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Communication: Evidence of hydrated electrons injected by a metallic electrode in a high voltage system

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In this work it is shown a strong evidence of the hydrated electrons production was shown in a film of condensed water, by directing the injection of electrons in localized and/or delocalized water electronic states using a system of high voltage *made in laboratory*. The results show that the water layers on the silica particles are electrically charged by injection of electrons from a metal electrode when silica is placed in high electric field. This charging process also appears to depend on the thickness of these water layers and of the spatial arrangement required by the silica surface. © 2010 American Institute of Physics. [doi:10.1063/1.3529422]

I. INTRODUCTION

Solvated electrons were observed for the first time in 1863 (Ref. 1) in liquid ammonia but only in 1962 (Ref. 2) in water. These species have been extensively studied due to their enormous importance in the understanding of the electron transfer process in water. They can also be used as interesting probes to give structural information about condensed water.^{3,4} The hydrated electron or aqueous electron e_{aq}^- can also be an important reagent in the chemistry of condensed phases and in the molecular biology.⁵

The first report of the isolation of water clusters with excess electron was made in 1981 by Armbruster *et al.*,⁶ using mass spectrometric studies. After this report many theoretical and spectroscopic studies were developed to understand how the excess electron is found in these water clusters.^{5,7-12}

Hydrated electrons are uncommon species produced by the injection of an excess of electrons into condensed water, producing species such as $(H_2O)_n^-$. Recent photophysics studies suggest that in water the electrons can be added in localized electronic states (one electron in a type *s* state or one electron in nearly three-fold degenerate type *p* state) or injected into the conduction band of the water, delocalized on hundreds of molecules in the condensed phase.⁵

Hydrated electrons are usually obtained from the photoexcitation or photoionization of water molecules that constitute the condensed phase or from solutes dispersed in that phase.^{5,7,11-14} Studies about structural relaxation of the water molecules around the electron, obtained by photoionization techniques, can supply important information on these hydrates.^{5,11} The e_{aq}^- can also be produced by the photoionization at a metal/water interface, introducing electrons of a metallic electrode directly into the electronic states of the water.^{13,14}

The hydrated electrons can be excellent probes to study electronic structures and, consequently, the spacial organization of condensed water and can allow one to obtain new structural informations about the condensed phase.

In this work, experimental evidence of the production of e_{aq}^- by the injection of electrons from a metallic electrode into the electronic structure of water condensed on the surface of silica gel particles will be shown. The innovation is in the production of hydrated electrons by a high voltage system without photoexcitation.

II. EXPERIMENTAL SECTION

A. Experimental assembly

The high voltage cylindrical cell ($d_{in} = 90$ mm, $d_{out} = 110$ mm, $h = 80$ mm) was made from PVC (Polyvinyl Chloride) with a removable top also of PVC having inner threads to attach it to the cell body. An o-ring on the upper side of the cell body permits sealing. At the bottom, a hemispherical glass plate (2 mm of thickness) was fixed to the cell body by a PVC ring with inner thread. The high voltage electrode (aluminum disk, $\phi = 90$ mm) was fixed inside the cover and the hemispheric glass plate at the bottom of the cell was placed on the ground electrode (aluminum disk, $\phi = 90$ mm). These electrodes were assembled to generate a vertical electric field, perpendicular to the electrodes ($0-375$ V mm⁻¹). The rate of charge transport, measured as electrical current, was amplified (amplifier built in the laboratory) and the acquisition was made by an analog/digital acquisition device (USB - 6009, National Instruments).

The high voltage system (cell + electrodes) was isolated in an acrylate box with lateral holes to permit dry airflow to the cell, inside the box. The relative humidity inside the box (RH_{box}) was maintained below 25% by recirculation of the air through a drying column containing silica gel with humidity indicator (Merck).

Control of the high voltage source, solenoid valve, Peltier element (temperature control of the dry air), and the acquisition of all data (electrical current and dry air temperature) were done with software developed in LABVIEW[®].

B. Pretreating and hydration of silica sample

The experiments used a sample of silica gel with the following characteristics: surface area = 616 m² g⁻¹, mean size

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of particle = 172 μm , pore size = 3.7 nm, and pore volume = 0.76 $\text{cm}^3 \text{g}^{-1}$.

The sample was dried at 393.15 K for 24 h. After drying, the silica sample was quickly weighed (1.0000 g) and transferred to a humidity chamber (RH = 74%; 298.15 K) for 72 h (adsorption equilibrium). Afterward, the sample was removed from the humidity chamber, weighed, and quickly transferred to the cell, which was closed and put inside the isolation box. The aluminum electrode, fitted on the inner side of the cover, was immediately connected to the positive terminal of the high-tension source.

Before starting the experiment, the RH inside the isolation box was reduced to less than 25% by recirculation of the box air through the drying column and, afterward, the experiment was started by the software.

The slow dehydration of silica gel inside was made by pulling out the water steam of the atmosphere from inside of the cell using a flow of 1 L min^{-1} of dry air.

