

Alkoxide Complexes of Some Tri- & Tetra-valent Metals: Part I— Conductometric & Potentiometric Studies on Some Aluminium Alkoxide Complexes in Non-aqueous Solvents

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Received 29 May 1975; accepted 27 October 1975

The conductometric and potentiometric titrations of aluminium chloride and alkoxides (methoxide, ethoxide and isopropoxide) with alkali metal (lithium, sodium and potassium) alkoxides have been carried out in solvents like methanol, ethanol and isopropanol. The formation of a number of species like $AlCl_2(OR)$, $AlCl(OR)_2$, $(AlOR)_3$ and $M[Al(OR)_4]$ have been detected and confirmed. The effect of change in concentration of the reacting species, alkali metal ions and alkoxide groups on the formation of these species has also been investigated and discussed.

THE chemistry of a number of alkoxides and double alkoxides has been recently reviewed by Mehrotra and coworkers^{1,2}. In view of some interesting features like covalent behaviour of some double alkoxy derivatives of strongly electro-positive alkali metals, attempts have also been made to establish the stoichiometry of some of these derivatives by titrimetric techniques using chemical indicators³⁻⁶ or by physicochemical methods.⁷⁻¹⁰

Preliminary synthetic efforts¹¹ showed that amongst simple expected products, $M[Al(OPr^i)_4]$ (where $M=Li, Na$ or K), the potassium derivative appears to have unexpectedly highest solubility in organic solvents. In view of this, conductometric and potentiometric titration techniques have been employed to detect the formation and stoichiometry of complex species in the reactions of aluminium chloride or alkoxides with alkali metal alkoxides in non-aqueous solvents. The effect of varying concentration of the reactants, change of solvent and the nature of the alkali metal on the nature of the species formed during the reaction, has also been investigated.

Materials and Methods

All titrations were carried out in a dry box under absolutely anhydrous condition.

Anhydrous $AlCl_3$ (BDH) was resublimed before use. $Al(OPr^i)_3$ was distilled under reduced pressure. Lithium, sodium and potassium metals (BDH) were used after cleaning the surface. Methanol, ethanol, isopropanol, benzene and acetic acid (BDH/SM) were dried by standard methods and distilled before use. $KAl(OPr^i)_4$ and $Al(OMe)_3$ were synthesized as described in literature^{11,12}.

The conductivity measurements were carried out using a TESLA conductivity bridge having a specially fabricated conductivity cell of cell constant 0.218 cm^{-1} .

E.M.F. and pH measurements were carried out on a Radiometer pH meter having glass and calomel containing saturated KCl solution in methanol as indicator and reference electrodes respectively.

Results and Discussion

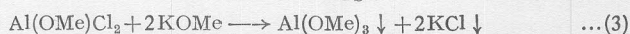
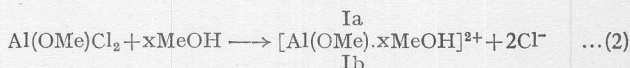
Conductometric titrations of $AlCl_3$ with MOR, where $M=Li, Na$ or K ; $R=Me, Et$ or Pr^i in non-aqueous solvents — Dissolution of a white precipitate, which appears on addition of KOMe to a solution of $AlCl_3$ ($5.57 \times 10^{-2}M$) in methanol continues up to the addition of one mole of KOMe per mole of $AlCl_3$ and the conductivity value shows a continuous increase up to one mole of KOMe (Fig. 1, curve A).

This may be due to the solubility of the products Ia (or Ib) (Eqs. 1 and 2) and limited amounts of KCl in MeOH.

Further addition of KOMe solution shows a decrease in conductivity and the formation of a bulky precipitate up to ~ 2.8 moles of KOMe/mole of $AlCl_3$. This decrease may be due to the formation of insoluble $Al(OMe)_3$ and KCl (Eq. 3). Beyond this, the flocculent precipitate dissolved and there was an increase in conductivity.

The second inflexion corresponded to the addition of ~ 3.8 moles of KOMe. The soluble species was found to be $KAl(OMe)_4$ (Eq. 4).

