

SOLUBILITY EQUILIBRIA
INVOLVING
METAL OXIDES
AND
CORRESPONDING
AQUEOUS METAL PERCHLORATES

BY

Forrest C. Hentz, Jr.
Associate Professor
Department of Chemistry
School of Physical Sciences and Applied Mathematics
North Carolina State University
Raleigh, North Carolina

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PREFACE

The 1963 "Proposal for a Water Resources Institute at North Carolina State College" contained the following paragraph:

"The urgency of the need for water resources development information calls for an expanded program of research or, possibly more realistically, a shift in research emphasis towards water resources. Such increased research activity, together with the inevitable increase in activity of water-oriented action agencies, will create an unprecedented demand for specialists trained in associated areas. In view of the tremendous nationwide interest expressed at all levels, this demand for personnel will soar far beyond the present capacities of this nation's universities to satisfy. Hence, it is urgent that provisions be made for training and especially for graduate study in water-related areas."

Since that time, an enormous increase in interest and in activity in water research has been realized at local, state, national, and worldwide levels. The interest has stirred innovation in all government agencies with the result that those generally interested in oceanography, water purification, conservation of natural resources, etc. have been attracted to the fundamental research of chemists whose interests lie in the area of aqueous solution chemistry. In the past two years, specialized symposia on the chemistry of aqueous solutions have been conducted by the American Chemical Society (1966) and the Gordon Research Council (1967), and one has only to scan the current programs of national scientific meetings in order to see a growing emphasis on basic research which is related to water resources.

This writer came to North Carolina State University in 1964 with an active interest in the basic chemistry of aqueous systems and was immediately attracted to the Water Resources Research Institute of the University of North Carolina. A proposal submitted to this agency subsequently provided the opportunity for the development of a small program of graduate research concerning the hydrolytic

behavior of metal ions. Since it is true that initial research generates many possibilities for further research, it is in this sense that the support of the Water Resources Research Institute of the University of North Carolina is gratefully acknowledged.

The author wishes to thank those students at North Carolina State University who have worked on this project: R. G. Beach, A. P. Brill, III, R. G. Stoner, Jr., and R. D. Wauchope. The efforts of Mrs. Anna G. Deese in the typing of this report are also appreciated.

-- Forrest C. Hentz, Jr.

January, 1968

INTRODUCTION

INTRODUCTION

This report consists of a discussion of the two phases of the project which are substantially complete (Report I and Report II). These have been included in much the same form as that submitted for publication. While it might seem that "Solubility Equilibria Involving Metal Oxides and Aqueous Metal Perchlorates" is a title only remotely related to the subject matter in this report, such is not the case. It should be remembered that equilibria can (and often should) be approached from opposite directions, especially in cases where slow kinetics are possible. Thus, in the research described herein, we have approached the solid oxide by stepwise hydrolysis of the metal ion initially in aqueous solution. The reverse process would, of course, involve the stepwise dissolution of the oxide in the presence of acid and/or metal-salt solutions.

It should not be implied that this report is, in the literal sense, a "completion" report. Neither should it be implied that the thorium and titanium systems are the only ones investigated in this project. Other systems which have been investigated in a preliminary way, but not nearly to a state of completion, are as follows:

- (1) Solubility studies of the systems MO-aq. $M(\text{ClO}_4)_2$, where M = Cd, Mg, Zn, and Pb. Here equilibrium is attained very slowly and problems arise from solubilities too low to allow investigation of the saturated solutions.
- (2) Hydrolysis studies involving the approach to precipitation of hydrous oxide of the ions: Mn^{2+} , Cr^{3+} , Fe^{3+} , etc.
- (3) The possibility of forming heteropolycations by addition of base to mixed metal-salt solutions, and the subsequent formation of "mixed basic salts."
- (4) The investigation of Zr(IV) in acid perchlorate solution, in much the same manner as Ti(IV).

Of the items listed above, (4) is actively in progress. It is fully anticipated that we will continue our research in this area of aqueous solution chemistry.

