

less soluble. Therefore, it is possible to conclude that the lower solubility of sample 6 is due to the lower free energy state of the well crystallized sample and that the larger surface area does not cause a substantial increase in solubility.

Yates²⁸ has recently pointed out that colloidal

(28) P. C. Yates, paper presented in symposium "Colloidal Silica and Silicates" at 137th National Meeting of the American Chemical Society, Cleveland, April 13, 14, 1960.

silicate-water systems may be thermodynamically stable because of adsorption of ions which materially lowers the surface free energy.

Acknowledgments.—The authors wish to thank Drs. H. H. Steinour and S. Brunauer for their many helpful discussions and suggestions. Thanks are also due to Dr. D. L. Kantro who kindly provided the water adsorption surface area measurements.

DETECTION OF METAL ION HYDROLYSIS BY COAGULATION: II. THORIUM^{1,2}

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Coagulation and stabilization concentrations for aqueous thorium nitrate solutions were obtained as a function of pH using silver iodide, silver bromide and silver chloride sols *in statu nascendi*. At pH < 4 the coagulation concentration shows a constant value corresponding to a four-valent species, Th⁴⁺ or Th(H₂O)_z⁴⁺. With increasing pH the coagulation concentration increases and levels off at a value characteristic for trivalent counterions. It is believed, therefore, that the initial hydrolysis step of Th⁴⁺ consists in formation of [Th(H₂O)_{z-1}OH]³⁺ species. At still higher pH's the coagulation concentrations again become much lower indicating high valent species, possibly a dimer [Th(H₂O)_{z-1}OH]₂⁶⁺. Reversal of charge is produced by the hydrolyzed Th-species, whereas the four-valent Th-ion does not reverse the charge. The problem of reversal of charge has been discussed and it is concluded that this effect is caused by OH-bridging of counterions.

Introduction

Hydrolysis of thorium ion already has been a subject of extensive investigations. However, owing to the complexity of the problem, unambiguous conclusions are difficult to make and therefore different authors have decided on different complex species as products of the hydrolysis process. Thus, Kraus and Holmberg⁵ believe that the main species in perchlorate medium are Th(OH)₂²⁺ and Th₂(OH)₆⁶⁺ whereas Hietanen^{6,7} using the "inert medium method" found evidence for polynuclear complexes of the type Th[(OH)₃Th]_n⁽⁴⁺ⁿ⁾⁺ and Hietanen and Sillén⁸ using the "self-medium method" claim the complexes are of Th₂(OH)₆⁶⁺ and Th₂OH⁷⁺ type. From Lefevbre's calculations⁹ it appears that the predominant complex species is Th₅(OH)₁₂⁸⁺ in addition to Th₇(OH)_z, Th₂(OH)₆⁶⁺ and Th(OH)₂²⁺. Faucherre and Schaal^{10,11} concluded that during the hydrolysis process a tetramer [Th₄O₄]⁸⁺ is formed. In an older work Chauvenet and Tonnet¹² and Chauvenet and Souteyrand-Franck¹³ proposed the species Th(OH)₂²⁺ and

ThO²⁺. Finally, Kasper's¹⁴ conclusion is that the main hydrolysis product is Th(OH)³⁺.

Obviously, more work is required in order to clarify the problem of the hydrolysis of Th⁴⁺. Especially desirable should be the introduction of new techniques that would give an independent clue as to the hydrolysis products.

In an earlier paper¹ we have shown that the coagulation technique can be successfully employed in investigating metal ion hydrolysis. It is well known that the electrolytic coagulation of lyophobic colloids is influenced in a very sensitive way by the charge of the counterion in solution. Thus, any change in counterion caused by its hydrolysis that gives rise to species of different charge will be reflected in the change of the critical coagulation concentration of the solution in question. From this change, the charge of predominant new species can be determined which in turn can lead to conclusions as to the hydrolytic processes taking place in such a solution. If data, obtained using the coagulation method, are combined or compared with results obtained employing other techniques, such as potentiometric titration, conductivity, freezing point depression, etc., more conclusive answers regarding the hydrolysis products can be expected. The coagulation technique has another great advantage when compared with other common methods since it utilizes solutions of extremely low concentrations, ranging from 10⁻⁴ to 10⁻⁷ mole/l. This eliminates the usual complications connected with the activity changes which appear at higher concentrations. Furthermore, since no addition of neutral salts are necessary in order to keep the activity coefficient constant, the hydrolysis products can-

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(2) Supported by the U. S. Atomic Energy Commission Contract No. AT(30-1)-1801.

