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DATE - March 30, 1962

PREPARATION AND PROPERTIES OF HIGH CONCENTRATION SOLS
PART IV: THORIUM HYDROXIDE SOLS

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Translated by C. E. Schilling

TRANSLATOR'S NOTE

This paper was probably originally written in English, then translated into German for publication in Kolloid-Zeitschrift. In the course of the present re-translation into English it was felt that under the circumstances a few translator's notes might help clarify a few outright errors, though in a few places it was necessary to resort to quite a literal translation in order to preserve what appeared to have been an unclear statement of the facts in the original (or possibly the German) version.

Thanks are due Drs. K. A. Kraus and M. H. Lietzke for help in checking the unclear sections mentioned above. Credit is also due Mr. K. H. McCorkle for his help in proofreading.

Translation of article from Kolloid-Zeitschrift Band 71 Heft 2 (1935), pp. 172-176.

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PREPARATION AND PROPERTIES OF HIGH CONCENTRATION SOLS, PART IV: THORIUM HYDROXIDE SOLS

by

N.R. Dhar and R. M. Mittra (Allahabad, India)[1]

Translated by C. E. Schilling

In previous work[2] we studied the preparation methods and the properties of highly concentrated sols of aluminum, iron, chromium, and zirconium hydroxide, of vanadium-pentoxide as well as silicic and molybdic acid. The concentration of the individual sols reached a value for iron oxide, Fe_2O_3, of 81 grams/liter; for alumina, Al_2O_3, 53.6 grams/liter; for Cr_2O_3, 127 grams/liter; and for ZrO_2, 100.2 grams/liter. These concentrated sols were exceptionally viscous.

In the current publication we present our results on the preparation and properties of high concentration thorium hydroxide sols.

Preparation of the Sols

Freshly precipitated, thoroughly washed thorium hydroxide $Th(OH)_4$ was peptized with small quantities of thorium nitrate $Th(NO_3)_4$. The resulting sol was then concentrated by heating directly over a flame. The sol at first was colorless, then turned increasingly more whitish as it concentrated. The color of the concentrated sol was red in thin layers and yellowish in thick layers, by transmitted light, and bluish white by reflected light. As a means of purification the sol was hot dialyzed. After a 20-hr hot dialysis the sol contained 192.04 grams ThO_2/liter of sol (0.729 molar) and 36.3 grams nitrate/liter of sol (0.585 molar). Thus the degree of purity of the sol = ThO_2/NO_3 = 1.24 moles/mole (Sol 1). After a 60-hr hot dialysis the sol contained 428.28 grams/liter of sol (1.62 molar) ThO_2 and 35.7 grams/liter of sol (0.576 molar) nitrate and its purity ratio was 2.81 (Sol 2). This sol appeared to be whitish and turbid and its blue cast was less noticeable than that of Sol 1. Upon dialysis for 100 hrs in hot water the sol contained 215.52 grams (0.924 mols) ThO_2 and 2.84 grams (0.0456 mols) of nitrate per liter and thus had a purity ratio equal to 20.26 (Sol 3).

A fresh sample of the sol was hot dialyzed for 140 hr until no nitrate was detectable in the dialysis wash water. The concentration of this sol was 240.85 grams (1.038 mols) of ThO_2 and 1.491 grams (0.024 mols) of nitrate per liter and its purity

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[1] Original translated into German by R. Riedel (Leipzig).

[2] R. N. Mittra and N. R. Dhar, J. Indian. chem. Soc. 9, 315 (1932); C. Ahobalacharya and N. R. Dhar, loc. cit. 9, 441 (1932); R. D. Sharma and N. R. Dhar, loc. cit. 9, 455 (1932).

ratio was 43.25 (Sol 4). This sol showed no tendency toward blue cast. All of these sols were too viscous to permit study of their properties. For this reason they were diluted before making viscosity determinations and coagulation studies.

Coagulation

The following results of coagulation tests were obtained for these 4 test sols:

Table 1

Sol 1 diluted to 7.68 g ThO_2/liter; five cc's of sol per test; 10 cc total volume; and waiting period 1 hr.