III. RESULTS AND DISCUSSION

The present work was developed from a casual observation of an electrostatic phenomenon in which the particles of silica gel are charged and hurled by an electric field. As described in Sec. II, a system was assembled similar to a parallel plate capacitor. In this system, a small amount of hydrated silica gel was put on the lower electrode (ground) and tension up to 30 kV was applied to the upper electrode, producing an electric field up to 375 V mm^{-1} between these electrodes. It was observed that the silica gel particles were hurled from the ground to the positive electrode, overcoming gravitational and adhesion forces. When all water adsorbed on silica is removed by heating to 393.15 K for 24 h, the particles do not move and charge transport disappears.

Those initial observations indicate that the water adsorbed on the silica surface is essential for the electrostatic charging. In these experimental conditions, electric charges can be generated in the water film by a *Faradaic* process (electrolysis) or by injection of electrons from the metallic electrode.

To evaluate the first hypothesis (the Faradaic process), silica with constant superficial humidity was exposed to the electric field and the rate of charge transport was monitored along the time of exposition. These results are shown in Fig. 1(a).

In Fig. 1(a) it can be observed that there are no significant changes in the rate of charge transport made by silica particles with constant superficial humidity and electric field, as would be expected in a Faradaic process. With this observation, a charging process by Faradaic reactions was discarded because this process should consume the chemical species, oxidizing or reducing that species. Thus, the maintenance of electric charge rate transport is strong evidence that a Faradaic process is not occurring or is negligible in the net charge transport process.

Here it is important to comment that real electric charges are transferred by silica particles between the electrodes. The silica deposited on ground electrode is charged and hurled to positive electrode (+30 kV) through 8 cm of atmospheric air. When the silica collides with the positive electrode the electric charges acquired from the ground electrode are removed and an electric current is registered. The electric current indicates a flow of electrons and a simple deprotonation or polarization as the redistribution of the superficial charge on the particle does not justify the experimental observations. Deprotonation allows a polarization of the particles generating a dipole that could orient the particles but would not push them, because the electric field would attract both poles of this possible dipole generated by polarization.

The results in Fig. 1(a) suggest that the charging process occurs by another mechanism, possibly, by the transfer of electrons from the ground electrode to the localized (*s* and *p*) and delocalized (conduction band, CB) electronic states of the adsorbed water, forming structures of the type $(\text{H}_2\text{O})_n^-$. In Fig. 1(b) the intensity of the electric field was also swept under constant superficial humidity, verifying that the electrostatic charging of the superficial film happens at a significant level only from 150 V mm^{-1} , equivalent to 12 kV in the assembled system. Based on the model of electron injection into the water film on the particles this behavior can suggest

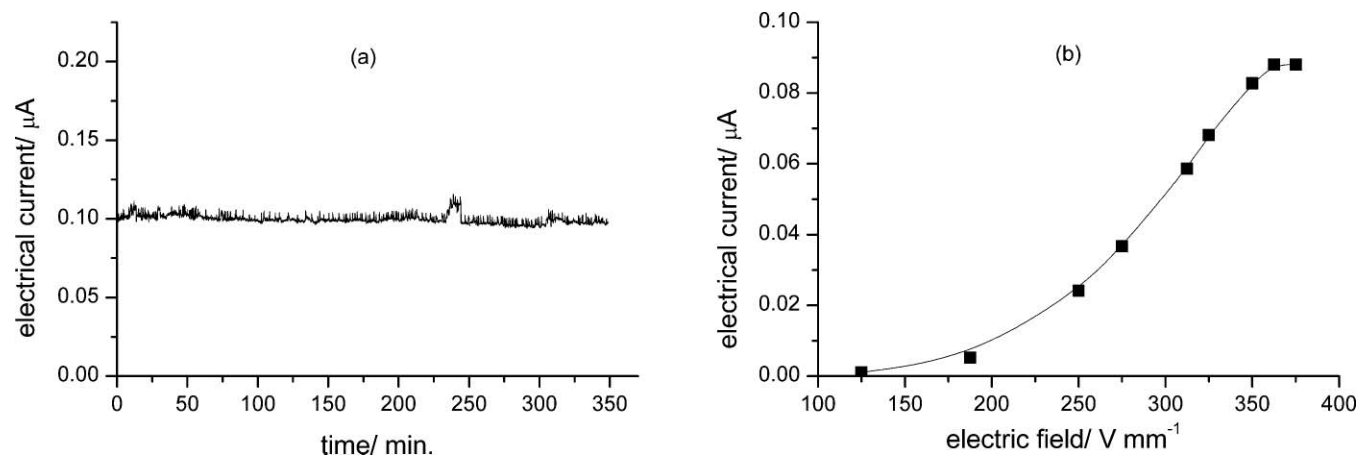


FIG. 1. (a) Rates of charge transport with constant superficial humidity and electric field. (b) Normalized rate of charge transport as a function of the intensity of the electric field applied.