(3) Participant in the NSF Summer Research Project, 1959.

(4) On leave of absence from Institute for Medical Research, Zagreb, Yugoslavia.

(5) K. A. Kraus and R. W. Holmberg, *THIS JOURNAL*, **58**, 325 (1954).

(6) S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

(7) S. Hietanen, *Rec. trav. chim.*, **75**, 711 (1956).

(8) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **13**, 533 (1959).

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(12) E. Chauvenet and J. Tonnet, *ibid.*, [4] **47**, 701 (1930).

(13) E. Chauvenet and Mme. Souteyrand-Franck, *ibid.*, [4] **47**, 1128 (1930).

(14) J. Kasper, Dissertation, The John Hopkins University, Baltimore, Maryland, 1941.

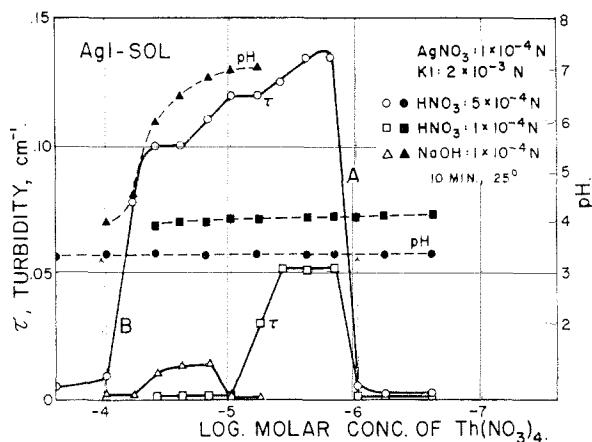


Fig. 1.—Coagulation curves of thorium nitrate for silver iodide sol *in statu nascendi*, 10 minutes after mixing the reacting components. Concentrations: AgNO_3 , $1 \times 10^{-4} \text{ N}$; KI , $2 \times 10^{-3} \text{ N}$; $\text{Th}(\text{NO}_3)_4$, varied; (○) HNO_3 , $5 \times 10^{-4} \text{ N}$, (□) HNO_3 , $1 \times 10^{-4} \text{ N}$, (Δ) NaOH , $1 \times 10^{-4} \text{ N}$. Full lines and open points represent turbidity measurements. A denotes the coagulation limit and B the stabilization limit. Dashed curves and blackened points give corresponding pH's.

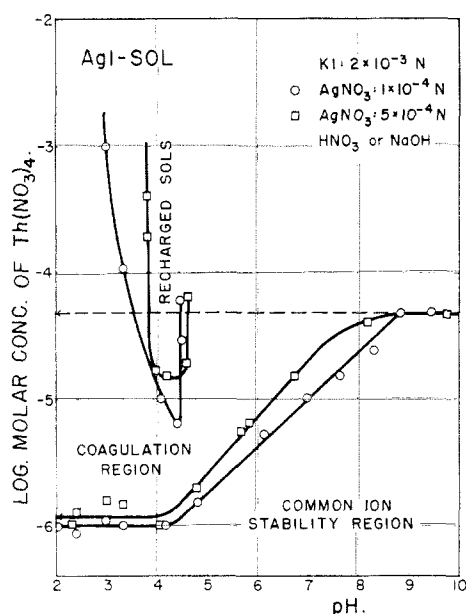


Fig. 2.—The plot of coagulation concentrations (lower curves) and stabilization concentrations (upper curves) against pH for thorium nitrate on silver iodide sol. Two different sol concentrations were employed: (○), $1 \times 10^{-4} \text{ mole/l.}$ and (□), $5 \times 10^{-4} \text{ mole/l.}$ AgI.

not be influenced by possible complexing with foreign ions.

We have used silver iodide, silver bromide and silver chloride sols *in statu nascendi* and coagulated them with solutions of thorium nitrate adding different amounts of nitric acid or caustic soda. The pH of these solutions was also measured. The plots of coagulation concentrations against pH revealed the changes in charges in ionic species in solutions.