Electrolyte	Molar Flocculation-Concentration	Conc. of ThO_2 in grams/liter of Sol
$KBrO_3$	0.0531	7.68
	0.0562	3.84
	0.0612	1.92
HIO_3	0.00475	7.68
	0.00325	3.84
KIO_3	0.00625	7.68
	0.00325	3.84
K_2SO_4	0.00105	7.68
	0.00062	3.84

This sol,* because of the influence of the $Th(NO_3)_4$, was so stable that it could only be coagulated by a saturated solution of KCl.

Coagulation Using a Mixture of $KBrO_3$ and K_2SO_4

1/8 Molar $KBrO_3$ in cc's	1/200 Molar K_2SO_4, Measured, for Complete Coagulation, cc's	Calculated, for Complete Coagulation, cc's
0	2.1	--
4.25	0	--
0.5	1.85	1.85
1.0	1.65	1.60
2.0	1.25	1.11

*Sol 1.

Table 2

Sol No. 2 diluted to 7.68 grams of thoria per liter

Electrolyte	Molar Flocculation-Concentration	Concentration of ThO_2 in grams/liter of Sol
KCl	0.29	7.68
	0.27	3.84
	0.25	1.92
$KBrO_3$	0.024	7.68
	0.021	3.84
	0.019	1.92
KIO_3	0.0017	7.68
HIO_3	0.0026	7.68
K_2SO_4	0.00044	7.68

Coagulation Using a Mixture of $KBrO_3$ and K_2SO_4

1/8 Molar $KBrO_3$ in cc's	1/200 Molar K_2SO_4, Measured, for Complete Coagulation, cc's	Calculated, for Complete Coagulation, cc's
0	0.875	---
1.90	0	---
0.25	0.775	0.759
0.50	0.675	0.644
1.00	0.420	0.414

Table 3

Sol No. 3 diluted to 11.52 g ThO_2/liter

Electrolyte	Molar Flocculation-Concentration	Concentration of ThO_2 in grams/liter of Sol
KCl	0.054	11.52
	0.046	5.76
	0.038	2.88
$KBrO_3$	0.0125	11.52
	0.0115	5.76
	0.0105	2.88
KIO_3	0.0013	11.52
HIO_3*	0.0029	11.52
K_2SO_4	0.00036	11.52

Coagulation Using a Mixture of $KBrO_3$ and K_2SO_4

1/20 Molar $KBrO_3$ in cc's	1/800 Molar K_2SO_4, Measured, for Complete Coagulation, cc's	Calculated, for Complete Coagulation, cc's
2.5	---	---
0	2.90	---
0.5	2.32	2.20
1.0	1.74	1.70
1.5	1.16	1.05

*Translator's note: "KIO_3" in the original article assumed to be a typographical error.

Table 4

Sol No. 4 diluted to 11.94 g ThO_2/liter

Electrolyte	Molar Flocculation-Concentration	Concentration of ThO_2 in grams/liter of Sol
KCl	0.038	11.94
	0.034	5.97
	0.030	2.985
$KBrO_3$	0.011	11.94
KIO_3	0.00125	11.94
HIO_3	0.004	11.94
$Th(NO_3)_4$	0.37	11.94
	0.37	5.97
HNO_3	0.460	11.94
	0.460	5.97
K_2SO_4	0.00026	11.94

Coagulation with a Mixture of $KBrO_3$ and K_2SO_4

1/20 Molar $KBrO_3$ in cc's	1/800 Molar K_2SO_4 Measured, for Complete Coagulation, cc's	Calculated, for Complete Coagulation, cc's
0	2.05	---
2.1	0	---
0.5	1.55	1.56
1.0	1.05	1.074

Sol 4 was very pure and for this reason was not as stable to electrolytes as were the other three sols. The following results show that it became very stable by addition of $Th(NO_3)_4$.

