TABLE II

Data plotted in Curve II

Myristic, mole %	Palmitic, mole %	F. p., °C.
100.0	0.0	54.1
91.3	8.7	50.4
79.7	20.3	46.7
74.6	25.4	45.5
72.5	27.5	45.2
70.6	29.4	45.4
69.4	30.6	45.6
63.9	36.1	46.7
56.3	43.7	47.3
51.5	48.5	47.3
45.3	54.7	48.7
37.4	62.6	51.9
28.3	71.7	54.7
16.0	84.0	58.3
0.0	100.0	62.3

TABLE III

Data Plotted in Curve III

Undecylic, mole %	Lauric, mole %	F. p., °C.
100.0	0.0	28.2
92.4	7.6	27.6
85.4	14.6	27.4
80.0	20.0	27.3
77.6	22.4	27.4
74.6	25.4	27.6
71.3	28.7	28.0
67.6	32.4	28.6
64.6	36.4	29.2
59.3	40.7	29.9
53.8	46.2	30.7
50.9	49.1	31.1
48.7	51.3	31.5
47.5	52.5	31.6
46.3	53.7	31.9
44.0	56.0	32.4
42.6	57.4	32.8
41.2	58.8	33.1
36.1	63.9	34.4
33.0	67.0	35.1
25.0	75.0	37.4
22.6	77.4	38.0
10.3	89.7	41.2
9.8	90.2	41.4
0.0	100.0	43.9

and lauric acids is 19.6°, at a composition of 0.725 mole of capric acid and 0.275 mole of lauric acid. Curve III shows the freezing points of mixtures of undecylic and lauric acids. An examination of this curve will indicate a small but definite change in direction near the middle of the system. This is somewhat similar to what Smith[6] obtained for the stearic–margaric system, and according to him is just what would occur if a compound was formed.

Summary

The following binary systems of fatty acids have been investigated, *viz.*: myristic–palmitic, capric–lauric, and undecylic–lauric.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA]

The Effect of Anions on the Titration of Aluminum Chloride

BY T. H. WHITEHEAD, J. P. CLAY AND C. R. HAWTHORNE

Introduction

The potentiometric titration of aluminum salt solutions by sodium hydroxide has been studied by a number of investigators.[1] All of these have noted the important role played by the anion of the aluminum salt. If the amount of aluminum in the salt is calculated on the basis of equivalents of sodium hydroxide required to produce an inflection of the titration curve in the region of *p*H 7, the values obtained are invariably too low. The most recent explanation offered for this discrepancy by Jander[1] is that the hydrolytic products of aluminum salts are complex compounds to which may be assigned Werner structures.

(1) Blum, THIS JOURNAL, **35**, 1499 (1913); Hildebrand, *ibid.*, **35**, 863 (1913); Davis and Farnham, *J. Phys. Chem.*, **36**, 1057 (1932); Treadwell and Zurcher, *Helv. Chim. Acta*, **15**, 980 (1932); Jander and Jahr, *Kolloid Beihefte*, **43**, 295 (1936).

One of the authors has reported[2] previously on the effect of anions in changing the *p*H values of basic aluminum salt solutions and aluminum oxychloride hydrosols.

The present paper is a study of the effect of several anions on the potentiometric titration of aluminum chloride solution in order to compare these effects with previous studies. The role of some cations also is noted.

Experimental

All reagents were of C. P. quality and tested for purity. Solutions were made up in Pyrex glassware and standardized in the usual manner.

All potentiometric titrations were carried out at 25° using a saturated quinhydrone electrode with bright platinum electrodes and saturated calomel half-cell.

(2) Whitehead and Clay, THIS JOURNAL, **56**, 1844 (1934).

Fifty cubic centimeters of 0.1 N aluminum chloride solution was used for each titration. Calculated amounts of the various salts were dissolved in the aluminum chloride solution before titration with sodium hydroxide solution. Each salt was tested in 50 cc. of water and if the pH value exceeded 7.0, enough hydrochloric acid solution was added to bring the pH value to 7.0. Then this same amount of acid was added to the aluminum chloride solution and added salt before titration with sodium hydroxide.

The aluminum content in each case was calculated from the amount of sodium hydroxide solution required to produce a pH value of 7.0 on the potentiometric titration curve. In every case this corresponded to the principal inflection of the curve.

Table I gives the results obtained when the various salts were added in such amounts as to make each anion concentration 0.0333 N.

TABLE I

Salt added	Milliequivalents of aluminum Present	Found
No salt	5.00	4.71
Potassium nitrate	5.00	4.66
Potassium acetate	5.00	4.62
Potassium sulfate	5.00	4.39
Sodium succinate	5.00	4.15
Potassium tartrate	5.00	3.72
Ammonium oxalate	5.00	3.71
Sodium oxalate	5.00	3.71
Potassium oxalate	5.00	3.71
Sodium citrate	5.00	3.38

These results show an order for the effect of the anions: citrate > oxalate ≧ tartrate > succinate > sulfate > acetate > nitrate. They also show the relative similarity of sodium, potassium, and ammonium ion in combination with oxalate ion.

TABLE II

Salt added	Milliequivalents of aluminum Present	Found
Potassium nitrate	5.00	4.61
Potassium acetate	5.00	4.46
Potassim sulfate	5.00	4.34
Sodium succinate	5.00	3.82
Potassium tartrate	5.00	3.68
Ammonium oxalate	5.00	3.32
Sodium oxalate	5.00	3.31
Potassium oxalate	5.00	3.31
Sodium citrate	5.00	2.84

Table II gives the results obtained when the same salts were added in such amounts as to make each anion 0.050 N in concentration.

Table II shows quite clearly that increased concentration of anion produced an increased effect upon the titration, shifting the inflection point more in each case, but the order of effect remained the same as in Table I.

Discussion

If the hydrolysis of aluminum chloride is pictured on the Werner–Pfeiffer basis, a basic aluminum salt will be postulated. It is well known that the addition of sodium hydroxide solution to aluminum chloride produces more basic salts of aluminum, so that according to the Werner theory there would be hydroxo groups attached to the central aluminum ion. If the anion of these added salts replaced hydroxo groups in the complex ion, these hydroxo groups would be forced into the outer solution and increase the basicity of the solution. Therefore a value of pH 7.0 would be reached more quickly when a salt was added than when no salt was added. This explanation is supported by the work of Jander[1] and by that of Thomas and Vartanian[3] who found that the effectiveness of acids in peptizing precipitated hydrous alumina varied with the anion of the acid. The order of acid anions given by them agrees with the anion order reported in this paper.

Conclusions

1. Certain anions affect the titration of aluminum chloride solution by sodium hydroxide.

2. The order of their effect is: citrate > oxalate > tartrate > succinate > sulfate > acetate > nitrate.

3. The cations, sodium, potassium, and ammonium seem to have relatively little effect on this titration.

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(3) Thomas and Vartanian, THIS JOURNAL, 57, 4 (1935).