Another aspect of this work is the general study of coagulation effects of thorium salt solutions on silver halide sols. Of particular interest was the determination of the correct coagulation concentra-

tion for the four-valent counterion, Th^{4+} , and the effect of pH on the reversal of charge of the sol particles. The very diversified coagulation phenomena caused by thorium ions on silver halide sols have been studied before.¹⁵⁻²¹ However, no systematic work on pH dependence of the coagulation and the reversal of charge has been done. Kruyt and Troelstra²¹ have investigated the influence of addition of HNO_3 and NaOH on coagulation effects of thorium nitrate solutions on silver iodide sols, but only presented the data in a schematic way and did not follow the appreciable pH changes which accompany the hydrolysis of the thorium ions. Our present work at low pH gives a precise coagulation concentration for Th^{4+} species for silver iodide, silver bromide and silver chloride sols *in statu nascendi* and, in addition, shows the correlation between the stability limit caused by the reversal of charge and pH in investigated sols. This has resulted in a better understanding of the reversal of charge phenomena.

Experimental

We have followed the coagulation of silver iodide, silver bromide and silver chloride *in statu nascendi* by mixing equal volumes (5 ml.) of silver nitrate solutions of constant concentration with solutions containing constant amounts of potassium halide component and varying amounts of thorium nitrate. The turbidity changes were measured by observing the light scattering at 45° in an Aminco light scattering microphotometer using the $546 \text{ m}\mu$ line. Nitric acid, when required, was added to the solution of halide and thorium components. However, when measurements were performed in the presence of NaOH , the silver nitrate and thorium nitrate solutions were mixed first, and the NaOH added to the halide solutions. This was done in order to prevent the formation of silver or thorium hydroxide due to the local supersaturations when the more concentrated stock solutions of NaOH were added. All measurements were performed at 25° . For a detailed description of the experimental technique and the method of analyzing the data in order to obtain the critical coagulation concentration we refer to our previous papers.^{22,23}

Half of the total amount of the prepared sol solution was used for turbidity measurements whereas the rest was utilized for pH measurements. A Beckman Model G pH meter was employed, the scale of which was calibrated with appropriate buffer solutions prior to taking pH readings.

All chemicals were of the highest purity grades further purified when necessary. Water was doubly distilled, the second time from an all-Pyrex still and regularly tested for pH and conductivity. All glassware was thoroughly cleaned and steamed before use.

Results

Three typical curves for coagulation of silver iodide sols by thorium nitrate solutions are given as an example in Fig. 1. The turbidities are taken from "time-turbidity" plots of each individual system 10 minutes after mixing the reacting components. This time has been found to be critical for

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- (17) J. Gillis and J. Eeckhout, *ibid.*, **19**, 49 (1937).
- (18) E. Matijević and B. Težak, *Arhiv kem.*, **22**, 62 (1950).
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- (21) H. R. Kruyt and S. A. Troelstra, *Kolloid-Beih.*, **54**, 262 (1943).
- (22) B. Težak, E. Matijević and K. Schulz, *This Journal*, **55**, 1557 (1951).
- (23) E. Matijević and M. Kerker, *ibid.*, **62**, 1400 (1958).

the coagulation of silver iodide sols.²² Two of the given curves represent systems to which HNO_3 (1×10^{-4} and 5×10^{-4} mole/l.) was added, whereas the third one was obtained in the presence of NaOH (1×10^{-4} mole/l.). In all cases the concentrations of AgNO_3 (1×10^{-4} mole/l.) and KI (2×10^{-3} mole/l.) were kept constant. In all curves two limits, the coagulation limit (A) and stabilization limit (B), appear, the latter being caused by the reversal of charge on the sol particles. The critical coagulation and stabilization concentrations are obtained by extrapolating the steepest part of limits A and B to zero turbidity. Corresponding pH 's are then read from pH curves at relevant concentrations, as indicated by arrows (for one curve) in Fig. 1. We have obtained such coagulation curves over a wide range of pH and plotted the coagulation and stabilization concentrations of $\text{Th}(\text{NO}_3)_4$ (expressed in moles/l.) against corresponding pH values.

Figure 2 gives such a plot for AgI -sol at two different sol concentrations. The lower curves represent the pH dependence of the coagulation limits and the upper curves that of the stabilization limits. The coagulation concentration of thorium ion increases from a lower limiting value at low pH 's to an upper limiting value at higher pH 's. Experiments could not be extended to even higher pH 's since the simultaneous formation of metal hydroxides would interfere with the coagulation of silver iodide. The reversal of charge effect is restricted to a rather narrow pH range for both sol concentrations being somewhat narrower for the sol of higher concentration.

