Composition and Stability of the Chelate between Aluminium (III) and Sulpho-Dichloro Hydroxy-Dimethyl Fuchson Dicarboxylic Acid (Trisodium Salt) and Analytical Applications of the Reaction

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With 8 Figures

Abstract

The reaction of sulpho-dichloro hydroxy-dimethyl fuchson dicarboxylic acid (trisodium salt) with aluminium (III) ions in aqueous solution to give a stable violet complex has been studied in detail, regarding the composition and stability of the chelate and its analytical applications. Absorbance as well as electrical conductance measurements have been performed to determine the composition of the chelate which comes out to be 1:1 (metal:chelating agent). The chelate has its maximum absorbence at 545 mμ, and is stable between pH 3.05 and 6.60. The system obeys Beer's Law over a concentration range of 0.013 to 0.980 p. p. m. of aluminium. The value of log K, as calculated by the absorbance data is 4.3 $\pm$ 0.1 at pH 4.0 $\pm$ 0.2, temperature 30 °C and ionic strength 0.2 (KCl). The corresponding free energy change of formation has also been evaluated. The effects of pH, temperature, time and diverse ions on the reaction have been studied and suggestions have been advanced on the possible position of the chelate ring in the complex. A procedure for the colorimetric micro-determination of aluminium has also been suggested.

Introduction

Among the members of the hydroxy-triphenylmethane group of dyes, many of which are well known to form coloured reaction products with metallic ions in solution and consequently are used as metallochromic indicators in complexometric titrations, as colorimetric reagents for the detection and determination of micro amounts of metals, and as spot reagents, is sulpho-dichloro hydroxy-dimethyl fuchson dicarboxylic acid (trisodium salt) commonly known as Chrome Azurol S (Colour Index 723). The reagent has the structure:

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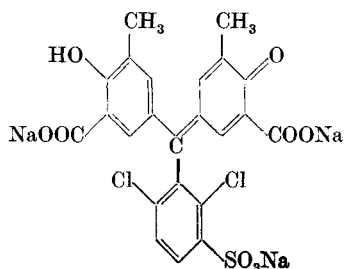
I. Chrome Azurol S (abbreviated as CAS)

The main use of the reagent has been as a metallochromic indicator in complexometric titrations[1-7]) due to its colour forming reactions with a number of metal ions. It has also been employed by a few workers as a colorimetric reagent[8-10]). The work on the composition and stability of the chelates of this reagent with metals had not been reported, and the present studies have hence been undertaken with this end in view.

As described earlier[11)12]), Chrome Azurol S forms stable coloured chelates in aqueous solution with a wide variety of metallic ions including copper (II), beryllium (II), magnesium (II), cadmium (II), aluminium (III), scandium (III), yttrium (III), lanthanum (III), and other lanthanons, cerium (IV), titanium (IV), zirconium (IV), thorium (IV), uranium (VI), iron (III), cobalt (II), nickel (II) and palladium (II) under different experimental conditions. The present communication records the investigations with the aluminium (III) — Chrome Azurol S chelate.

Experimental

Materials. Standard solutions of aluminium sulphate were prepared by dissolving the BDH Analar sample in double distilled water. BDH indicator Chrome Azurol S (trisodium

1) H. H. Willard and C. A. Horton, Anal. Chem. 22, 1190 (1950).

2) M. Theis, Z. analyt. Ch. 144, 106, 192, 275 (1955).

3) A. Musil and M. Theis, Z. analyt. Ch. 144, 427 (1955).

4) J. S. Fritz and M. O. Fulda, Anal. Chem. 26, 1206 (1954).

5) M. Malát and M. Tenérova, Chem. Listy 51, (11), 2135 (1957).

6) T. Matsuo, Bunseki Kagaku 7, 557 (1958).

7) S. P. Sangal and A. K. Dey, Z. analyt. Ch. 178, 415 (1961).

8) D. Ravinson and J. H. Harley, Anal. Chem. 25, 794 (1953).

9) B. J. Macnulty and L. D. Woolard, Anal. chim. Acta 14, 452 (1956).

10) L. Silverman and M. E. Shidelar, U. S. At. Energy Comm. NAA-SR-2686 21pp. (1958); Anal. Chem. 31, 152 (1959).

