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Colloidal Titration of Aqueous Zirconium Solutions with Poly(vinyl sulfate) by Potentiometric Endpoint Detection Using a Toluidine Blue Selective Electrode

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Zirconium oxy-salts were hydrolyzed to form positively charged polymer or cluster species in acidic solutions. The zirconium hydrolyzed polymer was found to react with a negatively charged polyelectrolyte, such as poly(vinyl sulfate), and to form a stoichiometric polyion complex. Thus, colloidal titration with poly(vinyl sulfate) was applied to measure the zirconium concentration in an acidic solution by using a Toluidine Blue selective plasticized poly(vinyl chloride) membrane electrode as a potentiometric end-point detecting device. The determination could be performed with 1% of the relative standard deviation. The colloidal titration stoichiometry at pH ≤ 2 was one mol of zirconium per equivalent mol of poly(vinyl sulfate).

Introduction

Zirconium chemicals are used in a wide range of industries, and with advances in modern technology, the diversity of their applications has increased.[1] In particular, tetragonal zirconia is one of the most important zirconium compounds for ceramic use, with excellent mechanical properties, such as high structure toughness, strength, and hardness.[2] We have studied the effective use of some zirconium oxy-salts as a depressive and fluidizing material of ceramic slurries,[3,4] and have developed a new direct-casting method based on aqueous-acidic high solids loading alumina slurries stabilized with zirconium acetate.[5] When the slurries were prepared, the concentration of zirconium oxy-salt was an important factor, and a simple and convenient determination of aqueous zirconium was required. However, the determination of zirconium is not very easy because zirconium(IV) has a marked tendency to form polynuclear hydroxy group-bridged zirconium species (polymerization) in aqueous solutions.[6] Pilkington *et al.* mentioned that accurate results in EDTA titration of zirconium could only be obtained after zirconium ions were converted to a depolymerized form.[7] Therefore, we studied a colloidal titration method as a means to measure the concentration of zirconium conveniently as it exists in the aqueous solution in a polynuclear configuration.

Colloidal titration is an excellent measurement method for determining the concentration of natural and synthetic polyelectrolytes.[8–12] Titration is based on the reaction between a positively charged polyelectrolyte (polycation) and a negatively charged one (polyanion). When the charges of the polyelectrolytes are neutralized by the addition of oppositely charged polyelectrolytes, the two ployelectrolytes tend to associate and eventually precipitate. According to Terayama, who was the first proposer of colloidal titration, the colloidal titration method has been applied to several poly-charged species, such as proteins and cells.[8] However, their stoichiometries are still not clear. Regarding the reaction between oppositely charged polyelectrolytes, most of the reaction is accurately stoichiometric. As a typical case, an aqueous solution of poly(diallyldimethyl ammonium) chloride (PDADMAC) can be titrated with an aqueous solution of potassium poly(vinyl sulfate) (KPVS) of known concentration. The reaction between oppositely charged polyelectrolytes has been studied on stoichiometry,[9,13-16] the stability constant,[17,18] and the effect of the polymerization degree.[19]

A few colloidal titrations were applied to measure metal ions in hydrolyzed, polymeric forms. Kikuchi and Kubota have investigated a chemical reaction of KPVS with a mixture of poly(aluminum chloride), PAC, ($[Al_2(OH)_nCl_{6-n}]_m$, $n = 3$, $m = 2.5$) as an inorganic macromolecule and [2-(diethylamino)ethyl]dextran hydrochloride. The general characteristics of the resultant polyelectrolyte complexes were also studied.[20] Tajima has reported that undeca(11-)tungstocobalt(II)phosphate, $[PW_{11}O_{39}Co(H_2O)]^{5-}$, was a useful standard for anionic colloidal titration.[21]

Although several titrimetric end point-detection methods can be applied to colloidal titration, Toluidine Blue (TB) method was employed because of its ample reported applications. Since visual detection is often difficult for the direct titration of polyanion, the TB concentration was monitored by potentiometry using a TB selective plasticized poly(vinyl chloride) membrane electrode.[19,22] We studied the hydrolytic behavior of zirconium(IV) in an aqueous solution, and demonstrated a new determination method of zirconium by colloidal titration.