REPORT

REPORT I

LIGHT-SCATTERING MEASUREMENTS ON HYDROLYZED SOLUTIONS

OF THORIUM(IV) NITRATE¹

(1) From a thesis submitted by Robert G. Stoner, Jr., to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the M. S. degree, 1967.

Abstract

Light-scattering measurements at 25°C on $\text{Th}(\text{NO}_3)_4$ solutions containing 0, 1, 2, and 3 bound hydroxyls per thorium atom (hydroxyl number, \bar{n}) have been made over the range 0.01-0.10M in total Th with each solution also 1.0M in NaNO_3 . The weight-average degree of polymerization calculated for each stage of hydrolysis agrees essentially with that found previously for a perchlorate medium; however, the estimated charges at the lower hydroxyl numbers are substantially less, indicating complexing of the thorium species by nitrate. The results indicate equilibrium solutions and degrees of polymerization near unity at hydroxyl numbers 0 and 1, and degrees of polymerization of 3-4 at hydroxyl number 2. At $\bar{n} = 3$, a degree of polymerization near 120 was found for clear solutions aged approximately one month; after an additional two-month aging period, an increase of some 25% in molecular weight was observed, with solutions of Th concentration above 0.07M showing faint visible turbidity. Some preliminary kinetic measurements for thorium solutions hydrolyzed to $\bar{n} > 3$ are reported.

Introduction

The hydrolysis of the thorium(IV) cation has been the subject of numerous investigations since the first reports^{2,3} of a tetrameric aggregate some twenty

(2) R. Schaal and J. Faucherre, Bull. Soc. Chim. France, 14, 927(1947).

(3) P. Souchay, ibid., 15, 143(1948).

years ago; however, a thorough description of the hydrolysis scheme has as yet not been possible. Recent studies^{4,5} in perchlorate solutions have indicated

(4) F. C. Hentz, Jr., and S. Y. Tyree, Jr., Inorg. Chem., 4, 873(1965).

(5) F. C. Hentz, Jr., and J. S. Johnson, ibid., 5, 1337(1966).

that in the range 0.01-0.10M hydrolysis becomes appreciable at hydroxyl number one (pH ~ 3) with formation of low molecular-weight species, and proceeds, in solutions at apparent equilibrium, to at least $\bar{n} = 2.5$ (pH < 4) where the weight-average polymerization number is near eight. At $\bar{n} = 3$, equilibrium was not attained in the ultracentrifuge,⁵ and the degree of polymerization was estimated in excess of 100 and was increasing from day to day; an instantaneous value of ca. 150 had been indicated previously by light-scattering measurements.⁴

The pertinent literature has been reviewed recently^{4,5,6} and the results for

(6) C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts, ibid., 4, 518(1965).

perchlorate medium are generally in agreement; nevertheless, questions remain as to whether equilibrium is established at $n < 2.5$ in non-perchlorate media (particularly chloride^{5,7}), and whether the hydrolysis is the same in the presence of

(7) S. Heitanen and L. G. Sillen, Acta. Chem. Scand., 8, 1018(1964).

other anions.⁸ We have therefore reinvestigated the thorium hydrolysis by means

(8) W. S. Brey, private communication.

of light-scattering measurements, this time in nitrate solutions at 25°C.

Experimental

Stock and Experimental Thorium Solutions--Stock solutions of the appropriate hydroxyl number were prepared by mixing analyzed solutions of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (Baker and Adamson AR) and 2M NaOH (carbonate-free), as before.^{4,5} From each stock solution eight experimental solutions of Th concentration 0.01-0.10M were prepared by dilution. The requisite amount of dried NaNO_3 was added to each solution so as to make each solution 1.00M in this salt.

Analyses--Thorium was determined gravimetrically as the oxide.⁹ Total

(9) W. F. Hillebrand, et al., "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, 1953, pp. 503, 542.

nitrate was determined by ion exchange using Rexyn 101(H) and titrating the eluted HNO_3 with standard base. The $\text{NO}_3:\text{Th}$ ratio in the unhydrolyzed stock solution was 3.95. (Found: Th, 0.4880M; NO_3 , 1.930M.)