11) A. K. Dey, S. C. Srivastava, R. L. Seth, S. N. Sinha and S. P. Sangal, Proc. 7th Int. Conf. on Coord. Chem., Stockholm (Sweden), Paper no. 7 B 5 (1962).

12) S. C. Srivastava and A. K. Dey, J. Inorg. Nucl. Chem., (in press) Inorg. Chem., (communicated).

salt; colour Index 723) was used for making the reagent solutions which were standardised by determining their sulphur content. Double distilled carbon-dioxide free water was used and always fresh solutions were prepared. Other reagents employed were of the reagent grade.

Absorbance measurements. A Unicam SP 500 spectrophotometer was employed for carrying out measurements of absorbance. All measurements were noted against distilled water blanks and 10 mm. matched silica cells were used. At wavelengths of 625 mμ or below, the ultrasensitive phototube was used and above this, the red sensitive phototube. The phototube circuit was kept at maximum sensitivity. The slit width under these conditions corresponds to very nominal band widths, and usually ranges between 0.030 mm and 0.080 mm.

Colorimetric measurements. A KLETT-SUMMERSON photo-electric colorimeter was employed using the KLETT filter no. 54 green (transmission 520—580 mμ). The KLETT test tubes in which the solutions were kept for measurements had a uniform diameter of 10 mm.

pH-measurements. pH of the solutions was measured with a LEEDS and NORTHRUP direct reading pH indicator with a glass-calomel electrode system.

Electrical conductance measurements. The measurements of electrical conductance were carried out with a LEEDS and NORTHRUP KOHLRAUSCH Slidewire with an audiofrequency oscillator in the circuit and using a dip type measuring cell having a cell constant 0.580.

Procedure

All experiments were carried out in an airconditioned room maintained at $30° \pm 1 °C$. The total volume of the mixtures was kept 50 ml (variation in the method of continuous variations using absorbance measurements was done within 25 ml and the volume then raised to 50 ml after adding potassium chloride for controlling the ionic strength). The pH of all the solutions and mixtures was adjusted to 4.0 ± 0.2 by adding sodium hydroxide or hydrochloric acid, and they were then thermostated at $30° \pm 0.01 °C$ for about an hour before use. The ionic strength was kept constant at 0.2 by the addition of potassium chloride.

The composition of the chelate was established by three different methods viz., (i) the method of continuous variations[13] (using absorbance and electrical conductance measurements), (ii) mole ratio method[14] and (iii) slope ratio method[15] (both using absorbance measurements).

Mole ratio method involves the preparation of a series of solutions containing a constant amount of the metallic ion, and with increasing ratios of the metal to the reagent (or vice-versa). The absorbances of the mixtures are when plotted against the concentration ratios, the curve rises from the origin as a straight line and breaks sharply at the stoichiometric ratio of the reactants in the complex.

The stoichiometry in the slope ratio method is arrived at by comparing the slopes of the two straight line plots obtained by varying one component in presence of a large excess of the other.

Evaluation of the stability constant. A convenient method for the calculation of the apparent stability constant is the method of ANDERSON and coworkers[16][17] based on the

13) P. JOB, Compt. rend. 180, 928 (1925); Ann. Chim. (10)9, 113 (1928).

14) J. H. YOE and A. L. JONES, Ind. Engng. Chem., Anal. Ed., 16, 111 (1944).

15) A. E. HARVEY and D. L. MANNING, J. Amer. chem. Soc. 72, 4488 (1950).

16) R. C. ANDERSON and S. E. TURNER, J. Amer. chem. Soc. 70, 1195 (1948); 71, 909 (1949).

17) R. T. FOLEY and R. C. ANDERSON, J. Amer. chem. Soc. 71, 912 (1949).

comparison of the composition of mixtures having identity of colour i. e., the same absorbance values. The necessary condition for the application of this method is that the interacting solutions forming the complex should be colourless. DEY and coworkers [18]) modified the method for calculating the stability of complexes where one of the reactants may be coloured. The method of continuous variations is employed using equimolecular solutions and the total volume is kept constant. The absorbances of the mixtures are noted at the λ_{max} of the complex and plotted against [M]/[M] + [Ke], where [M] is the concentration of the metal ion and [Ke] that of the chelating agent. The absorbance of the mixtures is due to the chelate and the reagent, as the metal ions are mostly colourless at high dilutions. With the progressive increase in the concentration of the metal ions, [Ke] decreases and in the descending portions of the curves, where [M] is in excess, a large majority of the reagent may be assumed to be bound up in the complex and the amount of the free chelating agent is negligible to contribute to the total absorbance of the system. The absorbance in these portions is therefore due to the chelate only. When a number of curves are plotted, then at the same value of absorbance, the respective amounts of the chelate formed are identical in every case.