White crystalline particles left at the bottom of the conductivity cell were found to be KCl on analysis. Further addition of KOMe only increases the conductivity of the solution linearly and does not indicate the formation of any other higher ionic or covalent species.



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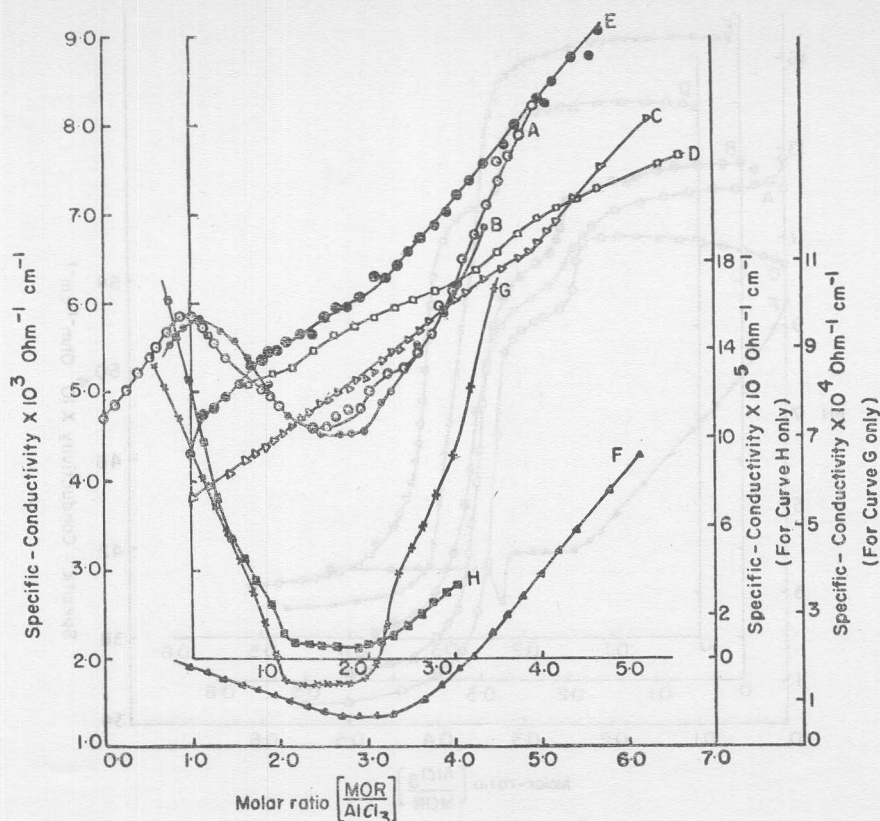


Fig. 1 — Conductometric titrations of AlCl_3 with MOR (where M = Li, Na and K; R = Me, Et and Pr) [Curve (A) KOMe $M/1.08$ vs 25 ml of AlCl_3 $M/17.94$ in MeOH; (B) KOMe $M/1.02$ vs 25 ml of AlCl_3 $M/19.16+0.8$ ml of KOMe $M/1.02$ in MeOH; (C) KOMe $M/1.53$ vs 25 ml of AlCl_3 $M/39.90$ in MeOH; (D) LiOMe $M/0.86$ vs 25 ml of AlCl_3 $M/25.68+0.8$ ml of LiOMe $M/0.86$ in MeOH; (E) NaOMe $M/1.11$ vs 25 ml of AlCl_3 $M/19.32$ in MeOH; (F) KOMe $M/0.96$ vs 35 ml of AlCl_3 $M/27.73+0.8$ ml of KOMe $M/0.96$ in MeOH (25 ml) + benzene (10 ml); (G) KOEt $M/1.00$ vs 25 ml of AlCl_3 $M/17.55+0.8$ ml of KOEt $M/1.00$ in EtOH; (H) KOPri $M/1.17$ vs 25 ml of AlCl_3 $M/22.00+1.0$ ml of KOPri $M/1.17$ in PrⁱOH]