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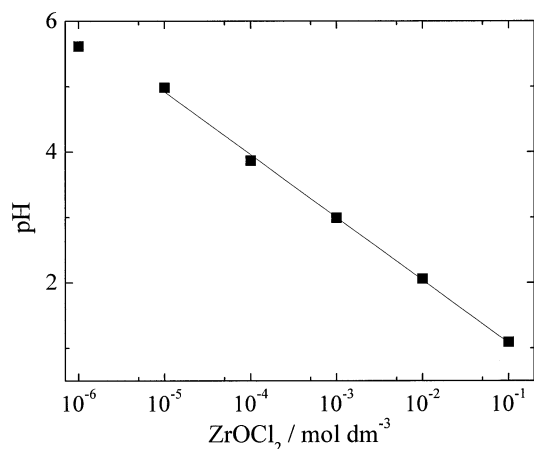E-mail: sakurada@apchem.gifu-u.ac.jp

Fig. 1   pH as a function of the concentration of $ZrOCl_2$.

Table 1   Precipitation reaction with several dyes at pH 4

	Anionic dye		Cationic dye
	Methyl Orange	Fluorescein	TB
Zr-Ac	+	+	−
$ZrOCl_2$	+	+	−
$ZrO(NO_3)_2$	+	+	−
PDADMAC	+	+	−
KPVS	−	−	+
NaCl	−	−	−

Experimental

Apparatus

The automatic titration apparatus used in the present study consisted of a reaction beaker with magnetic stirring, a potentiometer (Accumet 50, Fisher Scientific Co., Pittsburgh, PA, USA), an automatic burette (665 Dosimat, Metrhom Ltd., Herisau, Switzerland), and a personal computer to control the automatic burette and to treat the titration data. A glass combination pH electrode (Model 8172 ROSS Sure-Flow® pH Electrode, Orion Research, Inc., Beverly, MA) was used to determine the acidity of solutions. The hydrodynamic radii of hydrolyzed zirconium ion polymers were measured by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics Co. Ltd., Hirakata, Japan).

Chemicals

A standard potassium poly(vinyl sulfate) solution (KPVS) and a standard poly(diallyldimethyl ammonium) chloride (PDADMAC) solution for colloidal titration were purchased from Wako Pure Chemical Ind., Ltd. (Osaka, Japan). $ZrOCl_2$ and zirconium acetate (Zr-Ac) were obtained from Nacalai Tesque, Inc. (Kyoto, Japan) and Aldrich Chemical Company, Inc. (Milwaukee, WI, USA), respectively. 3-Amino-7-dimethylamino-2-methylphenothiazin-5-ium   chloride (Toluidine Blue, TB) (Chroma Gesellshaft Schmid Gmbh & Co., Kongen/N., Germany) was used as an indicator for colloidal titration. All other chemicals of reagent grade were used without further purification. The water used to prepare all of the sample solutions was distilled and purified with a Milli-Q system (Milli-Q Plus, Millipore Corporation, Billerica, MA, USA).

Titration procedure

The plasticized PVC membrane electrode was prepared as follows. A mixture of PVC (0.8 g), TB (1 mg) and tricresyl phosphate (1.2 g) was dissolved in 20 mL of tetrahydrofuran (THF). The THF solution was poured onto a flat petric dish (i.d. 85 mm), and the solvent was allowed to evapolate for 48 h at room temperature. A disc (i.d. 12 mm) cut out from the PVC membrane was fixed to a PVC tube (i.d. 10mm) using THF as an adhesive. A saturated potassium chloride solution was poured into the PVC electrode body, and an Ag/AgCl electrode was immersed. As a reference, an Ag/AgCl electrode (Model 2535A-06T, Horiba, Ltd., Kyoto, Japan) was used. The electrochemical cell was Ag/AgCl/satd. KCl/TB-sensitive PVC membrane/sample solution/satd. KCl/AgCl/Ag.

