[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Hydrous Thoria Hydrosols Considered as Polynuclear Basic Thorium Complexes

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The purpose of this paper is to submit evidence in support of the view that hydrous thoria hydrosols (more accurately, thorium oxychloride or basic thorium chloride hydrosols) may be regarded as polyolated and/or oxolated complexes, differing from thorium chloride crystalloidal solutions of low basicity in degree rather than in kind. This chemical point of view of the so-called metallic oxide hydrosols has been previously proposed for aluminum[1] and chromium oxysalt hydrosols.[2] In the present investigation, twelve basic thorium chloride hydrosols were studied, the results obtained with three of them ("C," "E," "F") being submitted here as typical.

Preparation and Description of Hydrosols.—Hydrosol "C" was prepared as follows. Portions of 3 N ammonium hydroxide (redistilled) were added to an aqueous solution of pure thorium chloride at room temperature with mechanical stirring. The addition of ammonium hydroxide was continued until the liquid became decidedly turbid, whereupon the stirring was continued for twenty-four hours. Then the liquid was dialyzed at room temperature against a highly permeable nitrocellulose membrane for five days using running distilled water.

Hydrosols "E" and "F" were prepared by the action of hydrochloric acid ("E") and of thorium chloride ("F") upon hydrous thoria at room temperature as follows. Hydrous thoria was precipitated from a thorium chloride solution by addition of ammonium hydroxide. Centrifugal washings and decantations were then applied until chloride ion had been removed. The hydrous oxide was then suspended in a small amount of distilled water and the desired amount of hydrochloric acid or thorium chloride dissolved in about 1500 cc. of water, was slowly added accompanied by vigorous stirring. After standing for twenty-four hours, the systems were dialyzed for six days as described above.

In all cases, at the conclusion of dialysis the hydrosols were centrifuged for one hour (1200 r. p. m., 42 cm. radius) and the supernatant liquid was siphoned into water-resistant glass bottles.

These three hydrosols which were turbid in appearance are described quantitatively in Table I. The micelles were positively charged.

TABLE I

COMPOSITION OF HYDROSOLS

Sol	Thorium milliequiv. per liter	Chloride milliequiv. per liter	Eq. Th/Eq. Cl	pH[a]
C	81.3	12.4	6.6	3.95
E	63.9	5.7	11	3.97
F	100.9	13.1	8	4.16

[a] The pH values are those measured immediately at the completion of dialysis.

Action of Neutral Salts.—The hydrosols were titrated with various potassium salts in the following manner. To 10-cc. portions of hydrosol in 30 cc. volume glass-stoppered bottles were added 10 cc. portions of salt solution. The bottles were rotated (7 r. p. m.) for 12 ± 3 hours at 25 ± 0.2° and the pH values were then measured. The quinhydrone electrode was used in cases where the pH value was below 8, the platinized-platinum hydrogen gas electrode being employed for systems with pH values near to or greater than 8.

