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The Reliquefaction of Zirconia Gels

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THE RELIQUEFACTION OF ZIRCONIA GELS

by

Hubert Joseph Kelly

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Master of Science in Chemistry.

By Hubert J. Kelly

Approved by JDP ortu

Date 14 May 1951

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Dedicated

to my wife

Ruth

- for her loving, steadfast assistance without
which this work would not be possible -

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I Introduction

The reliquefaction of the hydrogels of zirconia was first reported by Hurd, Fallon, and Hobday (7,6). Their gels, which were made at room temperatures and set in a few minutes, were observed to change again, merely on standing at the same temperatures, to water-clear sols. Heating such reliquefied gels to 60° C. resulted in their regelation, and upon subsequent cooling to room temperature reliquefaction again occurred. This heat-reversible gelation could apparently be repeated indefinitely.

Other examples of this unusual inverse effect of liquefying on cooling are mentioned by McBain (11) as being the gels of methyl cellulose in water and cellulose nitrate in alcohol. It is also interesting to note that Hurd, Jacober and Godfrey (8,5) encountered this inverse type of heat reversibility with titania gels.

However, the initial reliquefaction of zirconia gels at room temperatures seems to be unique. The following study was made to provide a further description of this phenomenon and to attempt to suggest the nature of it.

II Historical

The earliest investigations of hydrous zirconia, sols and gels, have been summarized by Weiser (21). Zirconia sols of varying

purity have been prepared by dialyzing solutions of zirconium nitrate, zirconium oxychloride, and zirconium acetate. The most pure sols are very sensitive to small concentrations of electrolytes, which precipitate zirconia. However, suitable concentrations of electrolyte or the heating of a pure sol may cause it to set to a typical gel. Sols and gels have been described as clear and transparent, opalescent, or opaque, depending upon their method of preparation and their purity.

Pauli (12) attempted an investigation of the constitution of the micelles of a zirconia sol prepared from ZrOCl_2 . By means of conductivity measurements, he postulated the presence of both cationic and anionic complexes of the composition $[\text{Zr}(\text{OH})_4 \cdot \text{ZrOCl}_2 \cdot \text{ZrO}]^{++}$ and $[\text{Zr}(\text{OH})_4 \text{Cl}_2]^-$. He attempted to show that, when the hydrogen ion concentration exceeded the chloride ion concentration, the anionic complex is present in the greater amount, but since the chloride ion concentration usually exceeds the hydrogen ion concentration in the typical zirconia sol, the cationic complex ordinarily predominates.

In 1935, Thomas and Owens (16, 17) investigated the hydrosol of ZrOCl_2 in order to include it in their general study of the colloidal oxides. They have discussed their observations by

developing the Pfeiffer-Werner complex theory for crystalloidal salts into the complex compound theory of colloidal oxides.

Whitehead (24) has written a review of the complex compound theory of colloidal oxides, and has included references to the hydrosol of zirconia in his paper.

As already noted, Hurd, Fallon and Hobday (7,6) made a study of the effect of pH on the setting time of the hydrogels of zirconia. It was during this investigation that the reliquesfaction phenomenon was first observed.

Marisic and Griest (10) received a patent on the Preparation of zirconia gel. Dehydration of a zirconia gel produces an excellent catalyst for the cracking of hydrocarbons. Their claims involve the formation of a stable hydrogel of zirconia by the addition of ammonium carbonate to an aqueous solution of $ZrOCl_2$, and water washing the gel at a temperature of 60°C or above to prevent loss of zirconia.

III Chemistry of Zirconium

Venable's (19) monograph on zirconium is the most comprehensive summary of zirconium chemistry. However, a greater understanding of the aqueous chemistry of zirconium has been provided by deBoer (2) who established the tendency of anions to become coordinately

bound to zirconium in the following order, $\text{OH}^- > \text{F}^- > \text{PO}_4^{3-} > \text{C}_2\text{O}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$.

Connick and McVey (1) have made an interesting study of the extent of hydrolysis and complex formation of zirconium in aqueous solutions. They have shown that even in a 2 M solution of HClO_4 the average zirconium species in low concentrations lies between Zr^{+4} and $\text{Zr}(\text{OH})^{+3}$. At higher concentrations of zirconium (or lower acidities) a polymerization occurs indicating appreciable hydrolysis even in very acid solutions. They calculated instability constants for the various complexes which form with the fluoride ion, the sulfate ion, the chloride ion, and the nitrate ion. The formation of these ions was studied under such conditions of acidity (2 M) and zirconium concentration that polymerization and hydrolysis were considered negligible.