An appropriate volume of the sample solution was accurately pipetted into a 100 mL beaker, and the solution was diluted to 50 mL with water (concentration of zirconium, $\sim 1.0 \times 10^{-4}$ mol dm^{-3}). Acetate buffer was used at less than 0.01 mol dm^{-3} in combination with hydrochloric acid to adjust the pH of the solution. After 1 mL of 0.1 mmol dm^{-3} TB solution was added, the solution was automatically titrated with 2.5 meq. mol dm^{-3} PVS solution with magnetic stirring. The titration speed was controlled at 0.1 mL min^{-1}.
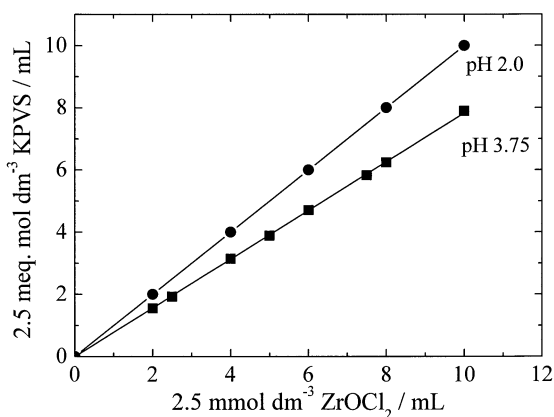
Results and Discussion

Aqueous chemistry

$ZrOCl_2$ is an acidic oxide, and its aqueous solution is strongly acidic. Therefore, we measured the pH of aqueous solutions of the salt with various concentrations. The results are shown in Fig. 1. The pH decreases linearly with the logarithm of the concentration of $ZrOCl_2$. The slope of the straight line indicates that a ten-times increase in the concentration of $ZrOCl_2$ induces a 1 unit pH decrease. That is, the zirconium salt behaves like a strong monoacid, such as HCl. For this reaction, Blumenthal[23] suggested the scheme of the hydrolysis reaction to be as follows:

$$ZrOCl_2 + H_2O \longrightarrow ZrOOH^+ + H^+ + 2Cl^-. \qquad (1)$$
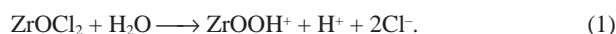
Equation (1) means that zirconium salt gives a charged species possessing one positive charge per one zirconium(IV) ion, but does not mean the existence of $ZrOOH^+$ as a single monomeric species. Singhal *et al.*[24] observed that there were tetramers and octamers of zirconium in acidic aqueous solutions using small-angle X-ray scattering (SAXS). In addition, unidentified polymeric species larger than the octamer were also formed under the condition when small amounts of NaOH were added. Blumenthal noted that Zr-Ac in an aqueous acidic solution did not dissociate simply into zirconyl cations and acetate anions, but formed more complicated zirconium species. Zirconium hydroxide precipitation from the acetate solutions did not occur up to a pH of about 5, where diacetatozirconic acid species were formed in the solution.[25] In addition, the zirconium ionic species possibly have a strong tendency to polmerize.
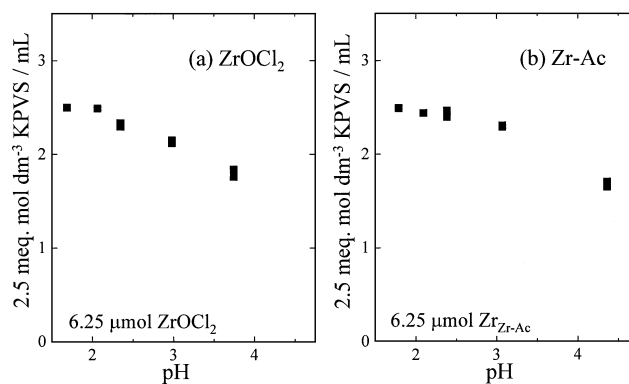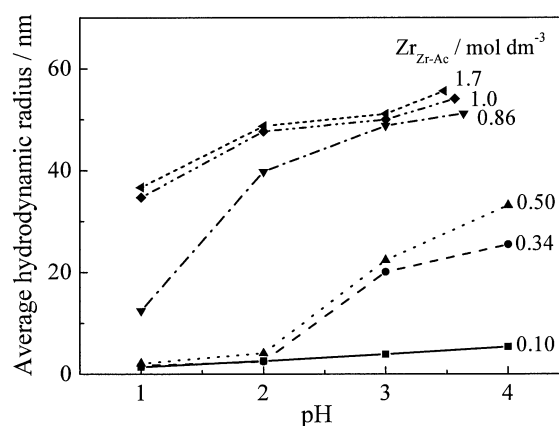
As a preliminary examination, we tested the precipitation reactions of some zirconium oxy-salts with anionic dyes, such as Methyl Orange and fluorescein, as well as with TB, which is cationic in solutions at pH 4. Table 1 shows these experimental results, together with those results with PDADMAC as a polycation, KPVS as a polyanion, and NaCl as a typical conventional electrolyte. Zirconium oxy-salts and PDADMAC react to form precipitates with anionic dyes; however, they do

