

Destruction of the Hydration Shell around Tetraalkylammonium Ions at the Electrochemical Interface

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Water molecules play important roles in chemistry, biochemistry, and physics. Hydrophilic and hydrophobic interactions of water with chemical substances greatly affect the kinetics and dynamics of chemical reactions. They can also alter the functionalities of the molecules. In biological systems, for example, hydrophobic phenomena are the driving force for protein folding and micelle and lipid-bilayer formation, etc. Tetraalkylammonium ions (R_4N^+) are often used as model systems to investigate hydrophobic phenomena.¹ X-ray² and neutron³ diffraction, Raman scattering,⁴ and IR absorption⁵ experiments have shown that water molecules around R_4N^+ are hydrogen-bonded to each other to form hydration shells by the so-called “hydrophobic hydration” process.¹

Hydration of cations is also an important issue in electrochemistry. Hydration shells prevent the direct contact of cations with the electrode surface, and the hydrated cations form the outer Helmholtz plane at the electrochemical interface.⁶ In the present study, the behaviors of hydrated tetraethyl-, -propyl-, and -butylammonium ions (Et_4N^+ , Pr_4N^+ , and Bu_4N^+ , respectively) at the electrified Pt–solution interface have been examined by surface-enhanced infrared absorption spectroscopy in the attenuated configuration (ATR-SEIRAS).⁷ Since cations can be concentrated at the negatively charged electrode surface and ATR-SEIRAS selectively probes the vicinity of the electrode surface (within ~ 5 nm from the surface),⁷ the hydrated cations can be examined with negligible interference from signals of hydrated anions. Herein we show for the first time that the hydration shells around Pr_4N^+ and Bu_4N^+ are destroyed at negatively charged surfaces.

Measurements were carried out chiefly in CO-saturated aqueous solutions containing R_4N^+ , under which the Pt surface is fully covered by strongly adsorbed CO.⁸ This system was chosen from the following two reasons. One is that in order to extend the potential range to be examined by suppressing the adsorption of protons and hydrogen evolution reaction [Figure S1 in the Supporting Information (SI)]. The other is that, since CO is hydrophobic, this system is also a model for examining the behavior of water molecules in hydrophobic interactions. As will be mentioned later, covering the surface with CO delays the destruction of hydration shells and facilitates the examination of the destruction process.

Figure 1 shows IR spectra of a CO-covered Pt surface in 0.02 M tetrapropylammonium perchlorate (Pr_4NP) measured during a potential sweep from 200 to -1000 mV (vs Ag/AgCl sat. KCl) at 5 mV s^{-1} . The vibrational bands of Pr_4N^+ at 1487, 1465, and 1388 cm^{-1} (assigned to the CH_2 and asymmetric and symmetric CH_3 deformation modes, respectively) grow in intensity as the potential is made more negative (Figure 1b), indicating the increase in the concentration of the cation at the interface due to the increase in the negative charge on the surface. The integrated intensities of these bands were reversibly reduced to the initial values on the reverse positive potential sweep (Figure 1c, red plot). Figure 1a shows the corresponding change in the O–H stretching region of