Even on repeating the above titrations under very carefully controlled conditions, the inflexions at ~ 2.8 and ~ 3.8 moles of KOMe per mole of AlCl_3 remained unaltered. It was therefore, conjectured that this might be due to initial reaction of AlCl_3 with solvent methanol to form a product of the type $\text{AlCl}_{2.7}(\text{OR})_{0.3} \cdot x\text{ROH}$ similar to reactions of anhydrous AlCl_3 with alcohols (MeOH, EtOH and PrⁱOH)¹³. In order to check this assumption, 0.5 mole of KOMe was first added to AlCl_3 before dissolving it into methanol. It was assumed that KOMe would have converted the AlCl_3 into $\text{AlCl}_{2.5}(\text{OMe})_{0.5}$. Titration of this species with KOMe gave a titration curve (Fig. 1, curve B) almost similar to curve A except that inflexion were seen at 3.0 and 4.0 moles of KOMe instead of at 2.8 and 3.8 moles of KOMe in curve A.

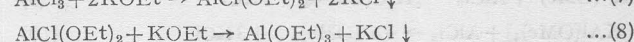
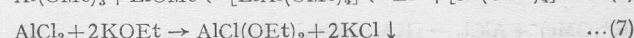
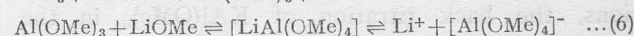
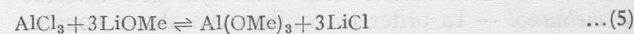
When a more dilute solution of AlCl_3 (2.51×10^{-2} M) was titrated, the conductivity continuously increased and only one inflexion point on the addition of ~ 4.0 moles of KOMe was observed (Fig. 1, curve C). The continuous increase in conductivity may be due to KCl formed remaining soluble, as its concentration does not appear to increase throughout the titration beyond its solubility limit. Therefore, the first and second inflexions obtained in earlier cases could not be detected. However the precipitation and dissolution follows a pattern similar to that observed with concentrated solutions.

Titration of AlCl_3 solution with LiOMe (Fig. 1, curve D) shows only two inflexions instead of three (Fig. 1, curve A). The disappearance of the first inflexion point may be due to much higher solubility of LiCl in MeOH. The two inflexions correspond to the reactions (5) and (6) respectively.

The titration with NaOMe showed an increase in conductivity and only one inflexion at ~ 2.0 moles of NaOMe (Fig. 1, curve E) corresponding to the formation of $\text{Al}(\text{OMe})_2\text{Cl}$.

In the titration of AlCl_3 with KOEt in ethanolic solution, the conductivity decreased up to the addition of ~ 2.0 moles (Fig 1, curve G), then remained constant up to the addition of 3.0 moles of KOEt solution and thereafter, started rising linearly. The probable reactions may be represented by Eqs. (7) and (8).

The lower degrees of association of $\text{AlCl}(\text{OEt})_2$ and $\text{Al}(\text{OEt})_3$ in ethanol compared to those of $\text{AlCl}(\text{OMe})_2$ and $\text{Al}(\text{OMe})_3$ in methanol may be responsible for this behaviour, as no flocculent precipitate was observed during the course of titration. The



