

ELECTROCHEMISTRY IN SUBCRITICAL AND SUPERCRITICAL WATER

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Introduction

Supercritical fluids have received significant interest recently because of their unique solvent properties. Gases such as carbon dioxide and ethylene have been used to perform a number of difficult separations. Some of these processes, for example the decaffeination of coffee, have been commercialized (1).

Water has not been studied extensively for use as a supercritical solvent because of the high temperature and pressure of its critical point ($T_C = 374^\circ\text{C}$, $P_C = 221$ bar). We are performing electrochemical research in supercritical water to take advantage of its unusual properties. The areas of study include the effect of temperature on the electrochemical potential of ions in water and the electrochemical reaction of organic compounds in aqueous solution.

The chemical behavior of an ion in water is of course influenced by water molecules that are oriented around it. A change in the structure of the solvation sphere around an ion will affect the electrochemical potential of the ion. Such a change in structure can be achieved by heating water to the critical region where the internal structure of hydrogen bonding is very sensitive to temperature changes. In this region, the electrochemical potential can also be a strong function of temperature. A study of these potential shifts should provide insight into the structure of solvation spheres in water and of water itself.

At high temperature, the breakdown of hydrogen bonding in water greatly reduces the dielectric constant. At the critical point, the dielectric constant of water is 3, approximately the same as that of benzene. Not surprisingly, water becomes miscible with non-polar organics at high temperatures. In the miscible region, it is possible to react organics electrochemically without using the more toxic and expensive organic solvents that are necessary for dissolution at 25°C . While many compounds will decompose in high temperature water, others, which are not active at normal conditions, will become subject to electrochemical attack at high temperature.

Though no definite predictions can be made, supercritical water appears to be a promising area for study. A cell has been designed which will operate at supercritical conditions, and preliminary data have been obtained for electrolyte solutions.

Experimental

The high temperature section of the electrochemical cell is made of an aluminum oxide ceramic. The volume of heated solution is less than 1 cm^3 , so the stored energy of the system is very small. All measurements were made with the solution stationary in the cell, but a high pressure pump allows the cell to be flushed with fresh solution. This prevents reaction products from contaminating the electrolyte. The platinum working and silver reference electrodes are in close proximity in the heated zone. The working electrode area is approximately $3 \times 10^{-4}\text{ cm}^2$. The platinum counter electrode is in a cool region downstream from the heated zone. All seals are made of teflon, and are in unheated parts of the cell.

Results

Cyclic voltammetry has been carried out in solutions of $0.05\text{M H}_3\text{PO}_4$, 0.2M NaHSO_4 , and 0.2M KCl . The pressure was held at 240 bar while the temperature was varied. The scan rate was 200 mV/sec .

In $0.05\text{M H}_3\text{PO}_4$, the potential difference between the evolution of hydrogen and

oxygen declined from 1.7 V at 25°C to 1.0 V at 375°C. At high temperature, the solution resistance increased dramatically indicating the dissociation of the acid was declining.

In 0.2M NaHSO₄, the potential difference between the evolution of hydrogen and oxygen declined from 2.0 V at 25°C to 1.3 V at 375°C.

In 0.2M KCl, the potential difference between the evolution of hydrogen and oxygen declined from 1.8 V at 25°C to 1.6 V at 300°C. The potential difference between the chloride/chlorine couple and oxygen declined from 0.2 V to <0.1V over this same temperature range.

Summary

The data presented here represent the first steps into a new area of electrochemistry. Much more data will be necessary before any major conclusions can be drawn. Even so, these results do show that electrochemistry can be carried out under near critical and supercritical conditions, and that there are significant changes in the behavior of ions in solution.

References

1. M. E. Paulaitis, J. M. L. Penninger, P. Davidson, and R. D. Gray, Chemical Engineering at Supercritical Fluid Conditions, Ann Arbor Science (1983).