Discussion of Results

Although the end-point of the potentiometric titration can be found with a precision of better than 0.01%, the titration of silver with thiocyanate is not suited to work of a highly exact nature. As a result of the side reactions, the variations between duplicate titrations at room temperature may amount to as much as 0.05%, the average result corresponding to an effective strength of the potassium thiocyanate of 0.08% less than the theoretical.

The Volhard method of locating the end-point leads to the same result when the precipitate is digested with a slight excess of silver before the final titration. In the ordinary Volhard method at room temperature without digestion, the average effective strength of the potassium thiocyanate is 0.02% higher than the theoretical, and 0.10% greater than the effective strength found potentiometrically or after digestion, because 0.10% of the silver nitrate is still adsorbed or occluded by the precipitate at the end-point. The relatively good results obtained by the ordinary Volhard method are thus due to a compensation of errors.

Potassium thiocyanate may be recommended as a standard substance in work of ordinary accuracy.

Summary

1. Potassium thiocyanate is easily obtained in a pure state and is a suitable standard substance for work of ordinary accuracy (±0.1%).
2. During the precipitation of silver with thiocyanate, or the reverse, slight side reactions occur in which cyanic acid is an intermediate product decomposing to ammonia and carbon dioxide. When a hot neutral silver solution is precipitated with thiocyanate the precipitate is colored tan by silver sulfide. The side reactions also take place in the absence of oxygen.
3. As a result of the side reactions, the average effective strength of the potassium thiocyanate in the potentiometric titration with silver at room temperature is only 99.92%.
4. If titrated at 70 to 90° an effective strength slightly greater than 100% is found. If the precipitation is carried out in hot dilute sulfuric acid (0.06 *N*), the deviation is several tenths of a per cent. greater.
5. The ordinary Volhard titration at room temperature leads to an effective strength 0.10% greater than the potentiometric titration, due to occlusion of silver nitrate at the end-point. If the precipitate is digested just before the end-point, the Volhard method gives results practically identical with the potentiometric method.
6. The solubility product of silver thiocyanate at 24° in 0.05 *N* neutral potassium nitrate solution is equal to 3.2×10^{-12}.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 4, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Formation of Zirconeate Hydrosols and their Disintegration by Certain Neutral Salts

BY ARTHUR W. THOMAS AND HARRY S. OWENS

In a previous publication,[1] the *p*H raising action of neutral salts upon basic zirconium chloride (sometimes designated as "zirconium oxide") hydrosols was ascribed to the replacement of OH groups from the polyolated micelles by the anions of the added neutral salts. If the strongly coördinatively bound OH group can thus be displaced from the central metallic atom by added anions, one would expect other coördinatively bound groups also to be displaceable.

Increases in chloride ion activity of "oxide" hydrosols have been reported to result upon addition of neutral salts.[2] Inasmuch as the order of effectiveness of the anions of the salts in raising the chloride ion activity is in general similar to those reported from this Laboratory for displacing OH groups from the micelle, the writers submit this as evidence for the expected displacement of chlorido groups. Removal and replacement of aquo groups from the central metallic atom by

---

[1] A. W. Thomas and H. S. Owens, THIS JOURNAL, **57**, 1825 (1935).

[2] (a) P. S. Wassiliev and A. J. Rabinowitch, *Kolloid Z.*, **56**, 305 (1931); (b) H. B. Weiser, *J. Phys. Chem.*, **35**, 1, 1368 (1931); (c) A. Lottermoser and T. Chang, *Kolloid Z.*, **65**, 62 (1933); (d) W. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929, p. 527.

added anions would likewise be expected. If so, then the positive charge of the micelle would be reduced and perhaps reversed.

The reversal of the sign of charge of cationic "metallic oxide" micelles by added electrolytes has been ascribed by some investigators to the adsorption of the added ions to the surface of the micelle. These investigators, reasoning from the physical point of view, base their arguments on *zeta* potential measurements such as those of Powis[3] with oil emulsions and of Kruyt[4] with glass–water interfaces. Their work has led to the following conclusion which is the main tenet of the adsorption advocates: "if the *zeta* potential is positive, it is influenced more by anions and the influence increases with the valency of the effective ions, unless the ion is strongly adsorbed."[5] Since the degree of adsorption of organic ions increases with valence and molecular complexity, one would not expect simple univalent organic anions to be as potent as divalent in reversing the charge of the cationic micelle. However, inasmuch as glycolate and lactate readily reverse the charge of basic zirconium chloride micelles while succinate or oxalate either do not or only under limited experimental conditions the weakness of the adsorption argument is apparent.