Table 5

20 cc's of 1/4 normal** $Th(NO_3)_4$ was added to 80 cc's of the sol to give a concentration of 9.55 g ThO_2/liter

Concentration of the Sol in g ThO_2/liter	Concentration of KCl in moles/liter
9.550	0.6878
4.775	0.7964

** Molar

From the foregoing experimental results the following conclusions can be drawn.

(a) When impure thorium hydroxide contains a large fraction of thorium nitrate it becomes more stable to coagulation by monovalent ions upon dilution. This behavior is due to the influence of stabilizing ions becoming more effective in dilute than in concentrated sols has already been shown in several publications from this laboratory.[3] This behavior shows up particularly in Table 5. In the presence of $Th(NO_3)_4$ a higher concentration of KCl is necessary to produce coagulation in dilute sols than in concentrated sols.

(b) The coagulation of both pure and impure sols shows an additive effect, if coagulated by a mixture of $KBrO_3$ and K_2SO_4, since thorium hydroxide sols show very little tendency to adsorb ions of its same charge from either of the coagulating electrolytes.

It is of interest to note that reasonably pure thorium hydroxide sols (purity ratio in the range 2.81 to 43.25) obey our dilution rule. According to this rule, without consideration of the valence of the flocculating ions, the greater the concentration of the sol, the higher the amount of coagulating electrolytes necessary to produce coagulation. Furthermore, our views have been stated in many publications to the effect that in general, high purity sols can be classified into two categories, which depend on their capacity to adsorb ions of the same charge when coagulated by electrolytes such as KCl, LiCl, $BaCl_2$, K_2SO_4, etc.

Several years ago B. N. Desai[4] studied the coagulation of thorium hydroxide sols of different purity ratios, and he also reported an abnormal behavior of impure sols upon dilution. It is clear, from the foregoing, that Desai's conclusion that the sols cannot be classified into two categories is untenable.

[3] S. Ghosh and N. R. Dhar, J. physic. Chem. 29, 435, 659 (1925); 31, 187, 649 (1927); Kolloid-Z. 37, 141 (1926); 43, 389 (1927).

[4] Kolloid-Beih. 26, 351 (1928).

In an earlier publication[5] it was shown that when the flocculation concentrations of mono, di, tri------x valent ions are N_1, N_2, N_3------N_X, then N_1, N_2, N_3------N_X behave like $1 : \frac{1}{2}\beta^{*} : \frac{1}{3}\beta^{2} : \text{------} \frac{1}{X}\beta^{X-1}$, where $\beta = e^{\frac{-qe/Dr}{kT}}$.

Here $0 < \beta < 1$ and β is a pure number, q is the charge on the colloid, D the dielectric constant of the medium, r is the thickness of the double layer, k the Boltzmann constant, and T the absolute temperature. From the relation stated above it follows that β gradually approaches unity as either q decreases or T increases.

Stated in another way this means that the flocculation concentrations of mono, di, and trivalent ions gradually approach the relation $1 : \frac{1}{2} : \frac{1}{3}$ as the charge on the colloid decreases. In real practice, the foregoing relation cannot be realized since the sol is likely to coagulate when the charge becomes zero. We should, however, determine that the ratio of the flocculation concentration of the ions of different valence does decrease as the charge on the colloid decreases. It was found that this relationship is applicable to different hydroxides of variable purity ratios. The following results show that the higher the purity ratio is for thoria sols, the smaller is the ratio of flocculation concentration for different ions:

Table 6

Purity	KCl/K_2SO_4	KCl/KIO_3	KCl/HIO_3
2.81	659	170.6	111.5
20.26	150	41.5	18.6
43.25	146	30.4	9.5

From the above results one can conclude that potassium iodate and iodic acid possess a much stronger coagulating influence than potassium chloride. These results agree with the emphatically stated opinion of Dhar[6] that iodic acid and iodates tend to polymerize and contain in solution the bivalent ion $(I_2O_6)^{=}$, and for this reason the iodate ions have the flocculation power approaching that of sulfate ions.

The fact that iodates undergo gradual polymerization was confirmed by the following determinations of molar conductivities of KCl and KIO_3 at 20°C:

[5] M. N. Chakravarti, S. Ghosh and N. R. Dhar, J. physic. Chem. 34, 330 (1930).