Light-scattering Measurements--Turbidity measurements at 4358Å were made with a Brice-Phoenix photometer (Model 2000) using dry, thiophene-free benzene as a secondary standard. The absolute turbidity of benzene was taken as $7.71 \times 10^{-4} \text{ cm}^{-1}$; using the opal diffusor supplied with the instrument, this quantity was

(10) D. K. Carpenter and W. R. Krigbaum, J. Chem. Phys., 24, 1041(1956).

determined to be $7.59 \times 10^{-4} \text{ cm}^{-1}$. One 3-cm square cell was used for all measurements. Solutions were clarified and the excess turbidities determined as before.⁴

Refractive index increments (4358\AA) were measured with a Brice-Phoenix differential refractometer (Model BP2000V) calibrated with KCl solutions.¹¹

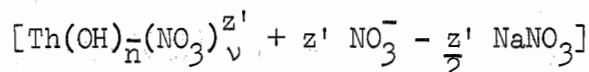
(11) A. Kruis, Z. Physik. Chem., B34, 13(1936).

Other Measurements—Solution densities were determined pycnometrically at 25°C. Measurements of pH were made at $25.0 \pm 0.1^\circ\text{C}$ using a Heath recording electrometer (Model EUA-20-11). The pH data were reproducible to ± 0.05 units except for solutions at $\bar{n} = 3.0$.

Results and Discussion

The light-scattering data were interpreted as before⁴ on the basis of a monomeric thorium component of the form

(12) G. Scatchard, J. Am. Chem. Soc., 68, 2315(1946).



where $z' = 4 - \bar{n} - v$. In this three-component system, the weight-average degree of polymerization, N_z , is related to the excess turbidity, τ^* , due to the thorium solute by

$$1/N_z = \frac{H'' M' \phi \psi^2}{\tau^*} - \frac{z'^2 M'}{2M_3} \quad (1)$$

$$H'' = \frac{32000\pi^3 n^2}{3N\lambda^4} \quad (2)$$

where ϕ is the solvent volume fraction, N is Avogadro's number, n is the refractive index of the solution, λ is the wavelength, and M_3 is the molarity of the background (NaNO_3). The primed quantities M' , z' , and ψ' refer respectively to the molarity, charge, and differential refractive index of the monomeric thorium component.

The definition of the thorium component also requires that ψ' and M_3 be expressed as

$$\psi' = \frac{\partial n}{\partial M'} - \frac{z'}{2} \frac{\partial n}{\partial M_3}$$

$$M_3 = 1.00 + \frac{z' M'}{2}$$

The small corrections of the stoichiometric hydroxyl number, \bar{n} , for free acidity were not made.

Turbidities, Refractive Index Increments, Solvent Volume Fractions, and Solution pH--For each hydroxyl number a plot of the gross solution turbidity as a function of M' was linear and converged to a common intercept at $M' = 0$. This intercept was subtracted from all measurements to give the excess turbidity, τ^* . Similarly, plots of the difference in refractive index between the thorium solution and 1.00M NaNO_3 (refractive index increment) were also linear with zero intercepts and slopes $\partial n / \partial M'$. Values of $\partial n / \partial M'$ decreased with increasing \bar{n} , being 6.04×10^{-2} , 5.14×10^{-2} , 4.00×10^{-2} , and 3.02×10^{-2} g-mole^{-1} for hydroxyl numbers 0, 1, 2, and 3, respectively. The differential refractive index for NaNO_3 , $\partial n / \partial M_3$, was found to be constant at 9.40×10^{-3} g-mole^{-1} over the range 0.5-1.2M and was used for calculation of ψ' . Solvent volume fractions were computed as before.⁴ The pH of each solution is tabulated with the data in Table I.

Degrees of Polymerization and Estimated Monomeric Charges--Equation (1) was applied by calculation of the reciprocal of the degree of polymerization, $1/N_{z'}$, for each series of solutions using z' as a variable parameter. The quantity $1/N_{z'}$ was then plotted vs M' , giving a family of lines whose slopes depend upon the z' chosen. The value of z' giving the slope nearest zero was assumed to best represent the system and allowed simultaneous evaluation of the weight-average degree of polymerization, N_w , and estimation of the monomeric charge, z' .¹³ Figures 1 and 2

(13) R. S. Tobias and S. Y. Tyree, Jr., J. Am. Chem. Soc., 81, 6385(1959).

show the results for the hydrolyzed solutions studied.