A chemical type of explanation has been suggested by Pauli,[6] who explains irregular series formation with "iron oxide" hydrosols by assuming that stable complex formers such as pyrophosphate or ferrocyanide react with the surface bound basic ferric chloride in the following way

$$Fe(OH)_2Cl + Na_4P_2O_7 \longrightarrow (FeP_2O_7)^-Na^+ + 2NaOH + NaCl$$

while trivalent ions of the same type do not form negative particles since they can react to form neutral molecules[7]

$$Fe(OH)_2Cl + K_3Fe(CN)_6 \longrightarrow Fe[Fe(CN)_6] + 2KOH + KCl$$

Further, he claims, with alkaline hydrolyzing salts like phosphates and citrates, the reversal always results with an excess of OH^- ion, whereas at lower concentrations the discharging by means of OH^- takes place with salts with high valence anions through the simultaneous action of the anion and OH^-. A model for this discharging and reversal reaction is

$$Fe(OH)_2Cl + KOH \longrightarrow Fe(OH)_3 + KCl$$
$$Fe(OH)_3 + KOH \longrightarrow (Fe(OH)_4)^-K^+$$

The charge on the sols can be due to ions varying in nature from $(Fe(OH)_4)^-$ to $(FeAnOH)^-$ in which "An" is a trivalent anion.

Inasmuch as the writers have in the case of basic zirconium chloride sols succeeded in reversing the micellar charge by the addition of certain acids, and addition of salts with anions of various valencies while maintaining the *p*H value below 7, the explanation by Pauli does not apply.

The writers have found that the anions listed in "Group A" of Table I reverse cationic basic zirconium chloride micelles to anionic zirconeate micelles while those in "Group B" do not.

TABLE I

Group A	Group B
Citrate[a]	Acetate
Glycolate[a]	β-Hydroxybutyrate
Lactate[a]	Chloride
Malate[a]	Ethoxyacetate
Mucate[a]	Ferricyanide
Pyruvate	Ferrocyanide
Tartrate[a]	Formate
Dihydrogen phosphate[b]	Fumarate
Pyrophosphate[b]	Glycine
	Maleinate
	Monochloroacetate
	Monohydrogen phosphate
	Oxalate
	Phosphate
	p-Hydroxyphenylglycine
	Propionate

[a] These salts were also found to peptize freshly prepared hydrated zirconium oxide to zirconeate hydrosols. The three salts in Group A not marked [a] were not tried. The salts in Group B would not, of course, be expected to peptize the oxide. [b] Provided medium was not too alkaline.

The conditions necessary for reversal of cationic to anionic micelles by added salts are: (1) ability of the salt anion to displace aquo groups from the cationic micelle, (2) the formation of a soluble anionic complex and (3) the equilibrium constant of the anionic complex must be near to or less than the solubility product of zirconyl hydroxide.

The first is essential to reversal of charge and inasmuch as the majority of anions in Group B possess known coördinative binding powers, they

---

[3] F. Powis, *Z. physik. Chem.*, **89**, 91 (1914).

[4] H. R. Kruyt, "Colloids," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1930, pp. 84–86.

[5] H. Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipsig, 1930, Vol. I, p. 367.

[6] W. Pauli and H. Neurath, *Kolloid Z.*, **70**, 135 (1935); W. Pauli, *Trans. Faraday Soc.*, **31**, 11 (1935).

[7] Pauli and Neurath[6] state that because the stabilizing agent is distributed over the surface of the oxide micelle, it is impossible for the stabilizing agent to react with quadrivalent radicals to yield neutral complexes.

must be able to displace aquo groups. If they do displace a number sufficient to reverse the charge, their failure to repeptize the precipitated cationic basic zirconium complexes resulting upon their additon to the hydrosol means that the complexes either are insoluble or unstable, or both.