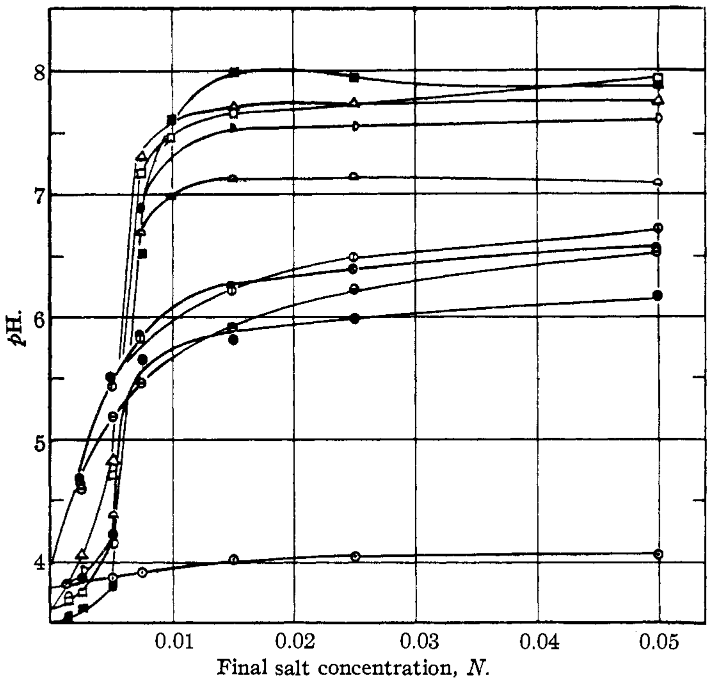

Fig. 1.—Effect of potassium salts on the pH value of Sol C: ⦶, acetate; ⊙, chloride (also nitrate); ■, citrate; ⊖, formate; △, malate; ⌓, malonate; □, oxalate; ⊗, propionate; ●, sulfate; ◗, tartrate.

In the case of the hydrogen electrode, the mixture was filtered to remove precipitate when oxalate was the added salt. No other salt caused precipitation when the pH value exceeded 8.

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[1] (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, THIS JOURNAL, **54**, 841 (1932); (c) T. H. Whitehead and J. P. Clay, *ibid.*, **56**, 1844 (1934); (d) A. W. Thomas and R. D. Vartanian, *ibid.*, **57**, 4 (1935).

[2] A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934).

The *p*H values of the 0.1 *N* potassium salt solutions were adjusted to *p*H = 6.4 ± 0.3[3] by the addition of potassium hydroxide in the case of the chloride, nitrate and sulfate and by addition of the proper 0.1 *N* acid to the other solutions. These values are given in Table II.

TABLE II

*p*H VALUES OF 0.1 *N* POTASSIUM SALT SOLUTIONS

Acetate	6.6	Nitrate	6.3
Chloride	6.2	Oxalate	6.4
Citrate	6.8	Propionate	6.4
Formate	6.4	Succinate	6.4
Malate	6.3	Sulfate	6.3
Malonate	6.4	Tartrate	6.5

The reaction time of twelve hours was well beyond that required for a "practical equilibrium" to be established.

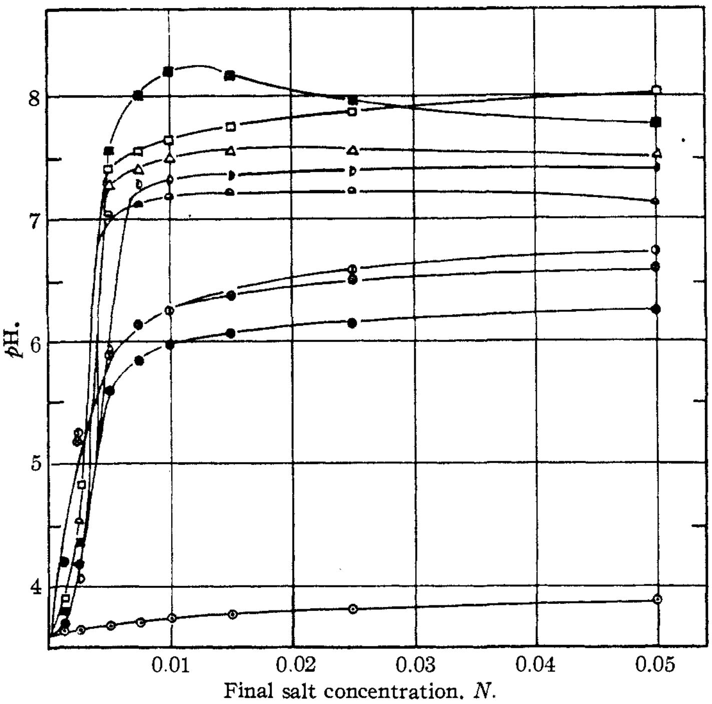

Fig. 2.—Effect of potassium salts on the *p*H value of Sol E: ⦶, acetate; ⊙, chloride (also nitrate); ■, citrate; △, malate; ⌓, malonate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

The results of the *p*H-salt titrations are shown in Figs. 1, 2 and 3.[4] It is seen that the *p*H raising order is in general: citrate > oxalate > malate > tartrate > malonate > succinate > acetate > propionate > formate > sulfate > chloride = nitrate. This series is similar to those obtained with basic aluminum[1] and chromic[2] salt hydrosols in so far as the above salts were studied with the latter named sols.