[6] N. R. Dhar, J. Indian chem. Soc. 5, 58 (1928).

* β used in place of italic "a" here for sake of clarity.

Dilution	4	8	16	32	64	128	256	512	1024
Molar conductivity of KCl	105.6	109.4	111.0	113.0	114.6	115.6	117.4	118.1	119.0
Molar conductivity of KIO_3	72.8	77.8	81.75	84.9	87.4	88.7	89.6	90.2	90.3

All other conditions being equal, these results show that the percentage increase in molar conductivity for KIO_3 upon dilution is larger than for KCl. It is known that the molar conductivity of an alkali salt of a dibasic acid exhibits a greater change on dilution than does an alkali salt of a true monobasic acid.

Viscosity

Ostwald, Smoluchowski, Kruyt, and others have expressed the opinion that an incremental change in charge on a sol produces a corresponding incremental change in its viscosity. Dhar and co-workers[7], however, have at hand experimental results for no less than 30 sols which show that the opinions of the above authors do not seem to prove correct. Dhar concluded that if all other factors remain constant, a decrease in charge on the colloidal particles causes an increase in hydration and pronounced increase in viscosity of the sol. Viscosity measurements made on dialyzed and undialyzed sols of the same concentration such as iron, aluminum, chromium, and zirconium hydroxides show that the viscosities of sols of low charge are remarkably high, compared with sols of high electrical charge. Exactly the same results were obtained for thorium hydroxide sols. The lower the purity, and more stable the sol, the lower the viscosity. This is indicated by the following results:

Table 7. Sol I

Content: 192.04 g ThO_2/liter

Purity ratio: 1.24

Concentration of Sol, g ThO_2/liter	Viscosity at 20°C H_2O = 1	Density at 20°C
192.04	3.5	1.2
96.02	1.69	1.1
48.01	1.20	1.05
24.005	1.086	1.02
12.002	1.04	1.02

After 3 months' aging period the viscosity of the sol rose from 3.5 to 8.2.

[7] N. R. Dhar, Z. Elektrochem. 31, 261 (1925); N. R. Dhar, D. N. Chakravarti and M. N. Chakravarti, Kolloid-Z. 44, 225 (1928); N. R. Dhar and S. Ghosh, loc. cit. 48, 43 (1929); N. R. Dhar and V. Gose, J. Indian chem. Soc. 6, 31, 641 (1929).

Table 8. Sol 2

Content: 428.28 g ThO_2/liter

Purity ratio: 2.81

Concentration of Sol g ThO_2/liter	Viscosity at 20°C H_2O = 1	Density at 20°C
428.28	4.63	1.42
214.14	1.998	1.20
107.07	1.365	1.10
53.53	1.14	1.05
26.76	1.05	1.01

After 3 months' aging the viscosity of the sol was 4.76 and upon addition of 0.1 cc of 1/2 M $Th(NO_3)_4$ solution to 7 cc of this sol the viscosity dropped to 3.08.

Table 9. Sol 3

Content: 215.52 g ThO_2/liter

Purity ratio: 20.26

Concentration of Sol g ThO_2/liter	Viscosity at 20°C H_2O = 1	Density at 20°C
215.52	258	1.20
107.76	11	1.10
71.08	5.63	1.07
53.88	3.4	1.05
26.94	1.83	1.02
13.47	1.32	1.01

After a two-months' aging this sol contained 71.08 g ThO_2/liter and had a viscosity of 6.73 which was 5.63 before aging. Upon mixing this sol with 0.5 cc of 1/2 M $Th(NO_3)_4$ the viscosity dropped to 2.63.

Table 10. Sol 4

Content: 240.85 g ThO_2/liter

Purity ratio: 43.25

This sol was too viscous to permit viscosity determinations to be run; for this reason it was diluted prior to making measurements.

