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Solution Chemistry of Some Cerium(IV), Thorium(IV) and Lanthanum(III) Compounds in Chlorosulphuric Acid

J. K. PURI, PRITPAL SINGH

Department of Chemistry, Panjab University, Chandigarh-160014, India

and JACK M. MILLER

Department of Chemistry, Brock University, St. Catharines, Ont. L2S 3A1, Canada

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Cerium(IV) oxide, -sulphate, -perchlorate, -acetate, -nitrate, -chloride are solvolysed in chlorosulphuric acid to form the $Ce(SO_3Cl)_4$ *species and behave as non-electrolytes in it. Thorium(IV) oxide, -nitrate, -acetate, -chloride are solvolysed in this medium to form the species* $H_2[Th(SO_3Cl)_6]$ *which behaves as a weak acid. Lanthanum(III) oxide, -sulphate, -acetate and chloride form the species* $H[La(SO_3Cl)_4]$ *in* HSO_3Cl *which behaves as a very weak acid. All these solvates polymerized at higher concentrations.*

Introduction

Various solvolysis in strong protonic acids have been reported [1–6] but not for cerium, thorium and lanthanum compounds. The species $[Ce_3(OH)_5]^{4+}$ is reported at pH 6.5 and in perchlorate solutions Ce^{4+} is reported [7] as $[Ce{-}O{-}Ce)]^{6+}$. Here we report on solvolysis in the stronger acid HSO_3Cl.

Experimental

Conductance measurements were carried out as described earlier [8]. The conductometric factor (γ) has been determined in the same way as described by Gillespie *et al.* [9] and Paul *et al.* [10]. A.R. grade samples of cerium, thorium and lanthanum compounds were used. Pyridine and acetic acid were freshly distilled before use.

Chlorosulphuric acid (BDH technical grade) was used as reported in literature [11].

Results and Discussion

Cerium(IV) oxide and -sulphate are sparingly soluble in HSO_3Cl at room temperature but their solubility increases on heating at 45 °C and colourless solutions of up to 0.052 and 0.085 molal concentrations could be obtained respectively. There is no significant change in the conductance of both these solutions. Beyond the above mentioned molal concentrations, further additions of the solutes results in the separation of white precipitate and the conductance values decrease which suggests that there is polymerization through chlorosulphate bridging in both cases. However, from their conductance data, the solution chemistry of cerium(IV) oxide and cerium(IV) sulphate in HSO_3Cl could be proposed as:

$$CeA + 6HSO_3Cl \longrightarrow Ce^{4+} + 4SO_3Cl^- + 2H_2SO_4 + 2HCl \quad (1)$$

$$CeA + 6HSO_3Cl \longrightarrow Ce(SO_3Cl)_4 + 2H_2SO_4 + 2HCl \quad (2)$$

$$CeA + 7HSO_3Cl \longrightarrow H[Ce(SO_3ClH)_5] + 2H_2SO_4 + 2HCl \quad (3)$$

$$CeA + 8HSO_3Cl \longrightarrow H_2[Ce(SO_3Cl)_6] + 2H_2SO_4 + 2HCl \quad (4)$$

[where $A = O_2$ or $(SO_4)_2$]

Reaction (1) is ruled out since these solutions are low conducting. If reactions (3) and (4) occur, there should be a decrease in conductance on the addition of HSO_3Cl but no such decrease is observed in any case. Moreover the solvolysed products were isolated, dried under vacuum and found $Ce(SO_3Cl)_4$ on analysis. Infrared spectrum of this compound shows absorption bands at 1170, 1035, 850, 760, 640, 570 cm^{-1} which confirms the presence of SO_3Cl^- group and thus supports that reaction (2) occurs. The low conductance of the solutions may be attributed to the presence of H_2SO_4 and HCl which behave as very weak bases in this solvent [11]. Since at higher concentration a solvate separates out without any change in conductance which indicates that there is some polymerization through chlorosulphate group. As expected from the closed shell electronic configuration the solutions are colourless and no

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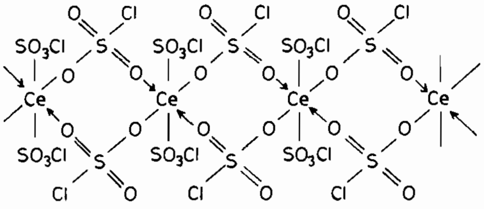
absorption bands are observed in the wavelength range 20,000–10,000 A°. Polymeric structures can be suggested in which cerium acquires most favourable hexa-coordination.