As pointed out in previous publications from this Laboratory, these increases in *p*H values are ascribed to the displacement of the coördinatively bound hydroxo (and possibly ol) groups from the thorium atom by the anions of the added salt. Salts producing a marked increase in *p*H value contain anions which have a stronger coördinative binding tendency than those producing smaller *p*H increases. This occurs whether the central metallic atom is part of a colloidal micelle or is a simple crystalloid ion.

Aquo and chlorido groups should likewise be displaced by the added anions. That the latter takes place is evidenced by increased chloride ion activity caused by the addition of salts to other oxide hydrosols.[5] The displacement of aquo groups by the added anions should lead to reversal of the sign of charge of the micelles. In certain instances this happens and the subject will be discussed in a subsequent paper.

Effect of Age.—Basic thorium chloride hydrosols stored at room temperature rapidly become more acid in reaction (to about *p*H 3) as shown in Fig. 4. This may be accounted for by three mechanisms: (1) aquo groups are converted to hydroxo groups and free hydrogen ion, (2) olation removing a product of reaction (1) favors (1) and, (3) oxolation of ol groups liberates hydrogen ion. At room temperature (3) would not be expected to proceed to any great extent. All of these reactions are favored by rise in temperature. Portions of the hydrosols which were boiled in a ground glass joined Pyrex glass reflux apparatus decreased in *p*H to the range of 2.1–2.5 depending upon the concentration of the sol. A typical example of the rate of change is shown in Fig. 5. When these heated sols were allowed to stand at room temperature, partial reversal of the reactions was noted as shown in Fig. 4. Conflicting statements are found in the literature concerning

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(3) With the exception of citrate where the *p*H value was adjusted only to 6.80.

(4) Basic thorium chloride hydrosols "age" rapidly, *i. e.*, they olate and/or oxolate rapidly at room temperature. For example, when dialysis of sol "E" was concluded it had a *p*H value of 3.97; three days later its *p*H value was 3.65 and in five days it was 3.45. This behavior accounts for the *p*H values at zero salt concentration not being identical inasmuch as one could not perform all the salt titrations in one day. The decrease in *p*H on "aging" is, of course, reflected also in the *p*H values attained upon addition of neutral salts.

(5) (a) H. B. Weiser, *J. Phys. Chem.*, **35**, 1, 1368 (1931); (b) S. Roychoudhury, A. Sen and A. Chatterjee, *J. Indian Chem. Soc.*, **11**, 23 (1934).