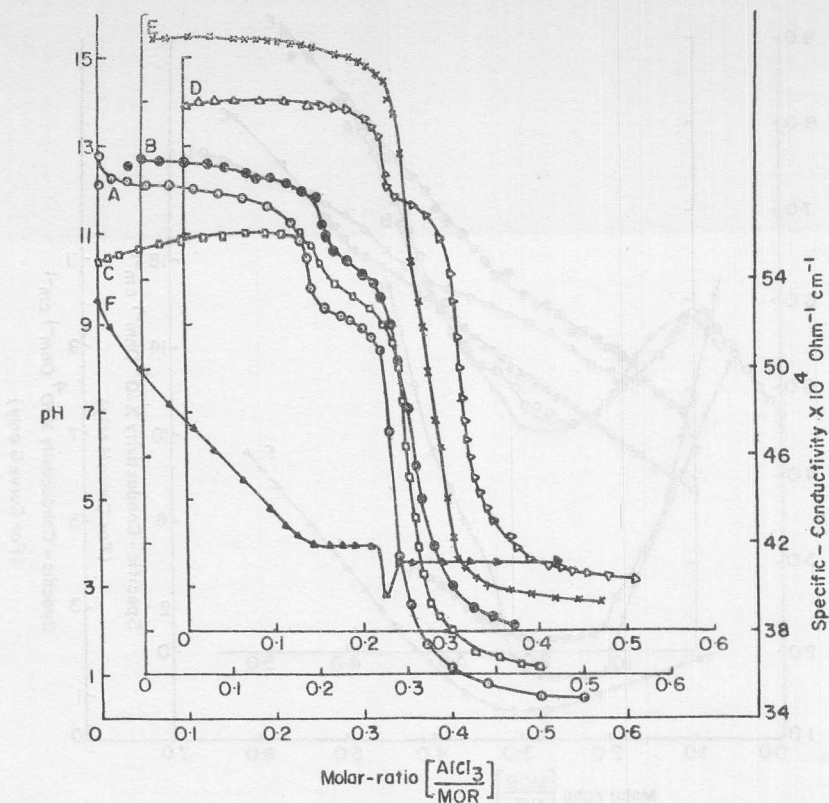


Fig. 2 — Potentiometric and conductometric titrations of 25 ml of MOR with AlCl_3 in ROH (where M = Li, Na and K; R = Me and Et) [Potentiometric titrations: Curve (A) AlCl_3 M/9.04 vs KOMe M/12.51 in MeOH; (B) AlCl_3 M/9.79 vs KOMe M/11.62 in MeOH; (C) AlCl_3 M/8.51 vs NaOMe M/10.16 in MeOH; (D) AlCl_3 M/11.85 vs LiOMe M/8.38 in MeOH; (E) AlCl_3 M/16.93 vs KOEt M/11.06 in EtOH. Conductometric titrations: (F) AlCl_3 M/7.13 vs KOMe M/11.54 in MeOH]

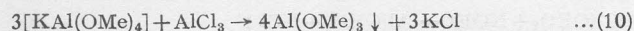
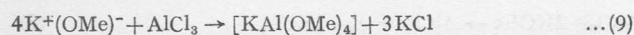
much lower solubility of KCl in ethanol (0.7 g/litre) compared to that in methanol (3.4 g/litre) would also lead to the observed differences in the titration curves.

The titration of AlCl_3 with KOPr^i in isopropanol follows a pattern (Fig 1, curve H) similar to that observed with KOEt.

The titration of AlCl_3 solution in a mixture of methanol (10 ml) and benzene (15 ml) media with KOMe follows a different pattern (Fig. 1, curve F) and formation of only one species, $\text{Al}(\text{OMe})_3$ could be detected. This difference can be understood in view of the lower solubility of KCl in methanol-benzene mixture compared to that in methanol alone.

Reverse conductometric titration of KOMe with AlCl_3 in anhydrous methanol — As expected, two inflexions corresponding to the molar ratios of 0.25: 1.00 and 0.33: 1.00 (AlCl_3 : KOMe) were observed. When AlCl_3 was added to KOMe in methanol (Fig. 4, curve F), the precipitation starts after the first inflexion point and is complete near the second inflexion point. The probable reactions may be represented by Eqs. (9) and (10).

Conductometric titration of 1:4 mixture of $\text{Al}(\text{OMe})_3$ and KOMe with acetic acid and hydrogen chloride in methanol — In order to confirm the above conclusions, the back titration of $\text{KAl}(\text{OMe})_4$ in the

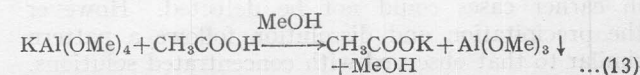
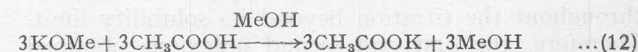
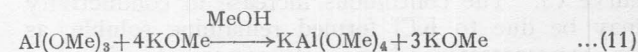


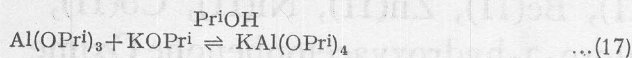
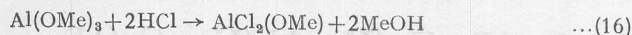
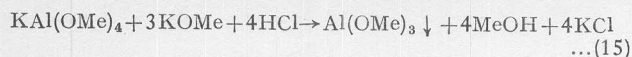
presence of excess (3 moles) of KOMe was carried out with acetic acid and hydrogen chloride in methanol.