Taken at face value, the results for the unhydrolyzed series were found to be $N_w \sim 0.6$ at $z' \sim 1$. The divergence of N_w from unity and the low charge is in marked contrast to that found in perchlorate^{4,5} and may be due to the formation of nitrate-thorium complexes^{14,15} or to activity coefficient variations¹⁶ in the system

(14) E. L. Zebrski, H. W. Alter, and F. K. Heumann, *ibid*, 73, 5646(1951).

(15) R. A. Day, Jr., and R. W. Stoughton, *ibid*, 82, 5662(1960).

(16) A. N. Kirgentsev and A. V. Lukyanov, Russ. Jour. Phys. Chem. (English Transl.), 39, 389(1965).

$\text{NaNO}_3\text{-Th(NO}_3)_4\text{-H}_2\text{O}$. Likewise, the results at $\bar{n} = 1$ ($N_w \sim 1.2$; $z' \sim 0$) indicate a predominately monomeric distribution of thorium species complexed extensively by nitrate anions. Further hydrolysis to $\bar{n} = 2$ leads to considerable aggregation of the thorium particles. Values of $N_w = 3 - 4$ were calculated on the basis of a charge near zero.

For solutions at hydroxyl number 3.0, the calculations required $z' = 0$ and equilibrium was not attained over a period of five months. After aging one month, an apparent N_w of ca. 120 was found for visibly clear solutions; remeasurements on the same solutions after an additional two months showed an approximate 25% increase in N_w . Except for the two most concentrated solutions ($C_{\text{Th}} > 0.07M$) all solutions were free of visible turbidity at the end of five months.

Preliminary Kinetic Measurements--Measurements of τ^* , Δn , and ρ as a function of time were made over a period of two months for solutions (thermostated at $25 \pm 1^\circ\text{C}$) at hydroxyl numbers 2.5, 2.75, 3.0, and 3.1. Our preliminary results indicate that 1M NaNO_3 solutions at $\bar{n} = 2.5$ ($N_w \sim 6$), and probably those at $\bar{n} = 2.75$ ($N_w \sim 20$), are at least at a state of pseudoequilibrium, although very slow changes cannot be ruled out. The turbidity and N_w increase slowly over a period of 90 days at $\bar{n} = 3.0$, as indicated above; however, a slight increase of

the stoichiometric hydroxyl number to 3.1 clearly leads to relatively rapid changes in the measured solution turbidity. For both series of $\bar{n} \geq 3$, only the solution turbidity shows measurable week-to-week changes; any changes in refractive index increment and density over a period of sixty days are immeasurably small. Assuming zero charge, increases in molecular weight are therefore paralleled by increases in solution turbidity. The results for $\bar{n} = 3.1$ are shown in Table II; extrapolation to zero time gives N_w approximately 100.

Conclusions--These results indicate that the hydrolytic aggregation of thorium, under comparable conditions, is much the same in nitrate as in perchlorate solutions. It is perhaps a significant difference that the estimated monomeric charges for the lower degrees of hydrolysis are, as might be expected, lower in the presence of nitrate. As in the case of perchlorate medium, solutions are at apparent equilibrium through at least $\bar{n} = 2.5$. Equilibrium is not attained in extensively hydrolyzed thorium solutions ($\bar{n} \geq 3$) and it is possible that the kinetic data will be difficult to reproduce and that these solutions will yield significant precipitates on sufficient aging at 25°C. We are continuing our investigations along these lines.