The effects obtained with the silver bromide sol are represented in Fig. 3. The general picture is similar to that of silver iodide. The only significant difference is in the trend of the coagulation concentration *vs.* pH curve at higher pH 's, where, after leveling off between pH 7 and 8, the curve drops again to values even lower than those obtained at low pH . Also, the reversal of charge region appears to be wider than in the case of AgI sols.

Finally, Fig. 4 gives the same plot for the silver chloride sol. The trend of the coagulation concentration *vs.* pH curve is similar to that of silver bromide, and the reversal of charge region is even wider than for both the silver iodide and the silver bromide sols.

Discussion

A. On Hydrolyzed Species of Thorium from Coagulation Effects.—It is apparent from Figs. 2, 3 and 4 that for all three silver halide sols, the coagulation concentration of thorium nitrate solutions decreases to a constant value below pH 4. This concentration is 1×10^{-6} mole/l. for AgI , 6×10^{-7} mole/l. for AgBr and 3×10^{-7} mole/l. for AgCl sol. The quantitative expressions for the Schulze-Hardy rule give precisely this range of values for four-valent counterions.²⁴⁻²⁶ Thus, we

(24) B. Težak, E. Matijević and K. F. Schulz, *ibid.*, **59**, 769 (1955).

(25) E. Matijević, K. F. Schulz and B. Težak, *Croat. Chem. Acta*, **28**, 81 (1956).

(26) E. Matijević, D. Broadhurst and M. Kerker, *This Journal*, **63**, 1552 (1959).

(27) B. Težak, E. Matijević and K. Schulz, *ibid.*, **55**, 1567 (1951).

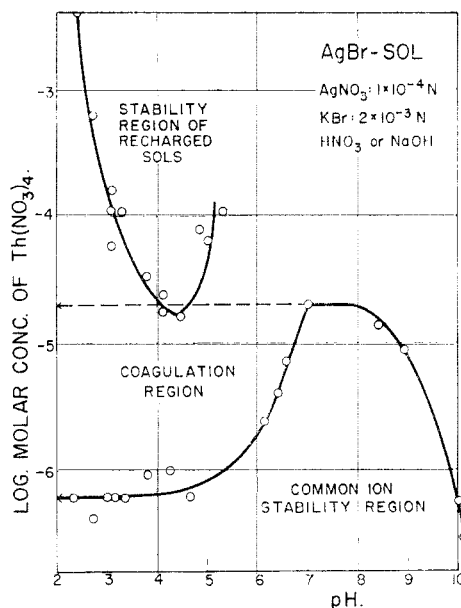


Fig. 3.—The same plot as in Fig. 2 for silver bromide sol: AgBr , 1×10^{-4} mole/l.

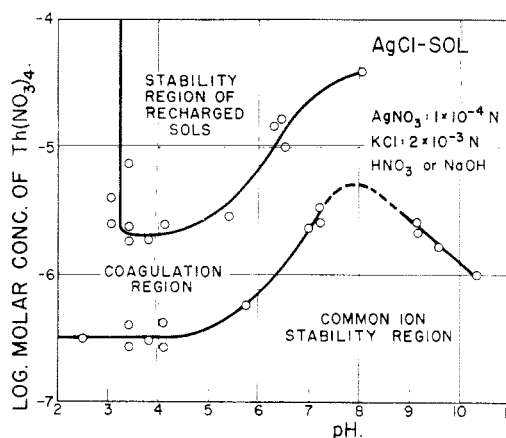
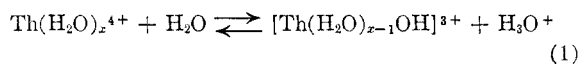


Fig. 4.—The same plot as in Fig. 2 for silver chloride sol: AgCl , 1×10^{-4} mole/l.