The concentration of the chelate can be calculated by the following procedure. In an equilibrium of the type involving a metal ion and a chelating agent in the ratio 1:1,

$$M + Ke \rightleftharpoons M(Ke),$$
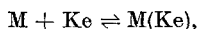
the a stability constant is given by:

$$K = \frac{x}{(a - x)(b - x)} \tag{i}$$

where x is the concentration of the chelate at equilibrium and a and b respectively are the initial concentrations of the metal and the chelating agent. Taking two concentrations of the reagents i. e., two values of a and b, where absorbance is the same, the value of x will also be the same.

Hence

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)} \tag{ii}$$

or

$$x = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)} \tag{iii}$$

x may thus be evaluated and therefrom K with the help of the expression (i).

The value of the stability constant has been calculated in the present case by the above method.

Results and Discussion

Behaviour of the Reagent as a Colloidal Electrolyte. It was found that Chrome Azurol S, like most of the organic chromophoric reagents displays the behaviour of a colloidal electrolyte and hence extremely dilute solutions should be employed for physico-chemical measurements [19]). In the present studies, solutions of the order $\approx 10^{-4}$ and 10^{-5} M were used.

[18]) A. K. MUKHERJI and A. K. DEY, J. Inorg. Nucl. Chem. **6**, 314 (1958); Anal. Chim. Acta **18**, 324 (1958).

[19]) S. C. SRIVASTAVA, R. L. SETH and A. K. DEY, J. Colloid Sci. **17**, 86 (1962).

Rate of Colour formation and stability of coulor at room temperature. The colour formation is observed to be instantaneous. The mixtures were, however, kept for about an hour after preparing them, to allow for necessary equilibration. A mixture containing 1.00×10^{-4} M each of Chrome Azurol S and aluminium ion retained its absorbance value even after several days, a condition which is adequate for the application of the reaction in analysis.

Influence of temperature. The colour intensity is independent of the changes in temperature over a wide range, as clear from the table below.

Table I

Influence of temperature

Concentration of aluminium ion $= 1.00 \cdot 10^{-4}$ M
Concentration of CAS $= 1.00 \cdot 10^{-4}$ M
pH of the mixture $= 4.0 \pm 0.2$

Tempera-ture °C	5	10	20	30	40	50	60	70	80	90	95
Colori-meter reading	400	400	400	400	400	400	400	400	400	400	400

Order of addition of the reagents. There was no significant change in the observations, when the order of the addition of reagents was alternated.

Beer's Law. To determine, whether or not the aluminium-CAS complex obeys Beer's Law, a calibration curve was prepared. A series of solutions were prepared containing a constant excess of the reagent and varying concentrations of the metal ion. The colour intensity was measured against a reagent blank. The data on plotting graphically showed that the complex concentration is proportional to the absorbance between the concentration limits of 0.013 and 0.980 p. p. m. of aluminium.

Nature of the complex in solution. The method of Vosburgh and Cooper was employed to determine the nature of the complex in solution. Mixtures containing varying proportions of metal to Chrome Azurol S (i. e. 1:0.5, 1:1, 1:2, 1:3 etc.) were prepared keeping the total volume 50 ml. Absorbances were then measured at suitable wavelength intervals between a range of 355 mμ and 700 mμ. The observations plotted graphically in Fig. 1 show that the region of maximum absorbance of the reagent lies at 490 mμ at pH 4. This is clear from the curve A in the figure. In curves B, C, D, E and F, the region of maximum absorption shifts to 545 mμ.