In the titration with acetic acid the conductivity decreased up to the addition of 3 moles of the acid, indicating the neutralization of 3 moles of KOMe taken in excess (Eqs. 11 and 12).

The conductivity decreased further on the addition of acetic acid and a white precipitate corresponding to the stoichiometry of $\text{Al}(\text{OMe})_3$, separated out after the addition of 4 moles of acetic acid (Eq. 13). The conductivity increased up to the addition of 6 moles of acetic acid and thereafter became constant.

The titration when repeated with methanolic hydrogen chloride solution (Fig. 2, curve B) showed a continuous decrease in conductivity and the first inflexion corresponding to the neutralization of added KOMe (4 moles) was observed. The second inflexion obtained on further addition of HCl solution may be due to the formation of $\text{AlCl}_2(\text{OMe})$ species. The probable reactions may be as shown in Eqs. (14-16)





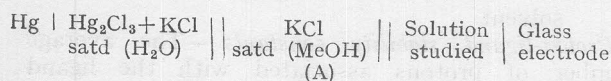
The difference in behaviour is due to the strong acidic character of HCl in comparison to acetic acid.

The formation of $\text{AlCl}_2(\text{OMe})$ species was further confirmed in a direct titration of Al(OMe)_3 suspended in methanol with HCl solution.

Conductometric titrations between aluminium alkoxides and potassium alkoxides—No inflexion was observed in the titration of Al(OMe)_3 with KOMe in methanol. However, when KOPr^i was added to Al(OPr)_3 solution in isopropanol, an inflexion at 1:1 molar ratio, indicating the possibility of a weak complex (Eq. 17), was obtained.

No definite inflexion was however, obtained in the reverse titration.

Potentiometric titrations of MOR with AlCl_3 in ROH where $M=\text{Li, Na or K}$; $R=\text{Me or Et}$ —The use of glass electrodes in non-aqueous solvents has been introduced successfully by different workers^{14,15}. In the present investigations, the electrochemical cell of the type (A) was set up for the measurement of pH and e.m.f. of solution mixtures.



Two sharp inflexions (Fig. 2, curve A) were obtained on titrating KOMe with AlCl_3 . The exact positions of inflexions were calculated by plotting a graph between $\Delta E/\Delta V$ (or $\Delta^2 E/\Delta V^2$) versus volume of AlCl_3 solution added. The inflexion points corresponded to the addition of 0.25 and 0.33 mole of AlCl_3 per mole of KOMe solution, confirming the formation of KAl(OMe)_4 and Al(OMe)_3 species.

It may be pointed out that contrary to the observations in conductometric titrations, potentiometric titration technique showed similar in-

flexions in concentrated as well as in dilute solutions (Fig. 2, curve B).

Unlike conductometric titration curves change of alkali metal from Li to Na or K in MOMe had no effect on the nature of titration curve (Fig. 2, curves C and D).

The different alkali methoxides show the formation of two different species at all concentrations, whereas the formation of only Al(OEt)_3 could be detected in the titration of KOEt with AlCl_3 in ethanol (Fig. 2, curve E). The titration of KOPr^i with AlCl_3 in isopropanol could not be accomplished due to poor solubility of AlCl_3 in isopropanol.

Titration of AlCl_3 with KOMe in methanol or KOEt in ethanol show the formation of only one species, i.e. Al(OR)_3 .

Acknowledgement

Thanks are due to CSIR, New Delhi for the award of a junior research fellowship to one of them (N.C.J.)

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