Cerium(IV) perchlorate dissolves fairly well in HSO_3Cl but after 0.15 molal concentration, a white precipitate settles out. There is a slight increase in the conductance of the solution and the solution thus formed is found to be acidic in character as observed by the addition of KSO_3Cl (a strong base of HSO_3Cl system [11]). However, from the conductance data and the above observations the possible solvolytic reaction in this case can be proposed as:

$$Ce(ClO_4)_4 + 4HSO_3Cl \longrightarrow Ce(SO_3Cl)_4 + 4HClO_4 \qquad (5)$$

The species $Ce(SO_3Cl)_4$ behaves as non-electrolyte whereas $HClO_4$ behaves as a very weak base [12] in HSO_3Cl.

Cerium(IV) acetate dissolves in chlorosulphuric acid to form highly conducting solutions, but at higher concentrations again a solvate is formed. However, the conductance value indicates the possible mode of solvolysis as:

$$Ce(CH_3COO)_4 + 8HSO_3Cl \longrightarrow Ce(SO_3Cl)_4 + 4CH_3COOH_2^+ + 4SO_3Cl^- \qquad (6)$$
$$(\gamma = 4.0)$$

In the above equation $Ce(SO_3Cl)_4$ which is formed during the dissolution of $Ce(CH_3COO)_4$ behaves as non-electrolyte whereas the acetic acid which is first formed gets fully protonated [7] in HSO_3Cl to produce four moles of SO_3Cl^- ions in the solution which is further supported by the experimental γ-value of 4.0. Anhydrous cerium(IV) nitrate behaves differently from the other cerium(IV) salts forming a light yellow highly conducting solution, a γ-value of >4 suggests the following reaction;

$$Ce(NO_3)_4 + 12HSO_3Cl \longrightarrow Ce(SO_3Cl)_4 + 4NO_2^+ + 4SO_3Cl^- + 4H_2SO_4 + 4HCl \qquad (7)$$

The formation of NO_2^+ ions has already been reported [13] in HSO_3Cl.

Behaviour of cerium(IV) chloride has been investigated by studying the behaviour of the compound $CeCl_4 \cdot 2C_5H_5N$ in chlorosulphuric acid. Here again white precipitates formed above 0.10 molal concentrations. With addition of more of the solute, conductance of the solution increased but at the same time, the volume of the precipitate was also found to increase. However, the experimental γ-values Fig. 1 indicate the possible solvolytic reaction as:

$$CeCl_4 \cdot 2C_5H_5N + 6HSO_3Cl \longrightarrow Ce(SO_3Cl)_4 + 2C_5H_5NH^+ + 2SO_3Cl^- + 4HCl \qquad (8)$$

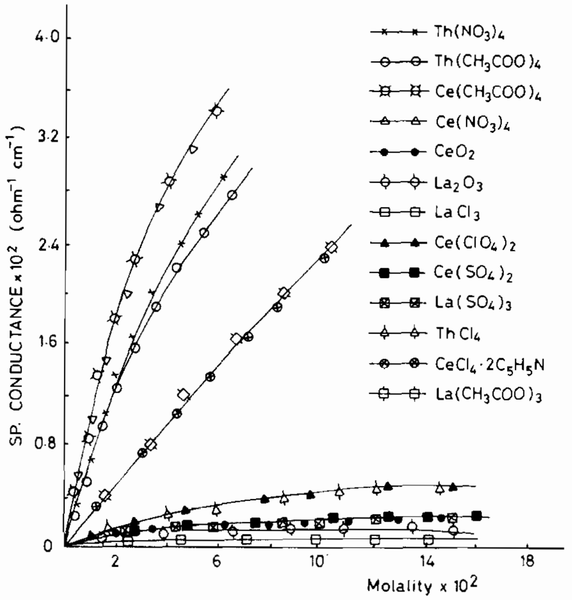


Fig. 1. Specific conductance of some cerium(IV), thorium (IV) and lanthanum(III) compounds in HSO_3Cl at 25 °C.