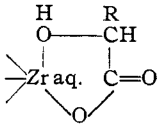
The anions in Group A must fulfill the conditions stated. The range of concentration in which charge reversal is effected is always very narrow. For example, the case of addition of potassium malate to Sol E[8] may be cited. At a malate concentration of 0.0035 *N* its micelles were positively charged, its *p*H was 4.65 and it was clear. At a malate concentration of 0.005 *N* it was a slightly turbid malato zirconeate hydrosol with a *p*H value of 7.40. Between these concentrations of malate the dispersed phase was all precipitated. Calculations show that more than 90% of the added malate was available to maintain equilibrium conditions and to react with the cationic micelle in some way other than displacement of OH groups. With the exception of the possible action of a small part of the malate in displacing chloride groups, part of the balance must have displaced aquo groups in order to confer the negative charge.

Inasmuch as hydrolysis (conversion of aquo to hydroxo groups) lowers the positive charge of basic metallic salt micelles, boiling of a sol (which process also favors olation and oxolation) should reduce the amount of added anion required to precipitate and reverse the charge of the micelles. A typical case may be cited. Sol E required (a) a concentration of 0.005 *N* potassium tartrate for precipitation and (b) 0.0088 *N* for conversion to tartrato zirconeate sol. After boiling under a reflux condenser for one hundred and ninety-two hours (a) = 0.0025 and (b) = 0.005.

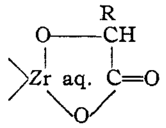
The zirconeate sols formed by addition of the Group A (Table I) salts to basic zirconium chloride sols were very stable, being unaffected by addition of alkali (excepting phosphate and pyrophosphate) and it is significant that all are α-hydroxy compounds.[9] It is interesting in this connection to refer to the chemistry of crystalloidal zirconium compounds. De Boer[10] has shown that the ability of ions to form complex compounds with zirconium is in the following order: α-hydroxy organic salts[11] (in alkaline solution) $> OH > C_2O_4 > SO_4 > Cl$ (in acid solution) and Mandl[12] found a similar order: α-hydroxy organic salts $> C_2O_4 >$ maleinate $>$ saturated monobasic or dibasic organic acid salts.

The stability of metal–α-hydroxy complexes has for many years been ascribed to the ability of the α-hydroxy group to react with the metallic ion. There are two possible types of compounds (1) comparable to the β-diketone chelates[13] and (2) one in which the hydroxy group acts as an acid.[14]

These types would be formulated as follows.



I



II

In "type I," negative micellar formation should be possible with radicals like monochloroacetate or ethoxyacetate, yet each of these acts like acetate when added to basic zirconium chloride sols. Evidently, ability of the α-substituted group to act as a donor of electrons to the metal has little effect on its ability of causing reversal of charge.

If "type II" illustrates the compound formed during chelation, then hydrogen ion should be liberated. An indication that such a reaction takes place is obtained from OH displacement experiments with salt mixtures, typical results of which are given in Table II. It is striking that mixtures of anions which do not reverse the charge of the micelles produced nearly the same *p*H values, while oxalate–lactate and oxalate–tartrate mixtures gave lower *p*H values. Chelation as illustrated by type II would account for the *p*H differences found and for the stability of the zirconeate hydrosols. Oxalate precipitates basic zirconium chloride sols without reversing the charge but subsequent addition of a salt of an α-hydroxy acid peptizes the precipitate to a complex zirconeate sol. Further, if sufficent α-hydroxy salt is first added to a basic zirconium chloride sol, subsequent addition of oxalate produces no precipitate. These behaviors are entirely in accord with the properties of crystalloidal zirco-

---

(8) Sol E had a *p*H value of 3.50 (at the time of this experiment), its total Zr and total Cl contents were 126.2 and 11 milliequivalents per liter, respectively. Its micelles were cationic.

(9) The enol form of pyruvate exists in increasing concentration as the *p*H is raised.

(10) J. H. de Boer, *Z. anorg. allgem. Chem.*, **165**, 1 (1927); J. H. de Boer and H. Emmens, *Rec. trav. chim.*, **49**, 955 (1930).

(11) Irrespective of valence.

(12) A. Mandl, *Z. anorg. Chem.*, **37**, 252 (1903).

(13) N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, p. 233.

(14) L. Dede, "Komplexchemie," Walter de Gruyter and Co., Berlin, 1928, p. 97. See also articles by Pickering and by Work in *J. Chem. Soc.* from 1900 to date.

nium solutions where in almost every case α-hydroxy groups form more stable complexes than any other groups.