This clearly shows that only one complex is formed in solution between aluminium and Chrome Azurol S under the conditions of study.
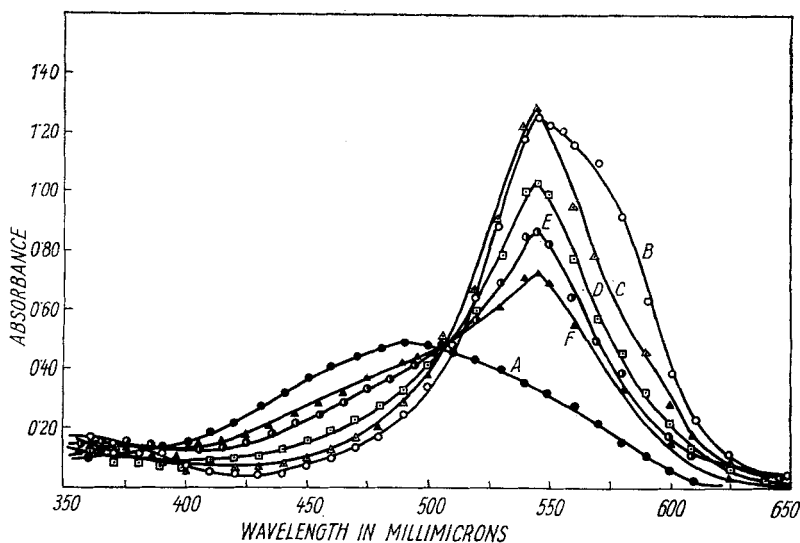

Fig. 1. Absorption spectra studies of mixtures of aluminium sulphate and Chrome Azurol S, pH 4.0 ± 0.2, 0.2 (KCl).
Curve A, Reagent $5.00 \cdot 10^{-5}$ M;
Curve B, $c = 10.00 \cdot 10^{-5}$ M; $p = 0.5$;
Curve C, $c = 5.00 \cdot 10^{-5}$ M; $p = 1.0$;
Curve D, $c = 2.50 \cdot 10^{-5}$ M; $p = 2.0$;
Curve E, $c = 1.66 \cdot 10^{-5}$ M; $p = 3.0$;
Curve F, $c = 1.25 \cdot 10^{-5}$ M; $p = 4.0$

Stoichiometry of the Components. The ratio of aluminium to Chrome Azurol S in the chelate has been established by the aforementioned methods using measurements of absorbance as well as electrical conductance. A few of the typical results are represented in Figs. 2—6.

The results obtained by the method of continuous variations are summarised in the tables below, where c represents the metal-ion concentration and p, the ratio c'/c, c' being the concentration of Chrome Azurol S.

Results summarised in the above tables clearly indicate that the ratio of $Al_2(SO_4)_3$ to Chrome Azurol S in the chelate is $1:2$ or metal ion to the chelating agent as $1:1$. The composition of the chelate may hence be represented as Al (CAS).

The results from the mole ratio method (Fig. 5) and the slope ratio method (Fig. 6) also lend a corroboration for the same composition of the chelate.

Table II

Composition of the chelate by the continuous variations method using
absorbance measurements

Figure	Curve	$c \cdot 10^4$ (M)	p	λ (mμ)	Peak occurs at volume of $Al_2(SO_4)_3$ (ml)	Composition of the chelate ($Al_2(SO_4)_3$:CAS)
2	A	2.00	1.00	545	8.33	1:2
	B	1.60	1.00	545	8.33	1:2
	C	1.33	1.00	545	8.33	1:2
(Fig. not shown)	A	2.00	1.00	560	8.33	1:2
	B	1.60	1.00	560	8.33	1:2
	C	1.33	1.00	560	8.33	1:2
3	A	1.33	1.50	545	10.70	1:2
	B	2.00	0.66	545	6.25	1:2
(Fig. not shown)	A	1.33	1.50	560	10.70	1:2
	B	2.00	0.66	560	6.25	1:2

Table III

Composition of the chelate by the continuous variations method using
conductance measurements

Figure	Curve	$c \cdot 10^4$ (M)	p	Peak occurs at volume of $Al_2(SO_4)_3$ (ml)	Composition of the chelate ($Al_2SO_4)_3$:CAS
4	A	6.66	1.00	16.7	1:2
	B	5.00	1.00	16.7	1:2
	C	3.33	1.00	16.7	1:2
(Fig. not shown)	A	3.33	2.00	25.0	1:2
	B	3.33	1.50	21.4	1:2
	C	6.66	0.50	10.0	1:2

Evaluation of the stability constant. The value of log K as
calculated by the method described earlier (Fig. 7) comes out to be 4.3 $\pm$ 0.1
at pH 4, temperature 30 °C and ionic strength 0.2 (KCl). The corresponding
free energy change of formation has been evaluated to be -6.0 ± 0.2 K
Cals.