TABLE I

Turbidities and Refractive Index Increments (4358Å),
Densities, and pH of Solutions at 25°C

\bar{n}	M'	$10^6 \tau^*(\text{cm}^{-1})$	$10^3 \Delta n$	$\rho(\text{gm-ml}^{-1})$	pH
0	.00976	4.5	.543	1.0569	3.03
	.02440	11.7	1.496	1.0632	2.73
	.03416	16.3	2.092	1.0666	2.69
	.04880	23.1	2.947	1.0733	2.55
	.07320	35.3	4.500	1.0840	2.43
	.09760	46.8	6.006	1.0948	2.33
	.1220	58.7	7.505	1.1060	2.22
1	.00801	6.8	.382	1.0555	3.34
	.02003	16.7	1.002	1.0609	3.32
	.02804	23.5	1.423	1.0642	3.26
	.04005	33.4	2.058	1.0693	3.19
	.06008	50.2	3.072	1.0775	3.12
	.08010	67.5	4.114	1.0863	3.09
	.1001	84.4	5.211	1.0946	3.07
.1202	101.0	6.202	1.1033	3.00	
2	.00679	10.8	.240	1.0546	3.68
	.01698	23.9	.609	1.0578	3.56
	.02377	32.9	.879	1.0596	3.54
	.03396	45.1	1.390	1.0633	3.50
	.05094	66.4	2.028	1.0693	3.47
	.06792	87.2	2.726	1.0745	3.37
	.1019	131.0	4.092	1.0853	3.29
*3	.00668	180.0	.171	1.0554	4.1
	.01335	383.0	.360	1.0569	4.0
	.02003	572.0	.580	1.0589	4.0
	.2670	757.0	.794	1.0605	3.9
	.04005	1140.0	1.200	1.0641	3.9
	.05340	1520.0	1.613	1.0677	3.9
	.06675	1900.0	2.030	1.0708	3.8
	.08010	2290.0	2.366	1.0755	3.8
.1068	3060.0	3.270	1.0826	3.8	
**3	.00668	237.0	.198		3.9
	.01335	506.0	.388	1.0565	3.9
	.02003	731.0	.607	1.0590	3.8
	.02670	980.0	.841		3.8
	.04005	1480.0	1.228		3.8
	.05340	1940.0	1.631	1.0680	3.7
	.06675	2460.0	1.944	1.0711	3.7
	.08010	2930.0	2.400		3.7
	.1068	3890.0	3.189	1.0821	3.7

