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Electrochemistry of Transition Metal Ions in Acetonitrile

Principal Investigator:

John W. Olver
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Junior Research Personnel:

George A. Forcier
Russell R. Bessette
Thomas E. Crumm
Eric W. Zink

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ABSTRACT

A new method for purification of acetonitrile was required using reduction of impurities with sodium and calcium hydride prior to distillation. Controlled potential electrolysis of zirconium halide solutions produced neither stable solutions of Zr(III) as anticipated nor Zr[0] in an identifiable form. Infra-red spectral studies of zirconium chloride solutions revealed $ZrCl_3^+$, $ZrCl_4$, $ZrCl_5^-$, and $ZrCl_6^=$ species. On electrolytic reduction the products formed react with solvent, electrolyte and residual water which is so difficult to remove.

We determined the dissociation properties of a series of useable polarographic electrolytes such as alkali and tetraalkylammonium halides, perchlorates, tetrafluoroborates, and trifluoracetates. Partial electrolyte association and in trifluoracetate cases triple ion formation (determined by conductance measurements) make precise interpretation of polarographic data very uncertain, and make quantitative correlation of spectral and polarographic data uncertain.

We undertook a study of the properties of the electrical double layer in acetonitrile at a mercury interface which shows extensive adsorption of both anions and cations on the electrode again complicating electrolytic data.

We studied the electrolytic properties in acetonitrile of copper(II) and copper(I) as a model case for reduction through lower oxidation states to the metal. These ions could be precisely coulometrically reduced to the lower states as in water and the precision was great enough to determine diffusion coefficients for the respective species by the Cottrell method.

Chronological List of Publications

1. "Simplified Purification of Acetonitrile for Electroanalytical Applications," G. A. Forcier and J. W. Olver, Anal. Chem. 37, 1447 (1965).

2. "High Sensitivity Coulometric Analysis in Acetonitrile," R. R. Bessette and J. W. Olver, J. Electroanal. Chem. 17, 327 (1968).

3. "Voltammetric and Spectral Studies on Zirconium in Chloride Media in Acetonitrile," J. W. Olver and R. R. Bessette, J. Inorg. Nucl. Chem. 30, 1791 (1968).

4. "Association of Common Polarographic Supporting Electrolytes in Acetonitrile," G. A. Forcier and J. W. Olver, Electrochemica Acta 14, 135 (1969).

5. "Measurement of Diffusion Coefficients for the Reduction of Copper(I) and (II) in Acetonitrile," R. R. Bessette and J. W. Olver, J. Electroanal. Chem. 21, 525 (1969).

6. "Dissociation of 1:1 Electrolytes Containing Trifluoroacetate Anion," G. A. Forcier and J. W. Olver, Electrochemica Acta, in press.

BACKGROUND

Previous work by the principal investigator (1) had shown that zirconium and hafnium as tetrachlorides could be reduced in acetonitrile to give at least the +3 states not observable in aqueous solution. Furthermore the reduction of Zr and Hf in excess chloride media occurred at sufficiently different potentials to allow feasible separation electrolytically.

The intent of the investigations under this grant was then two fold: first, to investigate and establish conditions for the production of uncommon lower oxidation states of zirconium and hafnium and for the electrolytic separation of the two elements, and second, to study the complexing properties of those elements with halides to identify critical species in the forementioned completed and proposed work.

SOLVENT

We were unable to produce by older methods acetonitrile sufficiently pure to repeat earlier cited work. After discovering that a new commercial production process was in use which led to new residual impurities we devised and perfected a new purification procedure for acetonitrile (2). The procedure involves distillation from successive sodium hydride, conc. H_2SO_4, and CaH_2 to give polarographically clean acetonitrile.

VOLTAMMETRY AND SPECTROPHOTOMETRY OF ZIRCONIUM

Controlled potential electrolyses of zirconium solutions in the potential range for reduction to Zr(III) or Zr[0] did not yield bulk separable quantities of either (3). Reactivity of any Zr(III) with electrolyte, residual water or solvent led to high current integrals. The reduction at a potential where Zr[0] was expected from the simple polarography led to unreproducible mixtures containing zirconium, oxygen, nitrogen and halide. Infrared spectral studies on solutions of zirconium with varying chloride content proved the presence of mixed complexes from $ZrCl_3^+$, through $ZrCl_4$ and $ZrCl_5^-$ to $ZrCl_6^-$ in chloride media. The spectra are given (3) and show the complex equilibria relevant to the zirconium case.

STUDIES ON COPPER

At this point a simpler case was chosen to establish controlled potential coulometry in acetonitrile since the zirconium work was so puzzling. Data precise to within ± 2% were obtained (4) for the reductions:

$$Cu(II) + e \longrightarrow Cu(I)$$

$$Cu(II) + 2e \longrightarrow Cu[0]$$

$$Cu(I) + e \longrightarrow Cu[0]$$

Copper behaved so well that diffusion coefficient data were determined for these three reductions by the Cottrell method (5).

ELECTROLYTE STUDIES

At this point it seemed clear that we did not know enough about electrolyte behavior in acetonitrile to explain and interpret the unexpected and generally negative electrolytic data on zirconium. We therefore examined the association properties of several common polarographic electrolytes including several alkali and tetraalkylammonium salts of perchlorate (6), halide (6), tetrofluoroborate (6), and trifluoracetate (7). Association and triple ion formation (in the last case) were observed but quantitative interpretation of the conductance data are tenuous since such quantities as activities and liquid junction potentials are uncertain. Secondary use of such data to interpret polarographic and spectral results therefore also tenuous.

We undertook a study of the electrical double layer in acetonitrile again using some of the common electrolytes described above. That work is in preparation for publication but generally shows considerable specific adsorption of both anions and cations on the electrode whereas in aqueous media cations generally do not adsorb.

CONTINUING WORK

One of the junior investigators supported on this grant is still working although his financial support has terminated. We still hope through his efforts to ascertain exactly why the gross electrolytic properties of zirconium and hafnium in acetonitrile differ from the micro properties observed polarographically. His approach has been to prepare $ZrCl_3$ as previously done and make a solution of that in acetonitrile. He will then study the electrolytic properties of Zr(III) to try to find the reason for failure of the direct reduction of Zr(IV) to Zr(III) and Zr[0].

References:

(1) Polarography of Hafnium and Zirconium in Acetonitrile (with James W. Ross), Journal of Inorganic and Nuclear Chemistry 25, 1515 (1963).

(2) "Simplified Purification of Acetonitrile for Electroanalytical Applications," G. A. Forcier and J. W. Olver, Anal. Chem. 37, 1447 (1965).

(3) "Voltammetric and Spectral Studies on Zirconium in Chloride Media in Acetonitrile," J. W. Olver and R. R. Bessette, J. Inorg. Nucl. Chem. 30, 1791 (1968).

(4) "High Sensitivity Coulometric Analysis in Acetonitrile," R. R. Bessette and J. W. Olver, J. Electroanal. Chem. 17, 327 (1968).

(5) "Measurement of Diffusion Coefficients for the Reduction of Copper(I) and (II) in Acetonitrile," R. R. Bessette and J. W. Olver, J. Electroanal. Chem. 21, 525 (1969).

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