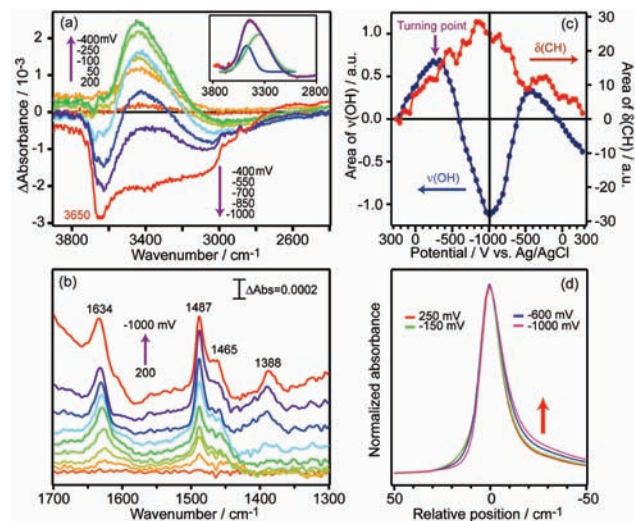


Figure 1. IR spectra of a CO-covered Pt electrode in 0.02 M Pr_4NP measured during a potential sweep at 5 mV s^{-1} . The reference spectrum was obtained at 300 mV. (a) High- and (b) low-frequency regions. The inset of (a) shows the spectrum measured at -400 mV and the curve-fitting results using Gaussian functions. (c) Integrated band intensities of (red) $\delta(CH)$ (1500 – 1430 cm^{-1}) and (blue) $\nu(O-H)$ (3750 – 2800 cm^{-1}). (d) Comparison of the spectral line shapes of on-top CO measured at 250, -150 , -600 , and -1000 mV. The peak position and intensity were normalized. The reference electrode was Ag/AgCl sat. KCl.

water. The negative potential sweep from 200 to -400 mV increases the absorption band centered at 3450 cm^{-1} (3477 and 3357 cm^{-1}), which is characteristic of H-bonded water. The concomitant growth of the Pr_4N^+ bands suggests that the observed OH band is of the hydration shell around Pr_4N^+ . The concentration of hydrated cations should remove water from the interface, but the OH bands of water are observed as positive peaks. This result is explained by the fact that the water molecules around R_4N^+ are more structured than in the bulk, and hence, the density of water is increased.^{1d} The observed spectra are in good agreement with those for the hydration shell in the bulk solution. It should be noted that the latter spectra were obtained after removing the interference from hydrated anions and bulk water by complicated multiple curve fittings.⁵

Interestingly, the O–H bands start to decrease at around -300 mV (Figure 1a), despite the continuous increase in the Pr_4N^+ concentration (which can also be found from the CH stretching modes of Pr_4N^+ at ~ 2900 cm^{-1}). In order to make clear the spectral changes at the more negative potentials, the difference spectra referenced to the spectrum at -400 mV are shown in Figure 2. The hydration-shell bands at 3464 and 3245 cm^{-1} monotonically decrease in intensity as the potential is made more negative. Additionally, a negative band appears at 3650 cm^{-1} at potentials more negative than -400 mV. This band is assigned to water molecules free from H-bonding and located on top of the CO

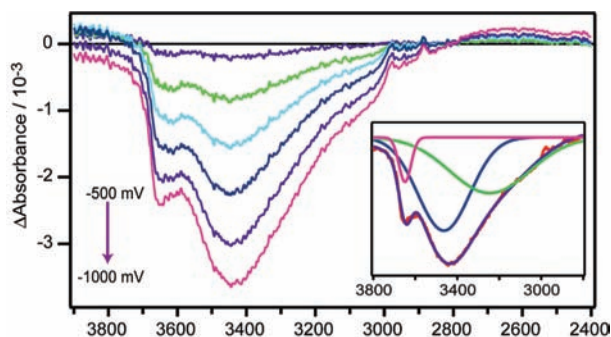


Figure 2. Potential difference IR spectra referenced to the spectrum measured at -400 mV. The inset shows the spectrum measured at -1000 mV and the curve-fitting results using Gaussian functions.

adlayer,⁹ as confirmed by the absence of this band on the bare surface (Figure S2 in the SI). We have reported previously that water is much more mobile on CO than on the bare surface, reflecting the weaker water–CO interaction (i.e., the hydrophobic nature of CO).¹⁰ Since cations are attracted to the electrode surface more strongly at more negative potentials, the decrease in the water bands suggests the removal of water on top of the CO adlayer and the decomposition of the hydration shell. The OH stretching bands were reversibly recovered for the reverse positive potential sweep, as shown in Figure 1c (blue plot).