In the above reaction the presence of pyridine which is fully protonated is known to be a strong base [12] of the chlorosulphuric acid system, whereas HCl behaves as a very weak base in it.

Thorium(IV) oxide has a limited solubility in HSO_3Cl and solution up to 0.01 molal concentration could be obtained on warming the solvent. Further addition of the solute results in the separation of a precipitate with no change in conductance of the solution. By analogy with the behaviour of tin, lead and silicon compounds [14] in chlorosulphuric acid and from the experimental γ-values (Table I) the possible solvolytic reaction could be proposed as:

$$ThO_2 + 8HSO_3Cl \longrightarrow H_2[Th(SO_3Cl)_6] + 2H_2SO_4 + 2HCl \qquad (9)$$

The species $H_2[Th(SO_3Cl)_6]$ thus formed during the reaction behaves as a very weak acid as has been shown by the addition of a strong base KSO_3Cl which causes a slight decrease in conductance of the solution. Moreover, H_2SO_4 and HCl also behave as very weak bases (loc. cit) in this system. Similarly thorium(IV) nitrate and acetate behave as:

$$Th(NO_3)_4 + 14HSO_3Cl \longrightarrow H_2[Th(SO_3Cl)_6] + 4NO_2^+ + 4SO_3Cl^- + 4H_2SO_4 + 4HCl \qquad (10)$$

TABLE I. Summary of the γ-Values at Different Concentrations of some Cerium(IV), Thorium(IV) and Lanthanum(III) Compounds in HSO_3Cl.

Compound	γ-Values at Different Concentrations			
	0.02 *M*	0.05 *M*	0.10 *M*	0.15 *M*
CeO_2	0.14	0.14	0.16	
$Ce(SO_4)_2$	0.15	0.16	0.18	
$Ce(ClO_4)_2$	0.22	0.24	0.28	0.32
$Ce(OAc)_4$	4.00	4.10	4.15	4.20
$Ce(NO_3)_4$	4.20	4.25	4.35	4.50
$CeCl_4 \cdot 2C_5H_5N$	2.30	2.10	1.87	1.65
$ThCl_4$	0.24	0.21	0.16	0.11
$Th(NO_3)_4$	3.50	3.35	3.25	3.15
$Th(CH_3COO)_4$	3.55	3.40	3.30	3.20
La_2O_3	0.12	0.12		
$LaCl_3$	0.11	0.07	0.05	0.05
$La(SO_4)_3$	0.16	0.15	0.13	
$La(OAc)_3$	2.80	2.70	2.60	2.50

$$Th(CH_3COO)_4 + 10HSO_3Cl \longrightarrow H_2[Th(SO_3Cl)_6] + + 4CH_3COOH_2^+ + 4SO_3Cl^- \qquad (11)$$

From the experimental γ-values (Table I), the number of SO_3Cl^- ions produced per mole of the solute in each case is found to be less than 4 which again supports the acidic character of $H_2[Th(SO_3Cl)_6]$. Moreover on addition of KSO_3Cl to these solutions a slight decrease in conductance was also observed in both cases which is further evidence for the presence of acidic species $H_2[Th(SO_3Cl)_6]$. The presence of NO_2^+ and $CH_3COOH_2^+$ ions have already been reported [7, 13] in HSO_3Cl.