TABLE II

EFFECT OF ADDITION OF SALT MIXTURES TO SOL B[a]

(I)[b]	(II)[b]	*p*H
..	0.05 Oxalate	7.42
0.001 Tartrate	.05 Oxalate	7.23
.005 Tartrate	.05 Oxalate	7.01
.05 Tartrate	.05 Oxalate	6.86
.05 Lactate	.05 Oxalate	7.02
.05 Acetate	.05 Oxalate	7.34
.05 Sulfate	.05 Oxalate	7.34
.05 Oxalate	.05 Tartrate	6.88

[a] "B" was a basic zirconium chloride hydrosol, *p*H value = 3.22, total Zr and total Cl = 89.1 and 11.2 milliequivalents per liter, respectively. [b] (I) Solid potassium tartrate, acetate. sulfate or an 85% solution of potassium lactate was first added to the hydrosol. Then (II) a solution of potassium oxalate (or of tartrate) equal in volume to the hydrosol was added and the *p*H value of the mixture determined. The numbers in Columns I and II denote the normality of the salts in the resulting mixture of hydrosol and salt solution.

Ability to chelate does not necessarily mean that the anion will be capable of reversing the sign of the charge on the cationic sol particles, as illustrated by the case of glycine. This compound readily chelates with metallic ions in solution;[15] however, it affects basic zirconium chloride sols to but a slight extent. The authors were unable to precipitate a dilute sol containing cationic micelles with a large excess of glycine. Weitz and Conrad[16] report similar findings with glycine and aminobenzoic acids mixed with basic ferric chloride ("ferric oxide") hydrosols.

Deolation to the Crystalloidal State.—Since powerful coördinative binding ions weaken the ol linkage,[17] the α-hydroxy organic salts might be expected ultimately to effect disruption of ol bonds. According to the postulates from this Laboratory that "metallic oxide" hydrosols are polyolated structures, the salts mentioned should decompose an "oxide" sol to the crystalloid state. This postulate was tested in the following manner. To each of three portions of a basic zirconium chloride hydrosol was added, respectively, an equal volume of 0.1 *N* potassium citrate, tartrate and glycolate. The resulting zirconeate hydrosols were dialyzed in nitrocellulose bags against distilled water at room temperature. The diffusate contained zirconium (tested by the phosphate method) in each case but not in the instance of a control dialysis of the untreated basic zirconium chloride sol. As the dialysis continued the amount of zirconium diffusing decreased, but on further addition of the original salt solution to the dialysate more diffusible complexes were formed. These diffusions and additions of salt were continued until there was but a trace of zirconium left in the dialysate. With the potassium citrate the time of dialysis required to disintegrate the colloidal micelles was three hundred and fifty to four hundred hours,[18] with potassium tartrate four hundred to five hundred hours,[18] with potassium glycolate the time required was still longer. This order of ability to deolate the colloidal micelles, citrate > tartrate > glycolate, is the same as the tendency for these anions to become coördinatively bound with zirconium, as shown by titration experiments with basic zirconium chloride hydrosols.[1]

Zirconeate Hydrolysis of Low *p*H Value.—Basic zirconium chloride sols (Zr in the cationic micelle) which are of low *p*H value can be changed to zirconeate sols (Zr in the anionic micelle) by the careful addition of any of the following acids: citric, glycolic, lactic, oxalic, pyruvic,[19] sulfuric and tartaric. Zirconeate sols thus formed can exist only on account of the strong tendency of basic zirconium complexes to oxolate.[1] The oxo linkages are resistant to acids and thus render possible the existence of polynuclear complexes. The micelles are negatively charged because the anions of the acids named, strong coördinative binders, replace aquo groups from the central metallic atoms.

Acid zirconeate hydrosols may be prepared also by the action of acids (with powerful coordinative binding anions) upon hydrated zirconium dioxide. In studying the course of the peptization of such an oxide by tartaric acid, both positive and negative zirconium micelles arose in the same solution. This is so contrary to the accepted notions of colloid chemistry that a description of the experimental procedure is important.