The removal of the free water on top of the CO adlayer and the decomposition of the hydration shell allow the direct interaction of Pr_4N^+ ions with adsorbed CO. Since the CO vibration is sensitive to the environment,¹¹ some changes in the CO spectrum are expected. Two slight yet clear changes were found in the spectral shape and the potential-dependent peak shift arising from Stark tuning effects and/or the change in electron back-donation from the surface¹² (Figure S3 in the SI). The change in the band shape is shown in Figure 1d, where the spectra measured at several potentials are compared by fixing the peak frequency and normalizing the peak intensity. A tail extending toward low frequency appears at potentials where the hydration shell is decomposed. Such an asymmetry in shape arises from the spatial inhomogeneity of the vibrations. Many other reasons also can cause such spectral changes, and hence, it is not very clear whether the observed changes reflect the direct interaction of Pr_4N^+ with adsorbed CO. Nevertheless, it should be stressed again that such spectral changes occur at potentials where the hydration shells are decomposed.

The structure and behavior of the hydration shells around other hydrophobic ions, Bu_4N^+ and Et_4N^+ , were also examined, as shown in Figure 3. Both ions give intense H-bonded water peaks at $3200\text{--}3500\text{ cm}^{-1}$ during the negative potential sweep, suggesting the formation of the hydration shells. In the case of the larger Bu_4N^+

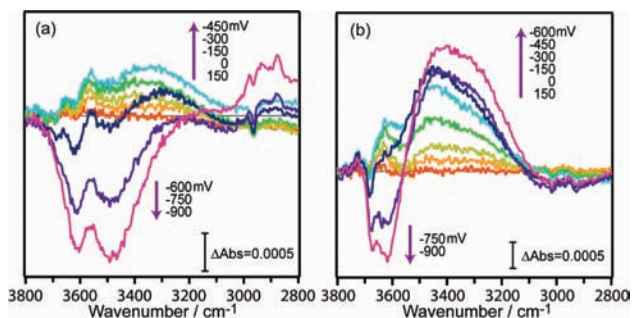


Figure 3. IR spectra of a CO-covered Pt electrode measured during a potential sweep at 5 mV s^{-1} in (a) 0.1 M tetrabutylammonium bromide and (b) 0.1 M tetraethylammonium perchlorate. The reference spectrum for each experiment was obtained at 300 mV .

cation, continuing the negative potential sweep below -600 mV decreases the intensities of the free-water and hydration-shell bands, suggesting the destruction of the shells in the same way as for Pr_4N^+ . In the case of the smaller Et_4N^+ cation, the free-water band decreases in intensity as for the other cations, but the intensity of the hydration-shell bands does not decrease. That is, the hydration shell around Et_4N^+ is stronger than those around Pr_4N^+ and Bu_4N^+ . The difference in the strength of the hydration shells may be related to the size of the cations. Finally, it is noted that hydration shells are easily destroyed at bare Pt surfaces and that their absorption bands are observed only as negative peaks in the same potential range because of the stronger interaction with the surface (Figure S3 in the SI). The results clearly demonstrate that hydration shells are destroyed more easily as the interaction with the surface increases. The destruction of hydration shells are the first step in reactions, and the approach presented in this communication will provide further insights into reactions of solvated molecules at interfaces.

In the present study, we succeeded in measuring IR spectra of hydration shells around hydrophobic ions (Et_4N^+ , Pr_4N^+ , and Bu_4N^+) by selectively concentrating the ions on a CO-covered Pt electrode surface. The interference from signals of hydrated anions was effectively eliminated. The method used in this work is a useful way to study hydration shells. We also found for the first time that the hydration shells around Pr_4N^+ and Bu_4N^+ are destroyed at negative potentials, while the hydration shell around Et_4N^+ was stable in the potential range examined. The different behaviors may be related to the stabilities of the hydration shells depending on the size of the central cation.

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Supporting Information Available: Experimental procedures, cyclic voltammetry, and IR spectra of water on a bare Pt electrode and of CO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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