It is reasonable, therefore, to assume that the peak II is associated with a change of orientation. The change in orientation of adsorbed TU can explain an interesting phenomenon, that the effect of the adsorbed TU on H_2 evolution at Ag electrodes in acidic and neutral media is markedly different.

The influence of adsorbed TU on the H_2 *evolution reaction*

Figure 4(a) and (b) illustrates the effect of TU on H_2 evolution at Ag electrodes in acidic and neutral media respectively. The *I–E* curves measured in the acid media with various concentration of TU show that there is a significant shift to negative potential (− 80 mV) for H_2 evolution even after only small additions of TU (10^{-4} M) to the solution (see Fig. 4(a)).

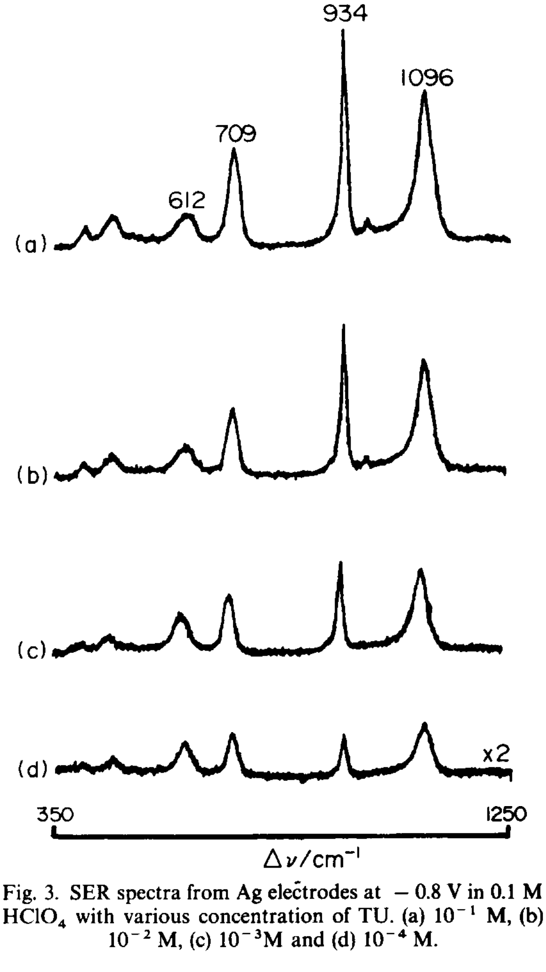

Fig. 3. SER spectra from Ag electrodes at − 0.8 V in 0.1 M $HClO_4$ with various concentration of TU. (a) 10^{-1} M, (b) 10^{-2} M, (c) 10^{-3}M and (d) 10^{-4} M.

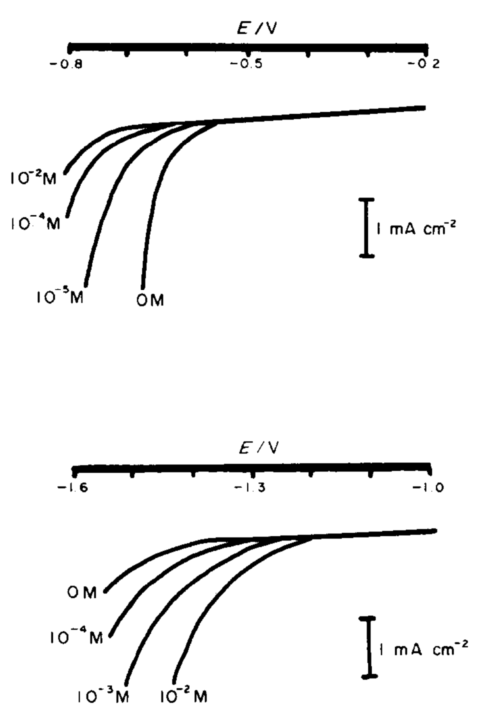

Fig. 4. Cathodic I–E curves of H_2 evolution on Ag electrodes in (a) 0.5 M $NaClO_4$ + 0.1 M $HClO_4$ and (b) 0.5 M $NaClO_4$ with various concentrations of TU. Scan rate is 50 $mV s^{-1}$.

Evidently, hydrogen ion discharge on the Ag electrode is inhibited by the adsorption of TU. In contrast, the adsorbed TU has a markedly catalytic effect upon H_2 evolution in the neutral media, in Fig. 4(b). It is possible that the different orientations of adsorbed TU in various potential ranges have opposite effects on the H_2 evolution. The differential capacitance curve in Fig. 2 shows that there are no significant differences for the adsorption behaviour of TU in neutral and acidic solutions, *ie* the peak II corresponding to the orientation change was observed in the same potential region (see Fig. 2(a) and (c)). H_2 evolution in the neutral solution occurs at very negative potentials, where TU has already changed its orientation to parallel to the surface. In contrast, the H_2 evolution takes place at relatively positive potentials in acid media and it is inhibited by TU adsorbed perpendicularly to the surface. It is more likely that only the essentially planar TU is a catalyst for the H_2 evolution on Ag electrodes. The amine group of TU (especially as this group is close to or touching the surface) may play a very important role for this catalytic effect. For example, the amine group may act as a bridge–forming ligand for water (or proton) discharge, thereby accelerating the Volmer process and hence increasing the activity of adsorbed hydrogen[18]. It should be emphasised that the influence for the adsorbed TU on H_2 evolution at Ga[3] is totally different from Ag electrodes although the metal–hydrogen bond strength of these two metals are very similar[18]. Szabo *et al* have claimed that the adsorbed TU at Ga can catalyse H_2 evolution both in acid and base solution. Moreover, it accelerates the rate of H_2 evolution to a larger extent in acid media than that in alkaline[3]. On the basis of the above assumption, one may suppose that TU can catalyse H_2 evolution either in alkaline or in acid media provided the adsorption of TU is *via* its amine group to the surface. This could be the case for TU adsorbed at Ga electrodes.