They reported the following order of stability of the simple complex ion of zirconium with anions, $\text{OH}^- > \text{F}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. This was in agreement with deBoer (2). They also list the order of abundance of the species of a particular type of complex ion, such as the following, $\text{ZrF}^{+3} > \text{ZrF}_2^{+2} > \text{ZrF}_3^+$; $\text{ZrSO}_4^{++} > \text{Zr}(\text{SO}_4)_2 \gg \text{Zr}(\text{SO}_4)_3^-$.

The average species of complex ion is a function of the concentration of the complexing anion. They found that chloride and nitrate ions are only slightly complexed. Among the organic

anions, the oxalate ion forms a very stable complex, but the next three dibasic aliphatic acids show little complexing power. An interesting observation is that zirconium is not complexed in a 1 M solution of acetic acid.

The latest treatment of the chemistry of zirconium is found in Sidgwick (14). The fact that zirconium is a transition element and may have a maximum covalency of 8 is significant to the complex compound theory of colloidal oxides. Although zirconium is an amphoteric element, the acidity of zirconium hydroxide is very weak, and it is insoluble in aqueous alkali. There is reported a very interesting series of basic zirconyl salts with the general formula, $(ZrO)_4O(ROO)_6$, and the chelation complexes of zirconium are numerous.

IV Apparatus

All zirconia gels were made in 16 X 150 mm Pyrex test tubes. The definition of the Time of Set and the Time of Reliquefaction required that the same size test tubes be used throughout.

A water bath was heated with blade heaters, and the temperature was controlled with a Cenco-de Khotinsky Thermo-Regulator. The variation in temperature was within 0.2°C . The water was kept in motion by a stirrer attached to a Cenco 150/60 cycle single

phase motor.

Two Bechman pH Meters, Models F and H-2, were used with a glass electrode and standard calomel cell to make the pH measurements. The meters were checked frequently with commercial buffer solutions, pH 2.00 and pH 7.00.

Volume measurements were made with 5 ml pipettes, graduated to tenths of a ml.

V Experimental Results

Part I Preliminary Work

A standard stock solution of known ZrO_2 concentration was prepared by dissolving 385 gms. of solid $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in water, filtering to remove a finely divided white residue, and diluting to 1 liter volume. An analysis of the solution indicated the ZrO_2 concentration to be 1.11 Molar. A trace of iron was also found to be present.

It was shown by Hobday (6), corroborating the work of Pauli (12), that the hydrolysis equilibrium of ZrOCl_2 solutions was established within three days, and that these solutions could be then considered as usable standards. The pH of the standard zirconium solution was 0.45.

A 1.50 N solution of sodium acetate was prepared from reagent grade $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$. The pH of this solution was 8.11. This solution had to be freshly prepared about every two months because of the appearance of a bacterial growth which made the solution slightly more acidic.

The following procedure was used in preparing the gels. A measured amount of the standard zirconium solution was pipetted into a test tube, and the tube stoppered. The sodium acetate solution, plus any desired diluent, was measured into another test tube, and stoppered. The two solutions were placed in the temperature controlled water bath for a period of twenty minutes. In order to standardize the conditions for gel formation, the mixing procedure was done with formal constancy. The test tubes were removed from the bath, quickly wiped, and the sodium acetate solution poured into the standard zirconium solution. To insure thorough mixing, the solution was poured back into the test tube which had contained the sodium acetate solution, and then back again into the test tube which had originally contained the standard zirconium solution. When mixing was completed, the test tube was immediately returned to the water bath. This whole mixing operation took approximately 15 seconds. When measuring the time of set of a gel, the time required for mixing was always included.

During gelation the mixture becomes increasingly opalescent until finally a white opaque gel is formed. The time of set was defined as the time interval from the beginning of the mixing procedure to the point when the rigidity of the gel structure was great enough to permit the test tube to be tipped upside down. Duplicate measurements of the time of set showed that a precision greater than 2% was obtainable when the time of set exceeded one minute. This is essentially Fleming's test tube method (4), as used by Hobday (6).

The reliquefaction of the gel is a very gradual process. The gel first softens, and becomes less opaque, i. e., light is being transmitted through it to a very limited extent. Then it loses its rigidity, and will flow. In its initial fluid condition, soft fragments of gel remain suspended in the liquid. As the process continues over a period of hours, these fragments are gradually consumed, and an opalescent sol results. Finally, the opalescence disappears, and the sol appears water-clear. That the resulting solution is indeed a sol is confirmed by the pronounced Tyndall effect which may be observed even ten months after reliquefaction.

In order to record a time of reliquefaction, the gel was defined as reliquefied when it lost its rigidity, and slipped

down the test tube when tipped upside down. This is a difficult point to determine, but if care was taken not to jar the weak gel, a precision of approximately 3% was attainable.

Part II The Effect of Added Electrolytes

The following gels were made to determine whether cations or anions were responsible for the increase in the rate of gelation when electrolytes were added. Hurd, Fallon, and Hobday (7) had reported this effect.