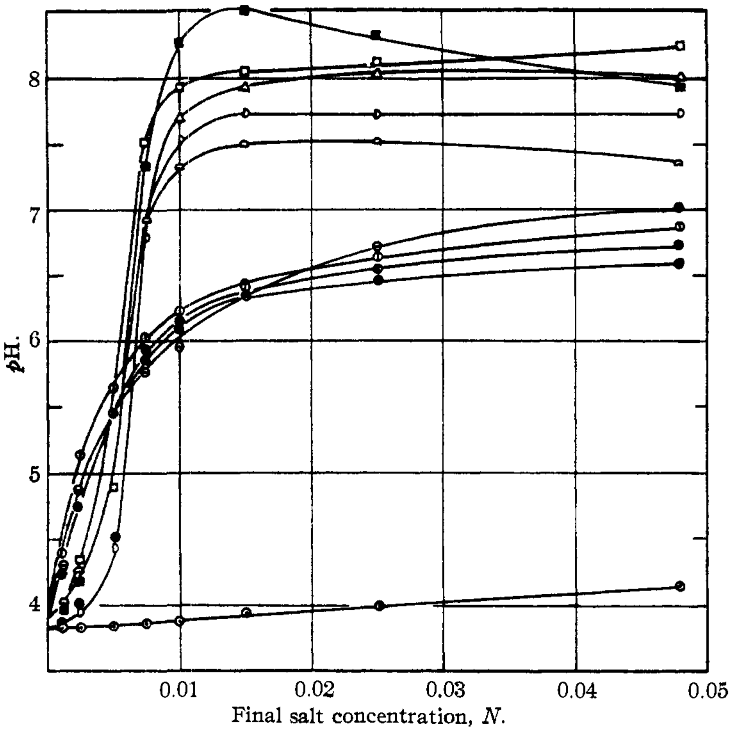

Fig. 3.—Effect of potassium salts on the pH value of Sol F: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; △, malate; ⌓, malonate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

pH changes in "oxide" hydrosols. That the pH may increase or decrease is explained by the present theory. A metallic "oxide" hydrosol which has been boiled, or which has not been sufficiently dialyzed, becomes less acid on standing due to hydrogen ion reacting with OH groups in the complex and also to partial deolation. A well dialyzed sol, on the other hand, becomes more acid upon aging due to conversion of aquo to hydroxo groups, to olation and to oxolation.

The conversion of hydroxo to ol groups should render a sol less responsive to the pH increasing action of added neutral salts since one would suspect ol groups to be more firmly held by the thorium atoms than hydroxo groups. Oxo groups would, of course, be unaffected by neutral salt additions.

The effect of previous heating on the pH raising effect of neutral salt additions is shown in Fig. 6. This behavior is the same as that noted in the case of basic aluminum[1b] and basic chromium[2] salt hydrosols.

Conductance Titrations.—Conductivity titrations of basic aluminum and basic chromium salt hydrosols with silver salts have revealed that the drop in conductivity is the greater, the stronger the tendency is for the anion to become coördinatively bound to the central metallic atom.[1b,2] Employing a technique essentially the same as that previously described, the data plotted in Fig. 7 were obtained.[6] The relatively effective coördinative binding ions, sulfate and acetate, produce steep drops in the conductivity. To be sure, part of the conductivity drop is due to combination between the chloride ions in the sol and the added silver ions, but the steep drop cannot be attributed entirely to this reaction, as previously stated.

The coördinative binding of the anion results in its being without effect upon the conductivity of the system and, further, if it is bound by replacement of aquo groups, it thereby lowers the positive charge upon the micelle and thus another conductivity lowering factor enters the picture. Silver nitrate produced a slight fall in conductivity in the case of sol "C" while in sol "F" it produced a slight increase in conductivity. Thus nitrate, known in general as a weak coördinative binding ion and in particular as regards thorium,

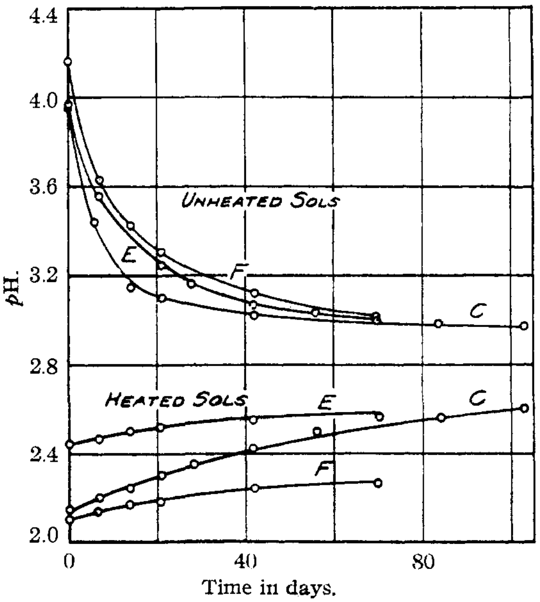

Fig. 4.—Change in the pH values of unheated and of boiled sols upon standing at room temperature.

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(6) The abscissas represent milliequivalents of solid silver salt added to 50 cc. of hydrosol.

shows some coördinative tendency in the case of sol "C" but not with sol "F."