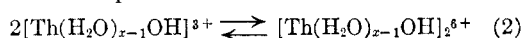
conclude that at low pH 's the four-valent thorium ion (Th^{4+} , or $\text{Th}(\text{H}_2\text{O})_x^{4+}$) is the predominant species in solution. This is in agreement with results obtained by Kraus and Holmberg.⁵ When pH becomes higher than 4 the coagulation concentration increases until at $\text{pH} \sim 7$, it levels off again at a much higher concentration of $\text{Th}(\text{NO}_3)_4$. This concentration is 5×10^{-5} mole/l. for AgI sol and 2×10^{-5} mole/l. for AgBr sol (for AgCl sol the value could not be determined unambiguously from Fig. 4). Again, calculations carried out before²⁴⁻²⁶ reveal that these concentrations correspond very well with critical coagulation concentrations of trivalent counterions. As a matter of fact, the experimentally obtained coagulation concentrations for La^{3+} and Al^{3+} under comparable conditions^{24, 25, 27} for AgBr and AgI sols are in a very good agreement with the above cited values. We should keep in mind that for comparison purposes the molarities of thorium nitrate solution have to be multiplied by 3 in this case, since coagulation concentrations are always expressed in normalities of counterions in

solution. It is, therefore, fair to assume that the thorium ion exists at $pH > 7$ in the form of trivalent hydrolyzed species. The simplest mechanism for such hydrolysis is given by the equilibrium equation



It appears, thus, that in *dilute* thorium salt solutions the initial major step in hydrolysis is the formation of the trivalent monohydroxy ion. This is very similar to what has been established for the hydrolysis of uranium(IV)^{28,29,32} and plutonium(IV) ions.^{28,30-32} Our findings are in agreement with conclusions drawn by Kasper.¹⁴ Kraus and Holmberg⁶ calculated a rather low equilibrium constant for reaction 1. Even so, they found that they had to take it into account at their *lower* concentrations of Th salt solutions in order to reconcile their experimental and calculated data. Since our working concentrations are still lower by 2 orders of magnitude it is reasonable that equilibrium 1 becomes predominant. In addition, we should also keep in mind that our results are obtained in aqueous solution in the presence of very small quantities of foreign ions, whereas Kraus and Holmberg worked in highly concentrated perchlorate solutions. The latter remark also refers to work by Hietanen^{6,7} as well as to that by Hietanen and Sillén⁸ which was performed at very high concentration of thorium ions (0.5 and 0.7 mole/l.).

Our results on silver bromide and silver chloride sol indicate that at our highest pH range a rather sharp drop in coagulation concentrations of thorium nitrate again takes place. Especially in the case of AgBr sol, the coagulation concentrations were even lower than those obtained for four-valent Th-ion, indicating an existence of species of charge higher than four. We could not pursue our investigations to still higher pH in order to obtain the lower limit of the coagulation curve which would give a definite answer as to the charge of counterions. However, the most probable next step in the hydrolysis equilibrium would be a dimerization of the trivalent species as



As a matter of fact, the existence of species $\text{Th}_2(\text{OH})_2^{6+}$ has been claimed by several investigators.^{5,8,9,12}

B. The Problem of Reversal of Charge.—From the colloid chemical point of view this work represents a contribution to two problems. Firstly, it gives the coagulation concentration of a four-valent counterion for three silver halide sols, which can be utilized for theoretical calculations.²⁶

In addition we have investigated systematically the dependence of the reversal of charge limit on several factors. It appears from Figs. 2, 3 and 4

that the higher the charge density of sol particles the smaller is the region of reversal of charge. Thus, the AgI-sol, which is known to be the strongest charged sol among three silver halides, shows a very narrow range where particles are of reversed charge. AgCl-sol, which shows the weakest charge has the widest range of reversed charged particles.

Another feature of our results is, that at lowest pH 's, where the counterion appears to have the highest charge, its ability to reverse the charge of sol particles completely disappears. Thus, the charge or valency of the counterion itself cannot be considered as solely responsible for the reversal of charge effect. This has been pointed out before by Krut and Troelstra,²¹ but they assumed that this effect was caused essentially by *insoluble* hydroxides. A similar conclusion was reached by Bosch and Haemers¹⁶ for coagulation of silver iodide by thorium nitrate. From our present experiments, it follows that *soluble* hydrolyzed thorium species cause the reversal of charge. Thus, the hydroxyl group in a counterion complex seems to be the main factor causing this effect. This is substantiated by adsorption experiments by Schulz and Herak,³³ who have shown that thorium species are strongly adsorbed on positive rather than on negative silver halide sols. There is more evidence available that the hydroxyl group is responsible for the reversal of charge. We have made a survey of ions that have been found experimentally to cause this phenomenon, and they all contain in their ionic structure hydroxyl groups, *e.g.*, all heteropoly ions,^{34,35} citrate ion,³⁶ hydrolyzed aluminum ion,¹ etc. It is especially interesting to note that the hexavalent hexol ion reverses the charge when incompletely dissociated but loses this ability when its hydroxyl groups become protonated.²⁶ Thus, we believe that hydroxyl groups in soluble counterion species are responsible for their adsorption on sol particles, which in turn causes the reversal of charge. This naturally does not apply to detergents and similar ions that reverse the charge,³⁷ but where the adsorption is not due to hydroxy bridges.