A solution of $ZrOCl_2\cdot 8H_2O$ was treated with ammonium hydroxide to complete precipitation of the zirconium. The precipitate was washed

---

(15) E. Ferrell, J. M. Ridgion and H. L. Reilly, *J. Chem. Soc.*, 1440 (1934).

(16) E. Weitz and W. Conrad, *Kolloid-Z.*, **68**, 230 (1934).

(17) E. Stiasny, "Gerbereichemie (Chromgerbung)," Verlag von Theodor Steinkopff, Leipzig, 1931, p. 351; A. W. Thomas and R. D. Vartanian, THIS JOURNAL, **57**, 4 (1935).

(18) Dialysis times, of course, have no absolute significance; the times given here are of relative value only.

(19) Pyruvic acid acts very slowly.

at room temperature by means of centrifugal decantations until the supernatant liquid was free from chloride ion. It was then suction filtered and air dried at room temperature for twenty-four hours. Portions of this hydrated oxide equal to 1 g. of zirconium oxide were immediately[20] placed in 200-cc. portions of water to which the amounts of tartaric acid reported in Table III were added. Then, with the exception of the last stated case in Table III, the systems were rotated at 7 r. p. m. at 25 ± 0.2° for twenty-four hours. In the last stated case, the system was boiled under a reflux condenser for twenty-four hours. Then all were centrifuged to throw down the unpeptized oxide. The supernatant liquids which were turbid to reflected light while clear to transmitted light were subjected to the tests recorded in Table III.

TABLE III

PEPTIZATION OF A HYDRATED ZIRCONIUM OXIDE BY TARTARIC ACID

Tartaric acid, g.	Temp., °C.	Dispersed zirconium calcd. as milliequiv. ZrO_2 per liter	pH	Migration in electric field[a]
0.08	25	6	4.95	+ and −
.16	25	9	4.41	+ and −
.62	25	15	2.80	+ and −
.62	100[b]	112	2.27[c]	.....

[a] Migration of zirconium-containing micelles; + to cathode, − to anode. [b] In this instance, instead of agitating the system at 25°, it was boiled in a Pyrex glass reflux condenser apparatus for twenty-four hours. [c] In this case, the pH of the hydrosol was lower than of the original tartaric acid solution.

The startling fact shown in the table is the coexistence of cationic and anionic micelles. This fact was demonstrated by electrophoresis measurements upon the freshly prepared sols in a Coehn tube. The cationic micelle migrated faster than the anionic, thus indicating a greater charge density for the former. Probably none of the anionic micelles (tartrato zirconeate) would have been present were the systems allowed to stand for a longer time, as in the case of the peptization carried out at boiling temperature. The basic zirconium tartrate (cationic) micelles arise owing to the combination of H^+ ions with hydroxo groups of the hydrated oxide, forming aquo groups and thus conferring a positive charge upon the polynuclear complex. The tartrato zirconeate (anionic) micelles arise owing to the preponderant coördinative binding of tartrate ions over H^+ ions through displacement of aquo groups. The polynuclear zirconium or zirconeate complex would ultimately disintegrate to small particles if the complexes were not highly oxolated.

This is probably the first reported instance of the occurrence of positive and negative micelles in the same solution. The sols were rather dilute, however, and hence one can conclude that the solubility products of the sundry complex basic zirconium zirconeates present were not exceeded.

The subject of these acid dispersions of zirconeate micelles is being investigated further by one of us (H. S. O.).

Summary

Certain neutral salts convert basic zirconium (cationic) micelles to zirconeate (anionic) micelles while others do not. Certain neutral salts disintegrate basic zirconium ("zirconium oxide") micelles to the crystalloidal state. Zirconeate hydrosols of low pH value may be formed by the action of certain acids upon hydrated zirconium oxide. The possibility of the coexistence of positively and negatively charged micelles has been demonstrated. The polyolation and oxolation theory of the structure of "metallic oxide" hydrosol micelles proposed by this Laboratory renders possible the prediction and understanding of these behaviors.

NEW YORK, N. Y.

RECEIVED JULY 9, 1935

---

(20) This hydrated zirconium oxide becomes refractory on aging, presumably due to oxolation. After forty-eight hours of standing at room temperature the amount peptizable by tartaric acid was decreased to about one-third of its former value. A specimen six months old was resistant to the action of boiling concentrated hydrochloric acid.