Fig. 2   Potentiometric titration curves for (a) ZrOCl₂ and (b) Zr-Ac.
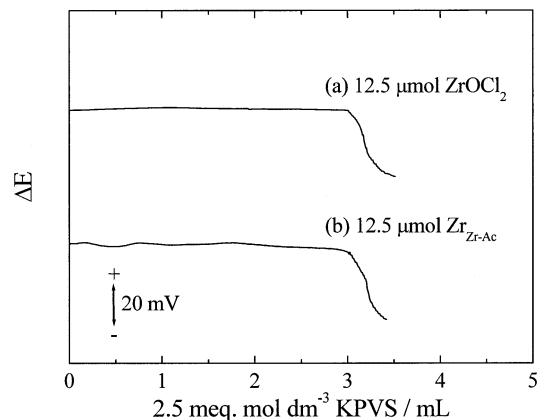
Fig. 4   Colloidal titration curves for (a) ZrOCl₂ and (b) Zr-Ac.

Fig. 3   Calibration curves of ZrOCl₂ at pH 2.0 and 3.75.

Fig. 5   Average hydrodynamic radius of zirconium species. Effect of the Zr-Ac concentration of the pH.

not react with cationic dye. On the other hand, polyanion KPVS reacts to form precipitates with cationic dye. NaCl that dissociates and forms simple, hydrated low-molecular weight ions in aqueous solutions does not react with both anionic dye and cationic dye. According to the results, it is concluded that the zirconium oxy-salts had positive charges and formed polymeric or cluster-like species in solutions.

Potentiometric titration curves

The potentiometric titration curves of ZrOCl₂ and Zr-Ac are shown in Fig. 2. In the vicinity of the endpoint, the observed change of the potential is about 40 mV and asymmetric. The asymmetric potential jump was similarly observed for chitosan titrated with PVSK using a TB-selective electrode as end-point detection tool.[19] Therefore, the endpoint was determined in the same way as for chitosan.[19] Figure 3 shows the calibration curves of ZrOCl₂ at pH 2.0 and pH 3.75. Both curves are straight lines passing through the zero point. Thus, each titration reaction is exactly stoichiometric. In addition, a line passing through the zero point means that the way of endpoint detection is valid. On the other hand, the slope indicates the net charge per zirconium atomic unit in the polymer chain, and that the charge at pH 2.0 is larger than that at pH 3.75. Similar straight lines going through the zero point were also obtained upon the titration of Zr-Ac. For all titrations, the relative standard deviation in five titrations was within 1% in the concentration range presently studied.

