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Overlayer adsorbates of NH$_4^+$ and SO$_4^{2-}$ on a Pt(111) surface studied by in situ IR spectroscopy

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Abstract

Adsorption of ammonium cations (NH$_4^+$) and sulfate anions (SO$_4^{2-}$) on a Pt(111) electrode in an (NH$_4$)$_2$SO$_4$ aqueous solution was studied by in situ infrared reflection absorption spectroscopy (IRAS). Adsorption and desorption of these ions on a coadsorbed NH$_3$HSO$_4$ first layer were observed on a Pt(111) electrode surface in a 0.02 M (NH$_4$)$_2$SO$_4$ solution.

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1. Introduction

The structure determination of a double layer that includes an overlayer on an electrode surface has been an important target for electrochemistry. Recent development in surface analysis has made it possible to reveal adsorbed structures in an inner Helmholtz layer on electrode surfaces. The structures of specifically adsorbed ions on a upd-modified surface have been thoroughly studied by in situ IRAS as well as in situ SXD and STM. In contrast with the extensive results of specifically adsorbed first layer species on electrode surfaces, there have been few results regarding second overlayer species on the first adlayer, partly because that the existence of a huge amount of solvent water molecules hinders the attempts to discriminate between the second layer species and a further overlayer in bulk phase.

One strategy for discriminating between a second layer species in an outer Helmholtz layer and a species in a further outer layer is to identify such a second layer of counter cations or anions on a known first layer species that is specifically adsorbed on the surface, because specifically adsorbed anions or cations are likely to form ions pairs with counter cations or anions, resulting in a non-specifically adsorbed overlayer on the electrode surface. Furthermore, the introduction of an ion salt that includes a fluoride anion into the solution is a useful method for probing overlayer adsorbates, because a fluoride anion, which is likely to form a very strong hydrogen bond through ion pair substitution, causes a combination change in the hydrogen-bonding scheme in ion pairs in a double layer.

In the present paper, we report that the adsorption of overlayer species of NH$_4^+$ and SO$_4^{2-}$ in a wide potential range in the double layer on a Pt(111) surface. F$^-$ was introduced into the solution to probe the structure of the overlayer of NH$_4^+$ and SO$_4^{2-}$. To our best knowledge, it is the first time that a strong ion pair between NH$_4^+$ and SO$_4^{2-}$ in an aqueous solution has been observed.

2. Experimental procedure

The details of IRAS measurement procedure were described elsewhere [1]. The IRAS measurements were performed on a system-2000 FTIR spectrometer (Perkin–Elmer) with a liquid nitrogen cooled MCT detector. All spectra were taken by synchronized normalized FTIR spectroscopic (SNIFTIRS) measurement or a potential step measurement with 8 cm$^{-1}$ resolution. The time for recording one spectrum was ca. 60 s.

A Pt(111) (Mateck) electrode was mechanically polished with successively finer grades of Al$_2$O$_3$ powder, followed by flame annealing and cooling in an Ar+$H_2$ stream before experiment. A Pt mesh and a saturated calomel electrode (SCE) were employed as a counter electrode and a reference electrode, respectively. All potentials reported in this paper are referred to SCE.

All reagents were of commercially available analytical-grade quality. Solutions were prepared using Milli-Q water.
3. Results and discussion

The NH$_4^+$ concentration in a solution of 0.02 M (NH$_4$)$_2$SO$_4$ + 0.02 M NaOH solution (pH 12.3) is three orders of magnitude smaller than that of NH$_3$. Therefore, SO$_4^{2-}$ anions are predominantly surrounded by counter cation of hydrated Na$^+$ rather than NH$_4^+$ in the bulk solution. Thus, the low concentration of NH$_4^+$ makes formation of hydrogen bonding between NH$_4^+$ and SO$_4^{2-}$ very improbable in the bulk phase solution. In contrast, in a double layer on an electrode surface a cathodic potential supply induces an increase in both NH$_4^+$ and hydronium cation concentration and hence a remarkable pH decrease at the electrode. Since the NH$_4^+$ concentration increases locally in the double layer on the surface after equilibrium, ion pair formation between an NH$_4^+$ cation and a SO$_4^{2-}$ anion is now conceivable in the double layer region on the Pt(111) electrode.