Effect of the orientation change of adsorbed TU on coadsorption with anions

A SER spectrum in Fig. 5(a) indicates the coadsorption of TU with ClO_4^- on an Ag electrode at − 0.2 V in a solution containing 10^{-4} M TU and 0.5 M $HClO_4$. After adding 2×10^{-3} M Cl^- to the cell, most bands were reduced in intensity only slightly (Fig. 5(b)). This means that Cl^- can neither replace TU nor the ClO_4^- coordinated with TU. However, there are some significant changes in the spectrum as the potential moved to − 0.5 V (Fig. 5(c)). The band at about 215 cm^{-1} from ν (Ag–Cl) mode emerged markedly while the intense band at 934 cm^{-1} for ClO_4^- decreased in intensity considerably. At − 0.7V (Fig. 5(d)), the 934 cm^{-1} band became very weak, which may have been due to solution phase species only. When the Ag electrode was pushed against the cell window, this band disappeared completely. It follows that the ClO_4^- as surface species were replaced eventually. It is well known that Cl^- can be specifically adsorbed at Ag electrodes and normally the SER band of ν (Ag–Cl) mode at about 220 cm^{-1} reaches the maximum in intensity at − 0.2 V. However, in the present case, this band was absent at − 0.2 V but appeared at − 0.5V and reached a maximum of intensity at around − 0.6 V. Another interesting feature in the spectrum at − 0.7 V (Fig. 5(d)) is that the band at 614 cm^{-1} is surprisingly high. This means that the replacement of anions on the surface may be connected strongly with the change in orientation of TU as they all occur in the same potential ranges. At the potentials positive to − 0.5 V, the TU coordinated with ClO_4^- is tightly adsorbed perpendicularly to the surface, which excludes Cl^- ion from the surface; and in this case one ClO_4^- ion may be coordinated with more than one TU at the surface. However, as the potential is taken more negative, some TU is desorbed and the remaining TU changes orientation to be essentially parallel to the surface. This may cause the coordination between TU and ClO_4^- to be broken because of the steric effect so that the SER intensity of ClO_4^- decreases markedly (*eg* see Fig. 5(d)). The spectra in Fig. 2 are also in good agreement with this assumption: the relative intensity of the 612 cm^{-1} band in the spectrum increases with the decrease in the intensity of the 934 cm^{-1} band, indicating that the more TU molecules change orientation, the less ClO_4^- ions are coadsorbed at the surface. Following the replacement of ClO_4^- by Cl^- ion, TU would tend to adsorb parallelly to the surface since Cl^- is much smaller than ClO_4^- so that the 614 cm^{-1} band increases considerably in intensity, However, bearing in mind the capability of Cl^- to be specifically adsorbed at Ag electrodes, the way of coadsorption with TU for Cl^- may be significantly different from that for polyoxyanions such as ClO_4^- and SO_4^{2-}. For example, it is of special interest that the frequencies of the SER bands from the adsorbed ClO_4^- are identical to those from the solution species, moreover, these frequencies are independent of the potential. This phenomenon may indicate the interaction of ClO_4^- with the surface is much weaker than that of Cl^-.

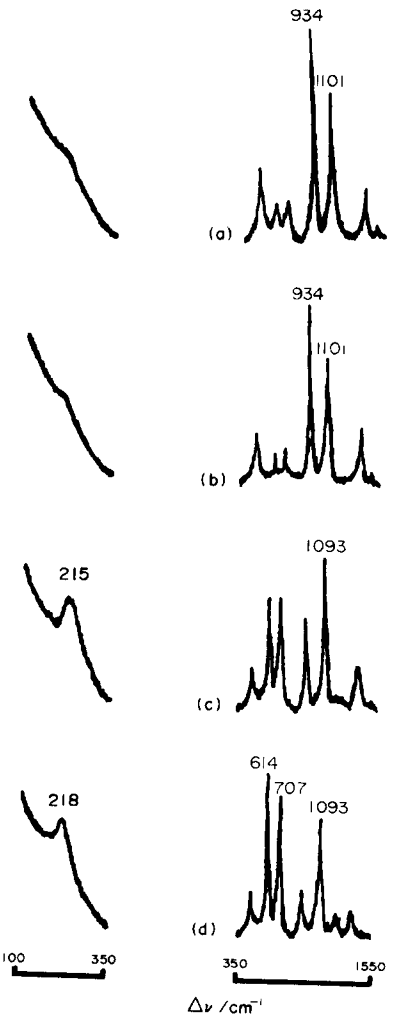

Fig. 5. SER spectrum form an Ag electrode at − 0.2 V in 10^{-4} M TU + 0.5 M $HClO_4$ (a) compared with spectra recorded at a range of potentials following the addition of 2×10^{-3} M Cl^- (b) − 0.2 V, (c) − 0.5 V and (d) − 0.7 V.

According to above experimental observations, one may be able to classify coadsorption as two aspects: parallel coadsorption and induced coadsorption[19]. In the parallel coadsorption, two or more than two species (such as TU and Cl^-, pyridine and CN^-[20]) can be observed simultaneously or individually, depending on the potential, composition and concentration of the solution. However, for the induced coadsorption, the SER signal of one of the coadsorbed species (such as polyoxyanions in the present study) can not be detected individually; it can only be observed simultaneously with that of another strong adsorbed species such as TU. Further work on this aspect is required in order to fully understand the nature of the coadsorption and the SER mechanism.

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