Effects of the pH

Since the total charge of the zirconium polymer depended upon the pH, the end point of the titration, *i.e.*, the volume of the titrant consumed at the charge neutralization of the polyelectrolytes, also depended upon the pH. Figure 4 shows such a study of colloidal titration curves.[9] For both ZrOCl₂ and Zr-Ac, the colloidal titration values were almost constant below pH 2.0, and decreased with the pH. Thus, the total amount of charge on the polymer chains, calculated from the colloidal titration value, remained the same below pH 2.0, according to Eq. (1), while it decreased upon raising pH because of the involvement of further hydrolytic processes. There is also a possibility that the pH-buffer component (acetate ion) had a role in decreasing the polymer charge through its coordination to zirconium ion. Also, the constant total charge below pH 2.0 agreed with a 1:1 reaction between the zirconium metal unit and the monomer unit of PVSK, supporting the validity of Eq. (1) below pH 2.0.   This remains the basis to determine the concentration of zirconium.

Under the condition of pH over 2, the aqueous zirconium species are expected to undergo further hydrolysis and the resulting coagulation reaction among the metal hydroxide polymer chains. Therefore, the average hydrodynamic radius of the solution species under various Zr-Ac concentrations was measured by DLS at several pH values. The pH was adjusted by combining acetate and hydrochloric acid as in the colloidal titration.   The obtained results are shown in Fig. 5.   The hydrodynamic radius increased with raising the pH and/or increasing the concentration of Zr-Ac. The results agreed with
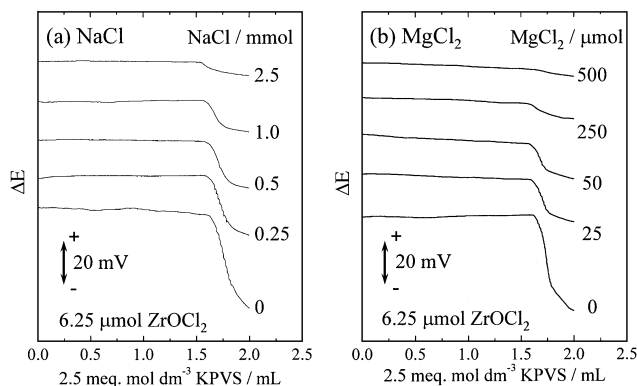
Fig. 6   Effects of the concentration of (a) NaCl and (b) MgCl$_2$ on the titration of 6.25 µmol ZrOCl$_2$.

a report of Pilkington, *et al*.[7] Unfortunately, no significant signal was obtained on DLS at a concentration of less than 0.1 mol dm^{-3} of Zr-Ac. Therefore, their sizes of zirconium-hydrolyzed polymers could not be clarified in this experiment. However, it is pointed out that the hydrodynamic radius of the polymer under our titration conditions should be less than 1 nm, since the titration was carried out at a much lower zirconium concentration (~1.0 × 10^{-4} mol dm^{-3}). According to Singhal *et al*., the radius of gyration for the octamer was 0.51 nm.[24]

Effects of salts

   It is well known that the reaction in the colloidal titration is inhibited by the presence of a large quantity of inorganic electrolytes. The titration curves in the presence of sodium chloride and magnesium chloride are shown in Fig. 6. In both cases of sodium chloride and magnesium chloride, the higher is the concentration of salts, the smaller is the change of potential after the end-point. However, the location of the end-point is not affected even by the presence of 2.5 mmol (50 mmol dm^{-3}) sodium chloride and 0.25 mmol (5 mmol dm^{-3}) magnesium chloride.

In conclusion, colloidal titration with poly(vinyl sulfate) was successfully applied to measure the zirconium concentration in an acidic solution by using a Toluidine Blue selective plasticized poly(vinyl chloride) membrane electrode as a potentiometric end-point detecting device. The determination could be performed with 1% of the relative standard deviation. The colloidal titration stoichiometry at pH ≤ 2 was one mol of zirconium per equivalent mol of poly(vinyl sulfate).

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