* Solutions aged one month

** Solutions aged three months

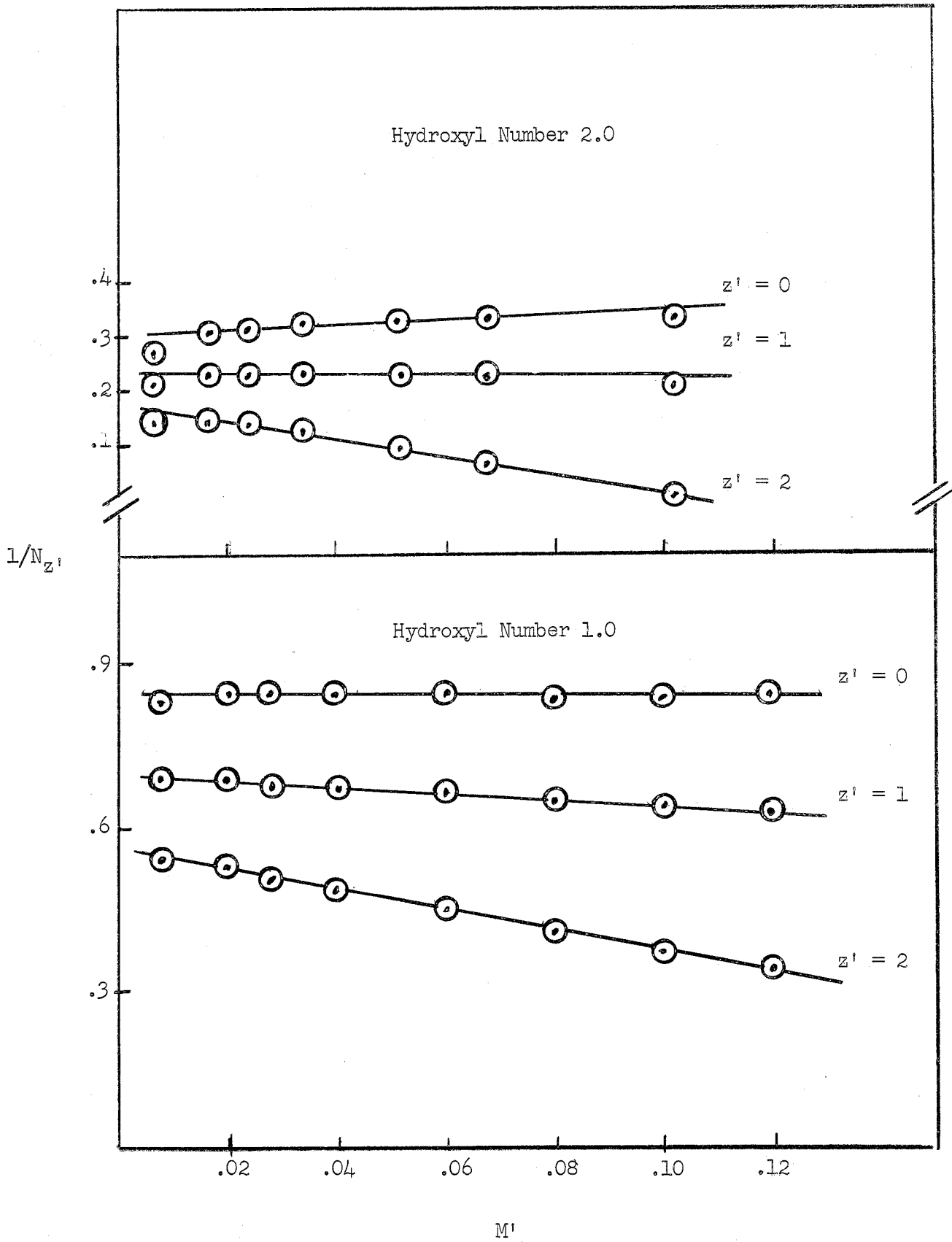


Fig. 1 - $1/N_{z^1}$ vs. M^1 with z^1 as a parameter; hydroxyl numbers 1.0 and 2.0

Fig. 2 - $10^2/N_{z'}$ vs. M' for hydroxyl number 3.0 (computed for $z' = 0$);
solution age shown.