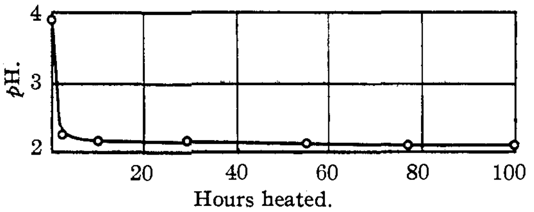

Fig. 5.—Change in pH value produced by boiling sol F.

Inasmuch as sols "C" and "F" had approximately the same ratio of Th:Cl, then the difference might be ascribed to the fact that they were prepared by different methods, inasmuch as one would hardly expect the 25% difference in concentration between the two sols to produce the divergence in nitrate penetration.

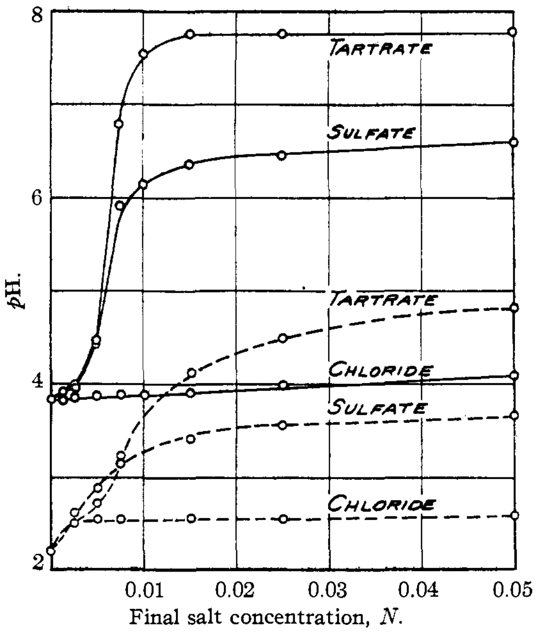

Fig. 6.—Effect of potassium salts on the pH value of sol F before and after boiling: ——— unheated sol; - - - - - boiled sol.

Summary

The pH values of basic thorium chloride (so-called "thorium oxide") hydrosols are raised by the addition of potassium salts. The order of effectiveness in general, similar to that found with certain other "oxide" hydrosols, is: citrate > oxalate > malate > tartrate > malonate > succinate > acetate > propionate > formate > sulfate > chloride = nitrate, the first named markedly increasing the pH value while the last named exerted very slight effect. The effect is ascribed to displacement of coördinatively bound OH groups by the anion of the added salt, the anion then becoming coördinatively bound. Dialyzed basic thorium chloride hydrosols rapidly become more acid on standing at room temperature; the rate increases upon heating and the reactions producing this effect show partial (or extremely slow) reversal. Heated basic thorium chloride hydrosols are less responsive to the pH increasing effect of added neutral salts. The interpretation of these behaviors can be made on the assumption of a polyolated and/or oxolated structure of the micelle, an extension to colloidal dispersions of the postulates which Werner and Pfeiffer applied to crystalloid basic salts.

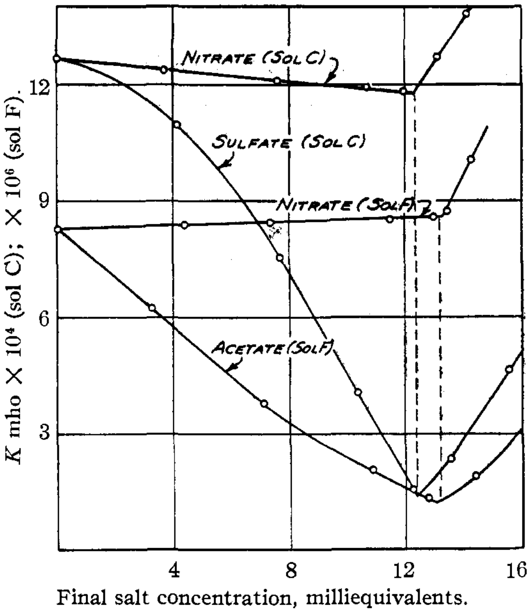

Fig. 7.—Effect of silver salts upon the specific conductivities of sols C and F.

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