Concentration of Sol, g ThO_2/liter	Viscosity at 20°C $H_2O = 1$	Density at 20°C
202.7	1268.5	1.18
140.2	126.1	1.15
101.35	31.62	1.1
50.67	4.4	1.05
25.35	1.99	1.025
12.66	1.407	1.014

The log of the viscosity plotted against the concentration produced a straight line. When this was extrapolated back to the original concentration the enormous value of 5250 was obtained for the viscosity. After one month's aging of the sol containing 140.2 g ThO_2/liter, the viscosity increased from 126.1 to 843.6. On addition of 0.1 cc of 1/2 M $Th(NO_3)_4$ to 7 cc of this sol, with shaking, the viscosity dropped to 65.

The foregoing results show that enormous increases in viscosity accompany increases in purity, even though the concentration of the sols were not very different from one another. Furthermore, the viscosities of these sols were very much diminished upon addition of the peptizing electrolyte, $Th(NO_3)_4$, which increased the charge and stability of the sols. These conclusive results prove that the greater the purity of the sol and the lower the charge on the particles is, the higher will be its viscosity.

From the above results it follows clearly that the viscosity-concentration curve for a thorium hydroxide sol of high concentration is steep, and that in the case of pure sols these curves run even steeper. Consequently, from the viewpoint of viscosity it appears that concentrated sols of thorium hydroxide behave as typical lyophilic colloids, just as was the case with other hydroxide sols investigated in this laboratory.

Aging

Periodic measurements of viscosity showed that concentrated thorium hydroxide sols became more viscous with age. This property has also been observed in cases of

other concentrated sols. On the other hand, if the sols are diluted, the viscosity can decrease with aging. This peculiarity is based on the fact that two opposing factors in the aging process are at work simultaneously. One is the slow decrease in the charge on the sol, which is caused by the decrease in adsorbing power of the particles. The decrease in electrical charge leads to an increase in viscosity. The second factor operates in an opposite manner. Since it depends on the decrease in particle adsorption tendency, the degree of hydration decreases as a result. This second factor leads to a decrease in sol viscosity. In concentrated sols the first factor appears to dominate the second, and for this reason the viscosity of concentrated sols increases with aging time. Conversely, the second factor dominates over the first in the case of dilute sols and the viscosity can decrease with aging.

The electrical conductivity of these concentrated sols increases upon aging, since a portion of the adsorbed electrolytes is set free upon aging as is shown by the results in Table 11.

Table 11

Sol Number	Conductivity x 10^{-2}	
	Fresh Sol	Aged Sol
1	2.4740	2.4820
2	0.2426	0.2519
3	0.1046	0.1087

Conclusions

1. The peptization of freshly precipitated thorium hydroxide sols with small quantities of thorium nitrate followed by hot dialysis produced highly concentrated sols of the following concentrations and purity ratios:

192.04 g ThO_2/liter (purity ratio: 1.24)
428.28 g ThO_2/liter (purity ratio: 2.81)
215.52 g ThO_2/liter (purity ratio: 20.26)
240.85 g ThO_2/liter (purity ratio: 43.25)

2. The first sol, which was very impure, did not obey the dilution law, which leads to the conclusion that the higher the concentration a sol has, the higher is the quantity of electrolyte necessary to produce coagulation when treated with $KBrO_3$. This sol does not obey the dilution law on account of the presence of a detectable quantity of $Th(NO_3)_4$. The other three sols obey the dilution law. All four sols showed an additive effect when they were coagulated by a mixture of $KBrO_3$ and K_2SO_4.

The coagulating power of potassium iodate and iodic acid is much greater than that of potassium chloride. From this it was concluded that solutions of potassium iodate and iodic acid contain the bivalent ion $(I_2O_6)^{=}$.

3. The viscosity of the pure sols is extraordinarily high and the viscosity-concentration curve is exceptionally steep. If the peptizing electrolyte $Th(NO_3)_4$ is added to these pure sols, a sharp decline in viscosity results. The viscosity of aged sols is greater than that of freshly prepared sols. These results convincingly prove that the viscosity is higher the greater sol purity ratio, and the lower the charge on the particle.

4. The electrical conductivity of thorium hydroxide sols at high concentration increases upon aging.

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