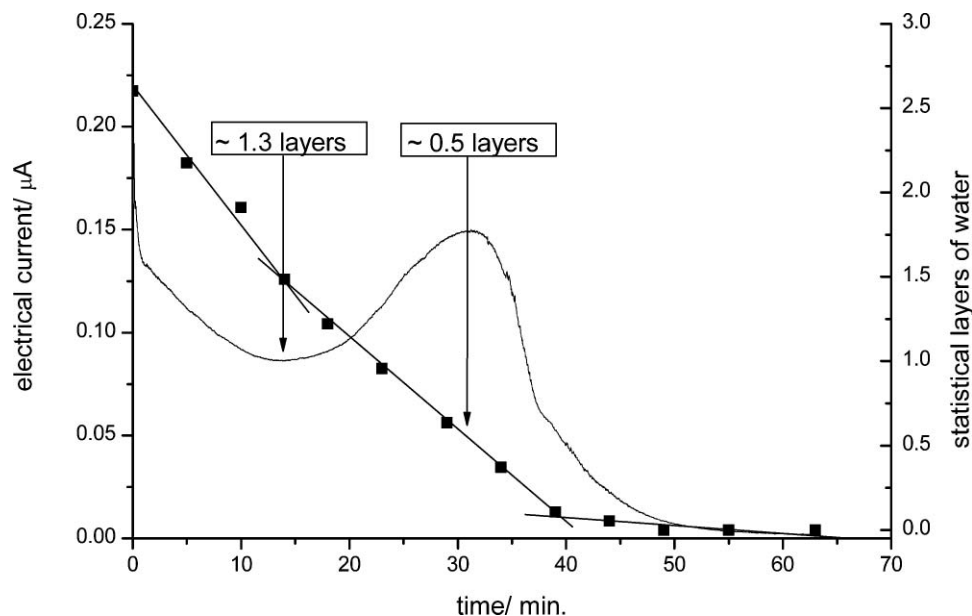


FIG. 2. Correlation between rate of charge transport and thickness of the surface water film with time of dehydration by a dry air flow.

that the Fermi level (E_f) of the electrode overcomes CB at that tension or can simply be related to the increase of the number of silica particles flowing in the electric field. The increase of electric field can hurl heavier particles to the positive electrode. To define this point, new studies will be realized with a new apparatus constructed to measure the relative number of silica particles flowing as a function of the electric field.

In a second step of this study, the thickness of the water film was reduced by a flow of dry air through the interior of the cell and the rate of charge transport and the thickness of the surface film were monitored along with the dehydration. The results are shown in Fig. 2.

When the charged particles collide with the positive electrode (30 kV), the excess of electrons are removed, discharging the surface film, and the particles fall back to the ground electrode, attracted by gravitational forces, restarting the charging and discharging cycle.

The profile of the rate of charge transport shown in Fig. 2 can give important information about the structural order of the adsorbed water. This consideration is very important and intriguing, but more studies are needed to prove this point.

It is well-known that the interaction between the $-OH$ groups on silica surfaces and water occurs by hydrogen bonds and dipolar forces changing the structure of adsorbed water in relation to bulk water. Some studies have shown that the influence of the surface on the structure of the water decays with distance from the surface, being negligible beyond ~ 3 water layers of coverage. The surface influence is stronger for the first monolayer and weaker for the more external layers.

The curves in Fig. 2 indicate that the changes in rate of charge transport and the thickness of the water layer on the surface are correlated. As can be seen, at the moment in which the electrical current begins to increase the first transition occurs (indicated in Fig. 2) in the kinetics of dehydration curve.

At this point the water film has ~ 1.3 monolayers. As the dehydration proceeds the maximum of the electrical current coincides with ~ 0.5 monolayers and the second transition in the kinetics occurs near to complete dehydration.

These results indicate that with dehydration the thickness of the water film is reduced and the outer water layer gradually becomes nearer to the surface, passing through different spacial arrangements until complete dehydration. Changes in the physical structure can alter the electronic structure and modify the absolute and relative energies of the electronic states. The relationship between rate of charge transport and the thickness of water film on silica shows an interesting relation, which can be used to study the electronic and structural arrangement of the water on silica or other similar systems.

If this suggestion is confirmed, the method of production of e_{aq}^- described in this work can permit the development of a new technique for the study of solid/liquid interfaces using electrons in excess, added by a metallic electrode, as probes.

IV. CONCLUSIONS

In this contribution the results show evidence of the production of hydrated electrons in the water condensed on the silica gel by the transfer of electrons from the metallic electrode to localized or extended electronic states of the water. With this, two important contributions may be cited: (1) a new method of production of e_{aq}^- , through the injection of electrons directly into localized or delocalized electronic states of adsorbed water under high voltage without photoinjection or photoexcitation and (2) the possibility to develop a new technique to study solid/liquid interfaces using excess electrons as probes of the electronic structure of the adsorbate is proposed.

The lack of reports about the production of hydrated electrons by this method can be due to the fact that e_{aq}^- can only

be generated without photoinjection or photoexcitation by high voltage, which makes it impossible to use in continuous aqueous environments due to the occurrence of electrical discharges. In the system described in this work, the water is condensed on the surface of the silica and the electrodes are separated by atmospheric air, providing insulating experimental conditions.

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