Thorium(IV) chloride is soluble in HSO_3Cl up to 0.12 molality. At higher concentrations, a light milkiness appears and a white compound separates out. The solutions are found to be of low conductivity. By analogy with the behaviour of Tin (IV) compounds [14] in chlorosulphuric acid, it may be assumed that $ThCl_4$ when dissolved in chlorosulphuric acid, first forms $Th(SO_3Cl)_4$ which at higher concentration forms species of the type $H_2[Th(SO_3Cl)_6]$ analogous to the compound $H_2[Sn(SO_3Cl)_6]$ and $H_2[Pb(SO_3Cl)_6]$ which behave as weak acids (loc. cit) in HSO_3Cl. The acidic behaviour of this species is further shown by the evidence that on addition of KSO_3Cl (a strong base of the system [11]) to the above solutions causes a decrease in the conductance of the solution due to the reaction:

$$H_2[Th(SO_3Cl)_6] \rightleftharpoons H[Th(SO_3Cl)_6]^- + H^+ \qquad (12)$$

However, from the experimental γ-values and the above observations, the possible solvolytic reaction may be proposed as:

$$ThCl_4 + 7HSO_3Cl \longrightarrow H_2^+SO_3Cl + H[Th(SO_3Cl)_6]^- + + 4HCl \qquad (13)$$

The mode of self-dissociation and ionization of chlorosulphuric acid may be represented as:

$$2HSO_3Cl \rightleftharpoons H_2^+SO_3Cl + SO_3Cl^- \qquad (14)$$

Therefore, the compounds which directly or indirectly increase the concentration of chlorosulphate ions (*i.e.* SO_3Cl^-) will behave as bases in HSO_3Cl and those which increase the concentration of chloroacidium ion (*i.e.*, $H_2^+SO_3Cl$) will behave as acids in this system. To ascertain whether a solute is an acid or a base, the change in conductance of the solution after each small addition of a strong base *i.e.*, KSO_3Cl or acetic acid is noted. A continuous decrease in the conductance of the solution is because of the removal of $H_2^+SO_3Cl$ ions from the solution as a result of the reaction:

$$H_2^+SO_3Cl + SO_3Cl^- \longrightarrow 2HSO_3Cl$$

which indicates the solute to be an acid.

If the solute is a base, then the added KSO_3Cl or CH_3COOH will not react with it and the conductance of the system will increase.

Conductometric titrations between $ThCl_4$ and various bases have been carried out in HSO_3Cl. There is a continuous decrease in the conductance of the solution on addition of the base solution. Fig. 2 suggests that the species $H_2[Th(SO_3Cl)_6]$ behaves as a weak acid. Three different types of bases have been used which ionize to give one SO_3Cl^- ion as:

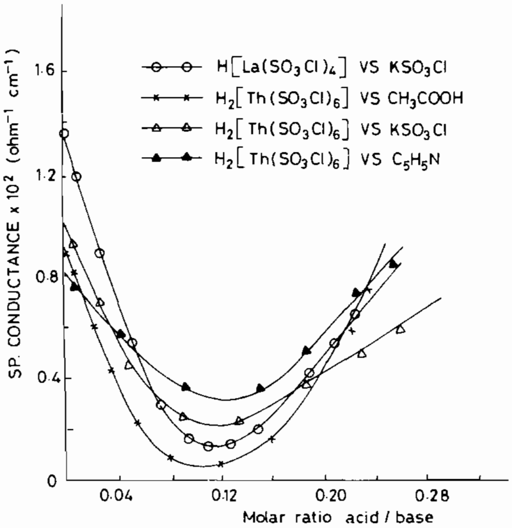


Fig. 2. Conductometric acid/base titrations of some acids and bases in chlorosulphuric acid at 25 °C.