The electrolytes were added to the sodium acetate solution. The temperature, the ZrO_2 concentration, the sodium acetate concentration, and the electrolyte concentration in equivalents were kept constant. The concentrations are based in every case upon the total volume after mixing all components, no allowance being made for concentration changes due to reactions upon mixing.

In order to compare results, a reference gel was made without the added electrolyte, and a ratio of the times of set with respect to this gel is tabulated in Table I.

A distinction should be made at this point between the sol formed preceding the gelation, and the stable sol resulting from the reliquefaction of the gel. The transitory nature of the "first" sol was realized. The stable sol is called the "second" sol in this paper.

Table I
Effect of Electrolytes

0.22 M ZrO_2 Temperature 30°C

0.96 M NaAc

T. of S. of reference gel 1.67 min.

Effect of Cations

Electrolyte	Electrolyte Conc.	T. of S. mins.	Ref. Ratio	pH
KCl	0.016N	1.67	1.00	4.98
KCl	0.16N	1.00	0.60	4.97
MgCl_2	0.016N	1.67	1.00	4.97
MgCl_2	0.16N	1.00	0.60	4.92
AlCl_3	0.016N	no gel	0	4.96
AlCl_3	0.16N	no gel	0	4.62

Effect of Anions

Electrolyte	Conc. of Electrolyte	T. of S. mins.	Ref. Ratio	pH
KCl	0.16N	1.00	0.60	4.98
K_2SO_4	0.16 N	0.74	0.44	4.99
$\text{K}_3\text{Fe}(\text{CN})_6$	0.16 N	1.60	0.96	----
$\text{K}_4\text{Fe}(\text{CN})_6$	0.16 N	1.67	1.00	----

In all cases, the gels reliquefied. However, the gels which set the fastest had the longest times of reliquefaction. This general relationship was also observed by Hurd, Fallon and Hobday (7).

The fluoride ion has a unique effect, especially upon reliquefaction. Two gels were prepared with added sodium fluoride. Table II indicates the concentrations of the gels, their times of set and reliquefaction. The temperature was controlled at 30°C. The sodium fluoride was added to the sodium acetate solution. Gel #3 is included in this table to facilitate comparison. Gel #4 was made to show that an equivalent amount of additional acetate ion would not be the cause of this effect.

Placing the "second" sol from Gel #2 in the 60°C water bath caused regelation, and when returned to room temperature, reliquefaction occurred. However, it was no longer rapid, as it had been initially, and the "second" sol retained a slight opalescence. This "second" sol was kept at room temperature (26°C.), and at the end of one month it set to a soft gel. This gel slowly but steadily increased in rigidity during the next three months. Its opalescence increased with time, and it acquired a yellowish brown color. It showed no signs of syneresis or reliquefaction.

Table II
Effect of Fluoride

0.22 M ZrO_2

Temperature 30°C

Gel	Conc NaAc	Conc NaF	T. of S.	T. of R. mins.	pH
1	0.96M	0.016M	.47 min	32	4.92
2	0.96M	0.16M	instantly	5	4.90
3	0.96M	_____	1.67 min	70	5.09
4	1.12 ^M	_____	2.00 min	52	5.26

Part III The Effect of Added Non-electrolytes

In each case the non-electrolyte was added to the sodium acetate solution. The concentrations of ZrO_2 and sodium acetate were kept at constant values, and the temperature employed was $30^\circ C$. The concentrations of ethyl alcohol (95%), pyridine, and the higher concentration of urea were estimated from specific gravity and solubility data (9). Table III records the observations made.

The gel made with alcohol present reliquefied to a water-clear sol, as did the gel made with the low concentration of urea. The time of reliquefaction was much longer for the gel made in the presence of alcohol. The higher concentration of urea, although preventing gelation, did not prevent the mixture from becoming opaque and very viscous. In time, the opacity of this mixture slowly disappeared and its viscosity decreased, as though undergoing the same process that caused reliquefaction, and a water-clear sol resulted. However, the gel containing pyridine did not reliquefy.

Since pyridine had prevented reliquefaction, its effect on a "second" sol was studied by adding 0.5 ml of pyridine to 4.0 ml of the "second" sol which had resulted from the reliquefaction of the reference gel listed in Table III. No apparent change occurred.

Table III

0.22 M ZrO_2

0.96 M NaAc

Temperature 30°C

Added Non-Electrolyte	Conc of Non-Electrolyte	T. of S.	pH
ethyl alcohol (95%)	~2.6M	0.74 min	5.02
urea	0.16M	1.67 min	4.94
urea	~3.2M	no gel	4.95
pyridine	~1.0M	instantly	6.10
reference gel	----	1.67 min	4.96