Acknowledgment.—We wish to record our thanks to Mr. Charles Rapp for his assistance in a part of the experimental work.

DISCUSSION

R. H. OTTEWILL (University of Cambridge).—Is it possible that the decrease in coagulation concentrations found at high pH values for silver chloride and silver bromide can be explained by the formation of silver oxide on the surface of the particles? Silver oxide appears very prone to form on silver bromide and it would be expected to be more so for silver chloride and less so for silver iodide. It is interesting that no decrease is found for silver iodide. It could be very useful to have some complementary measurements by another technique, *e.g.*, microelectrophoresis, to prove that the surface of the sol particles is not appreciably charged in this region.

E. MATIJEVIĆ.—Dr. Ottewill's suggestion is a possibility. However, we believe that it is more likely that with

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(29) R. H. Betts and R. M. Leigh, *Can. J. Research*, **28B**, 514 (1950).

(30) K. A. Kraus in "National Nuclear Energy Series," Div. IV, Vol. 14B, No. 3.16, Edited by G. T. Seaborg, J. J. Katz and W. M. Manning, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

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(33) K. F. Schulz and M. J. Herak, *Croat. Chem. Acta*, **30**, 127 (1958).

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the AgI sol the decrease in coagulation concentration at higher pH's does not occur because of an interaction of the iodide ion and the complex thorium ion with a corresponding change in charge. The iodide ion might act as a "penetrator." At the present moment there is no proof for either assumption.

J. TH. G. OVERBEEK (University of Utrecht).—With reference to Dr. Ottewill's remark, I want to report that in our measurements and those of P. L. de Bruyn at M.I.T. on the adsorption of I^- and Ag^+ ions on AgI difficulties were encountered at high pH (9 or 10) but very definitely before the normal solubility product of silver oxide is reached. The silver iodide became darkly colored and adsorption was poorly reproducible.

E. MATIJEVIĆ.—In our experiments no changes in colors were observed. In the pH range investigated the silver halide sols retained the same appearance.

J. TH. G. OVERBEEK.—If the transition of the flocculation value in going from valence 4 to valence 3 is exclusively due to the reaction $Th^{4+} + OH^- \rightarrow ThOH^{3+}$, one might expect the transition to be very similar for the three silver halides. However, according to Figs. 2, 3 and 4, the transition increases in steepness in the order AgI, AgCl, and AgBr.

E. MATIJEVIĆ.—Some differences in the transition range probably are caused by specific properties of the three silver halide sols. It is known that these sols show slightly different effects when coagulated with mixtures of ions.

J. TH. G. OVERBEEK.—How is it possible that the reversal

of charge concentration in Fig. 2 is lower than the flocculation concentration for the trivalent $ThOH^{3+}$ if the reversal is due exclusively to this trivalent ion?

E. MATIJEVIĆ.—As shown in Fig. 1, the pH in neutral and basic solutions depends strongly on the concentration of the thorium salt in solution. Thus, for the same coagulation curve the concentration limits for coagulation and stabilization appear at different pH's. Since the stability limit is always at high Th-salt concentrations, the corresponding pH is lower, giving the stability range of recharged sols as presented in Fig. 2.

S. LEVINE (University of Manchester).—What is the evidence for the dimerization described by your Eq. (2)?

E. MATIJEVIĆ.—The dimer is only given as a possible explanation for the drop in coagulation concentrations at high pH's. It was, however, detected by a number of investigators cited in the introduction of this paper.

R. R. IRANI (Monsanto Chemical Company).—Do you feel that your technique is applicable to the hydroxyl complexes of ferric ion, particularly since several species have been reported to coexist and their relative concentrations change with pH, *e.g.*, $Fe(OH)^{+2}$, $Fe_2(OH)_2^{+4}$, $Fe(OH)^+$, etc.

E. MATIJEVIĆ.—In principle, there is no reason why the method could not be employed for hydrolysis of ferric ion. The coexistence of several species could imperil the deductions. However, if one of the species becomes predominant its charge will be indicated by the coagulation behavior.