$$C_5H_5N + HSO_3Cl \longrightarrow C_5H_5NH^+ + SO_3Cl^- \qquad (15)$$

$$KSO_3Cl \xrightarrow{HSO_3Cl} K^+ + SO_3Cl^- \qquad (16)$$

$$CH_3COOH + HSO_3Cl \longrightarrow CH_3COOH_2^+ + SO_3Cl^- \qquad (17)$$

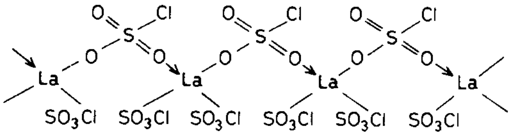
When complete removal of $H_2^+SO_3Cl$ ions has taken place, further addition of the base solution results in an increase of the conductance. The conductance composition curves pass through a minimum which occurs at about a base/acid molar ratio of 1:1 which suggests that thorium(IV) chloride behaves a monobasic acid. A slight displacement of the minima in the conductance composition curve for different bases may be due to the formation of HCl which has been shown to behave as a weak base in chlorosulphuric acid.

Lanthanum(III) oxide has a limited solubility in HSO_3Cl and so has the lanthanum(III) sulphate and solutions up to 0.01 molal concentration only could be obtained. Further addition of the solute results in the separation of white precipitates. The solutions are found to be of low conductivity and acidic in character which has been observed by the addition of a base which causes a decrease in conductance of the solutions. However, the conductance data indicate the possible solvolytic reaction as:

$$La_2O_3 + 11HSO_3Cl \longrightarrow 2H[La(SO_3Cl)_4] + 3HCl + 3H_2SO_4 \quad (18)$$

$$La_2(SO_4)_3 + 8HSO_3Cl \longrightarrow 2H[La(SO_3Cl)_4] + 3H_2SO_4 \quad (19)$$

The low value of $\gamma = 0.25$ suggests that the acid $H[La(SO_3Cl)_4]$ is a very weak acid in HSO_3Cl. Moreover, it has also been observed that with increase in concentration, the conductance value decreases suggesting that there is some polymerization occurring through chlorosulphate bridging. Possible polymeric structure where each lanthanum atom acquires tetra co-ordination can be proposed as:



Weak acidic character of $H[La(SO_3Cl)_4]$ in HSO_3Cl has been established by carrying out acid/base titrations against potassium chlorosulphate. There is no sharp break in the conductance-composition curve rather there is a broad minima suggesting that the acid is quite weak. Possible neutralization reaction may be explained as:

$$K^+ + SO_3Cl^- + 3H_2SO_4 + 3HCl + H_2^+SO_3Cl + La(SO_3Cl)_4 \longrightarrow K^+ + La(SO_3Cl)_4 + 2HSO_3Cl + 3H_2SO_4 + 3HCl \quad (20)$$

Lanthanum(III) acetate forms highly conducting solutions in chlorosulphuric acid which are basic in character. After 0.12 molality, a white precipitate separates out. Further addition of lanthanum(III) acetate results in further increase in conductance of the solution along with the increase in volume of the precipitates. From the values of γ, a possible solvolytic reaction may be proposed as:

$$La(CH_3COO)_3 + 7HSO_3Cl \longrightarrow H[La(SO_3Cl)_4] + 3CH_3COOH_2^+ + 3SO_3Cl^- \quad (21)$$

It may be assumed that lanthanum(III) acetate first disproportionates to give free acetic acid which gets fully protonated in it to give highly conducting solution which has already been reported in literature [11].

Anhydrous lanthanun(III) chloride is fairly soluble in HSO_3Cl with no significant change in the conductance of the solution and solutions up to 0.12 molal concentration could be obtained. However, the experimental γ-value indicates the possible solvolytic reaction as:

$$LaCl_3 + 3HSO_3Cl \longrightarrow La(SO_3Cl)_3 + 3HCl \quad (22)$$

The solid solvate which separated out at higher concentrations was washed with anhydrous methylene chloride, dried under vacuum and analysed as corresponding to the composition $La(SO_3Cl)_3$. Infrared spectra of this compound were measured and show absorption bands at 1165, 1030, 855, 765, 640, 570 cm^{-1} and confirm the presence of SO_3Cl^- group.

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