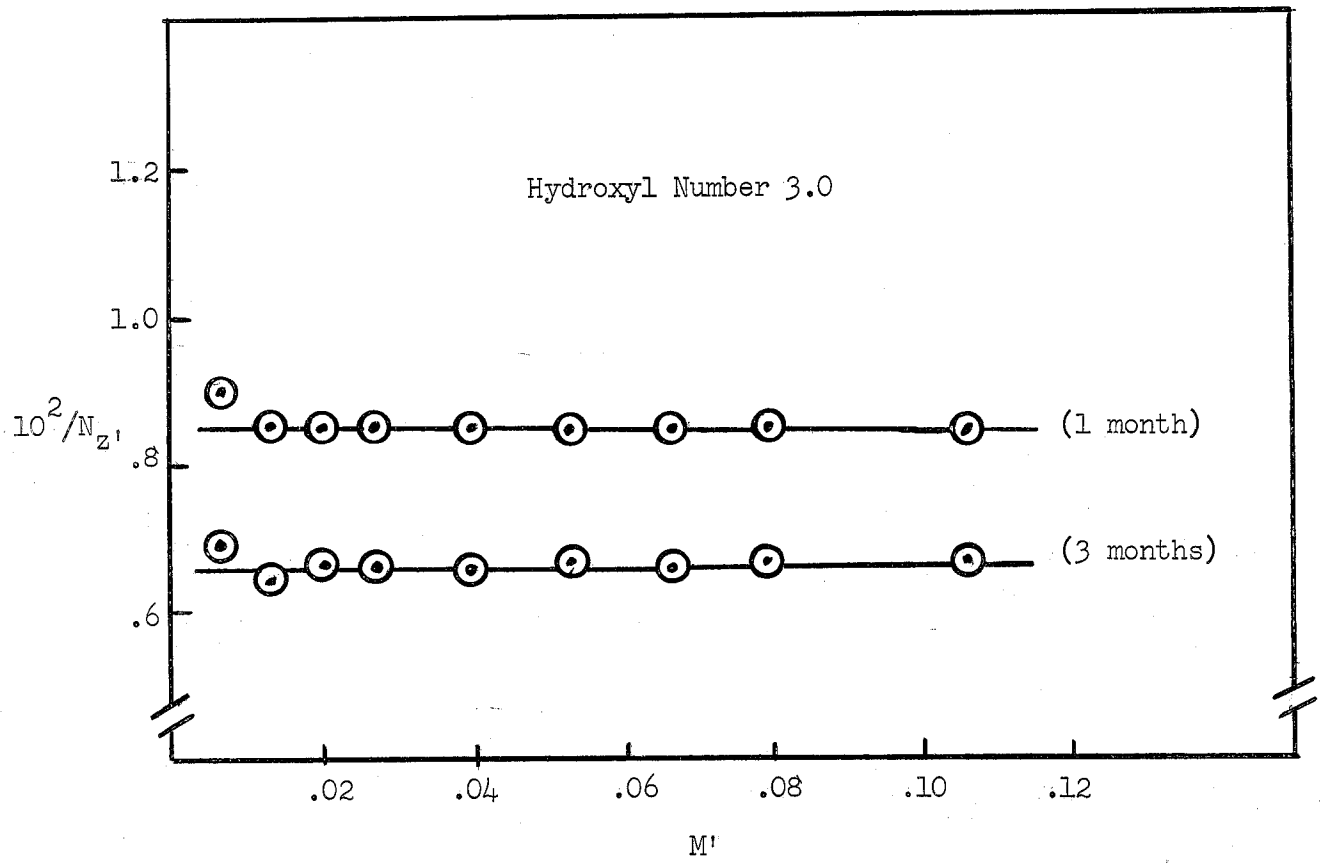


TABLE II

Preliminary Kinetic Data for Hydroxyl Number 3.1 (Values of N_w are representative of the data for $C_{Th} = 0.01-0.10M$)

<u>Solution Age (days)</u>	<u>$10^4 \tau^*$ (cm^{-1}) (a)</u>	<u>N_w (b)</u>
3	12.8	100
7	14.0	109
11	14.3	111
25	16.8	130
41	19.6	150
60	22.5	170

(a) Representative turbidity data for $C_{Th} = 0.0547M$; solution visibly clear over two months.

(b) Computed for $z' = 0$; $\partial n / \partial M'$ constant at $3.00 \times 10^{-2} \text{ g-mole}^{-1}$ during aging period.

REPORT II

LIGHT SCATTERING MEASUREMENTS ON PERCHLORIC ACID SOLUTIONS OF TITANIUM(IV)¹

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- (1) From the predoctoral work of Mr. R. D. Wauchope, candidate for the Ph.D. degree in chemistry, Department of Chemistry, North Carolina State University, 1968.
-

Several investigators²⁻⁴ have found evidence for monomeric titanium(IV)

- (2) D. Delafosse, C. R. Acad. Sci., Paris, 240, 1991(1955).
- (3) J. Beukenkamp and K. D. Herrington, J. Am. Chem. Soc., 82, 3025(1960).
- (4) A. K. Babko, G. I. Gridchima, and B. I. Nabivanets, Zh. Neorg. Kim., 7, 132 (1962); J. Inorg. Chem. USSR, 7, 66(1962).
-

species in aqueous acidic media, although there is disagreement as to the nature of these species. The possibility of a true "titanyl" ion $[\text{TiO}]^{2+}$, existing in solution seems small,⁵ but monomeric hydroxo species have remained an open question.

- (5) J. Selbin, Angew. Chem. internat. Ed., 5, 714(1966).
-

We have undertaken a light-scattering study of solutions of "titanyl perchlorate", $\text{TiO}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$,⁶ in 2M and 3M perchloric acid in hopes of clarifying the situation.

- (6) V. Krishnan and C. C. Patel, Indian J. Chem., 2, 425(1964).
-

Experimental Section

Turbidities (4358Å) of month-old, visibly clear, titanium solutions and of 2.00M and 3.00M perchloric acid were measured on a Brice-Phoenix light scattering photometer, calibrated by the Brice "working standard" method.⁷ The results are

(7) B. A. Brice, M. Halwer, and R. Speiser, J. Opt. Soc. Amer., 40, 768(1950).

shown in Table 1. Refractive index increments at 4358Å were measured with a Brice-Phoenix differential refractometer calibrated with KCl solutions.