Fig. 1 shows SNIFTIR spectra of a Pt(111) electrode surface in a 0.02 M (NH$_4$)$_2$SO$_4$ + 0.02 M NaOH solution as a function of electrode potential. The spectra are referenced to the spectrum taken at the background potential of −750 mV, where cations and anions are hardly adsorbed on the electrode surface. The bands at 1458 and 1105 cm$^{-1}$ can be assigned to $\delta$ NH$_4^+$ symmetric bending absorption [2] and $\nu$ SO stretching absorption of SO$_4^{2-}$ [3], respectively. The wavenumber of the $\delta$ NH$_4^+$ band is relatively lower by approximately 30–60 cm$^{-1}$ than those in ammonium solid salts, suggesting that NH$_4^+$ may form a strong hydrogen bond with SO$_4^{2-}$ [2,4]. The band at 1105 cm$^{-1}$ shows a typical value of a sulfate anion in aqueous solutions. The positions of the two bands ($\delta$ NH$_4^+$ and $\nu$ SO), remained constant (1458 and 1105 cm$^{-1}$) at all the potentials, while the intensities for both bands showed simultaneous variations throughout the whole potential region examined. The pair bands start to appear at −550 mV and reach a maximum intensity around −150 mV, which is the potential of zero charge (pzc potential) [5–7], and gradually decrease in intensity at the more positive potentials. It is well known that sufficient water molecules including hydroxide anions or hydronium cations can hydrate to Na$^+$ or SO$_4^{2-}$ ions, at the very negative or positive potentials, whereas at the pzc potential where hydrated molecules become sparse, the NH$_4^+$−SO$_4^{2-}$ ion pair in the double layer was formed by the NH$_4^+$ evolution derived from a pH decrease. Adsorption of NH$_3$ molecule began to appear at −250 mV (1264 cm$^{-1}$, umbrella mode), and the NH$_3$ coverage reached a maximum at 450 mV (1305 cm$^{-1}$), then decreased gradually at further positive potentials. The broad potential dependent absorption seen at 1210–1230 cm$^{-1}$ can be assigned to the band for a bisulfate anion coadsorbed with an ammonia molecule. Coadsorption of the NH$_3$ molecule with a bisulfate anion was observed within the potential range at 150–650 mV. At 850 mV, the band at 1200 cm$^{-1}$ for a bisulfate solution species became dominate, along with the onset of OH$^-$ adsorption. These results are in good accord with our previous results for Pt(111) in sulfuric acid solution [8,9].
The interfacial pH control and substitution by $F^-$ (NaF) can help to discriminate between a second layer adsorbate and further overlayer species in bulk solution. When NaF salt is introduced into a (NH$_4$)$_2$SO$_4$ solution (0.02 M (NH$_4$)$_2$SO$_4$ + 0.02 M NaF), $F^-$ could exhibit much stronger hydrogen bonding with NH$_4^+$ (NH$\cdot\cdot\cdot$F$^-$) than NH$\cdots$O (SO$_4^{2-}$) and the overlayer structure of NH$_4^+$ and SO$_4^{2-}$ pair could be different from the case that the solution is free of $F^-$. Fig. 2 shows SNIFTIR spectra of Pt(111) in a 0.02 M (NH$_4$)$_2$SO$_4$ + 0.02 M NaF aqueous solution as a function of electrode potential. All of the spectra are quite similar to those in Fig. 1 (0.02 M (NH$_4$)$_2$SO$_4$ + 0.02 M NaOH solution), except that peak intensity (1096 cm$^{-1}$) of the SO$_4^{2-}$ species is remarkably reduced because that strong hydrogen bonding of NH$_4^+\cdots$F$^-$ is preferentially formed so that NH$_4^+$ is surrounded by the $F^-$ anion, resulting in that SO$_4^{2-}$ ion is excluded from the surface anion–cation ion pairs.

Fig. 3 shows time dependent spectra at potentials of $-50$ mV (a) and $+50$ mV (b) on a Pt(111) electrode in a 0.02 M (NH$_4$)$_2$SO$_4$ solution (pH 5.31). The spectra are referenced with regard to the background spectrum at a potential of $+250$ mV, where the coadsorbed NH$_3$ and HSO$_4^-$ layer extends over the surface in a saturation coverage. The band at 1459 cm$^{-1}$ greatly decreased in intensity within 10 min in (a), while it remained nearly constant in (b) as time elapses. At $-50$ mV, where no specifically adsorbed first layer, NH$_3$ + HSO$_4^-$ coadsorbs, exists, both NH$_4^+$ and SO$_4^{2-}$ ions cannot be stabilized on the bare surface and desorb easily from the surface because of the lack of an anchoring first layer adsorbate on Pt(111). In contrast, at $+50$ mV, where the first adlayer is firmly present, both NH$_4^+$ and SO$_4^{2-}$ ions can be stabilized in such a way that NH$_4^+$ interacts with HSO$_4^-$ and also SO$_4^{2-}$ with NH$_3$ through firm hydrogen bonding. As a result, the IR peak intensities of these ions remained constant. It is the firm hydrogen bonding network extending to the outer layer in the double layer that makes the double layer structure significantly different from that in the solution phase.

4. Conclusions

Overlayer adsorbates of an NH$_4^+$ and a SO$_4^{2-}$ on a coadsorbed NH$_3$ + HSO$_4^-$ first layer, NH$_4^+\cdots$HSO$_4^-$ and SO$_4^{2-}\cdots$NH$_3$, were observed on a Pt(111) electrode surface by in situ IR measurements. Hydrogen bonding formation between the first and the second layer stabilizes the second layer and leads to a different structure of the double layer on the Pt(111) surface from that of the solution phase.

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