The excess turbidities (τ^* , the solution turbidities minus the turbidities of the medium) are quite low, indicating a low degree of polymerization. In appearance, the data were linear with respect to titanium molarity, and the values for the two series of solutions in the two media were consistent. A least-squares treatment was thus used to smooth the data. The degree of aggregation ($N_{z'}$) for a charge z' was then calculated for each solution at trial values of 0, +1, +2, and +3 for z' , using the Tobias-Tyree equation for a three component system⁸,

(8) R. S. Tobias and S. Y. Tyree, Jr., J. Amer. Chem. Soc., 81, 6385(1959).

$$\frac{1}{N_{z'}} = \frac{H'' \phi_2 M' \psi'^2}{\tau^*} - \frac{z'^2 M'}{2M_3}$$

$$\psi' = \frac{\partial n}{\partial M'} - \frac{z'}{2} \frac{\partial n}{\partial M_3}$$

$$M_3 = [\text{HClO}_4]$$

Table 1. Turbidities, τ , and excess turbidities, τ^* , of $\text{TiO}(\text{ClO}_4)_2$ solutions in 2M and 3M perchloric acid

Ti conc. $\times 10^2$	0.000	1.157	2.313	3.470	4.048	4.626	5.204	5.783	6.361	6.939	7.517	8.096	8.674	9.252**	
$\tau \times 10^5$	6.06	6.58 [†]	8.57 [†]	6.98 [†]	6.61	6.58	6.73	6.66	6.71	6.53 [†]	6.86	6.94	7.00	7.03	
(exp.)	3M	6.48	6.99 [†]	6.70	6.82	6.93	6.99	6.91	7.01	7.03	7.09	7.12	7.23	7.09 [†]	
$\tau^* \times 10^6$	0.00	1.2	2.4	3.6	4.2	4.6	5.4	6.0	6.6	7.2	7.8	8.4	9.2	9.8	
(calc.)	3M	0.00	0.9	1.9	2.8	3.2	3.7	4.1	4.6	5.0	5.5	6.0	6.4	6.9	7.3

[†] omitted from least squares treatment

** Solutions of higher $[\text{Ti}]^{4+}$ showed evidence of precipitation after one month.

and the results extrapolated to $M' = 0$ (infinite dilution in Ti). The resulting values of $N_{z'}$, are given in Table 2.

Table 2. $N_{z'}$ values at $M' = 0$

	$z' = 0$	+1	+2	+3
$N_{z'}$ 2M HClO ₄	0.48	0.59	0.81	1.14
$N_{z'}$ 3M HClO ₄	0.40	0.53	0.69	0.97

Results and Discussion

Since in both series a trial charge near three is required to give a reasonable value of $N_{z'}$, i.e., at least a monomer, these data strongly indicate that in equilibrium solutions where the K_{sp} of titanium hydroxide has not been exceeded, the predominant titanium species present is a monohydroxo ion, $[\text{TiOH}]_{(aq)}^{3+}$, probably in equilibrium with a smaller amount of the lower-charged $[\text{Ti}(\text{OH})_2]_{(aq)}^{2+}$ ion. The singly-charged species proposed by Beukenkamp and Herrington, $[\text{Ti}(\text{OH})_3]_{(aq)}^+$, which was indicated by ion-exchange studies on solutions supersaturated with respect to Ti(IV) hydroxide, may therefore be the precursor to the precipitation of hydrous titania. There is no evidence at present that titanium(IV) can form the type of polyions apparently exhibited by zirconium^{9,10} without proceeding on to the formation of colloidal particles with the hydroxide ultimately precipitating.

(9) J. S. Johnson and K. A. Kraus, J. Amer. Chem. Soc., 78, 3937(1956).

(10) R. L. Angstadt and S. Y. Tyree, Jr., J. Inorg. Nucl. Chem., 24, 913(1962).