Suggestions on the structure of the chelate. The reagent
alone shows maximum absorption at 425 mμ in a neutral or slightly acidic
medium, and at 465 mμ and 490 mμ in an acidic medium. In a strongly
alkaline medium where the structure suggests the removal of the phenolic
hydrogen by ionisation the λ_{max} is however, found to lie at 595 mμ. Hence
in the present case, it is likely that chelation occurs between the phenolic

oxygen and the adjacent carboxylic oxygen and not between the quinoid oxygen and the oxygen of the adjacent carboxylic group, because the λ_{max} of the chelate (545 mμ) is found to lie nearer to 595 mμ than to 425 mμ or 465 mμ. This would lead to the formation of an anionic complex species
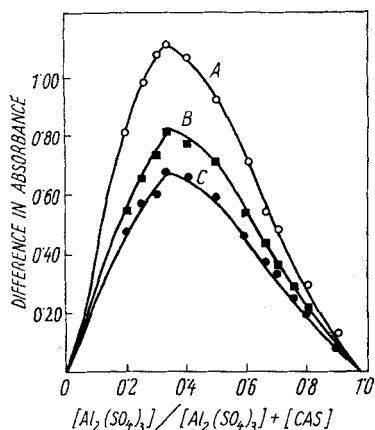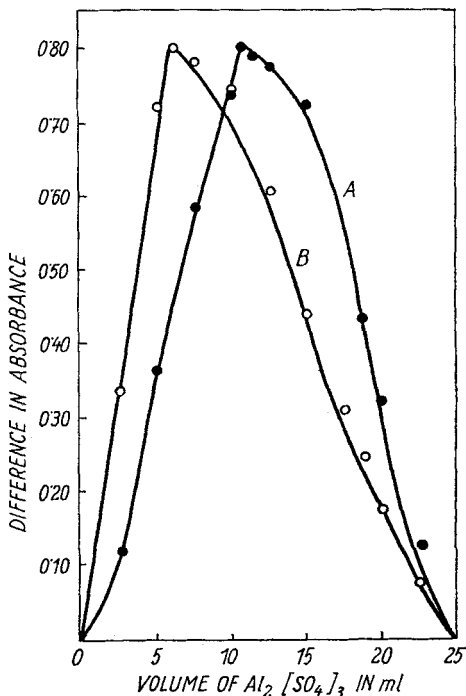

Fig. 2. Determination of the composition from absorption spectra studies of equimolecular solutions at 545 mμ; p = 1, pH 4.0 $\pm$ 0.2, μ 0.2 (KCl).
Curve A, c = 2.00 $\cdot$ 10^{-4} M;
Curve B, c = 1.60 $\cdot$ 10^{-4} M;
Curve C, c = 1.33 $\cdot$ 10^{-4} M

Fig. 3. Determination of the composition from absorption spectra studies of non-equimolecular solutions at 545 mμ, pH 4.0 $\pm$ 0.2, μ 0.2 (KCl).
Curve A, c = 1.33 $\cdot$ 10^{-4} M; p = 1.50;
Curve B, c = 2.00 $\cdot$ 10^{-4} M; p = 0.66

and this fact has been confirmed by the complete adsorption of the purple colour of the chelate when passed through a column of ion exchange resin Amberlite IR-45 (OH) (BDH AnalaR).

Effect of hydrogen-ion concentration on the stability of the chelate. The absorbances of mixtures containing aluminium sulphate and Chrome Azurol S in the ratio 1:2 (c = 2.5 $\times$ 10^{-5} M; c' = 5.0 $\times$ 10^{-5} M) at different pH were measured at various wavelengths. The results have been plotted graphically in Fig. 8. It may be seen that the wavelength of maximum absorbance of the chelate remains the same (545 mμ) between
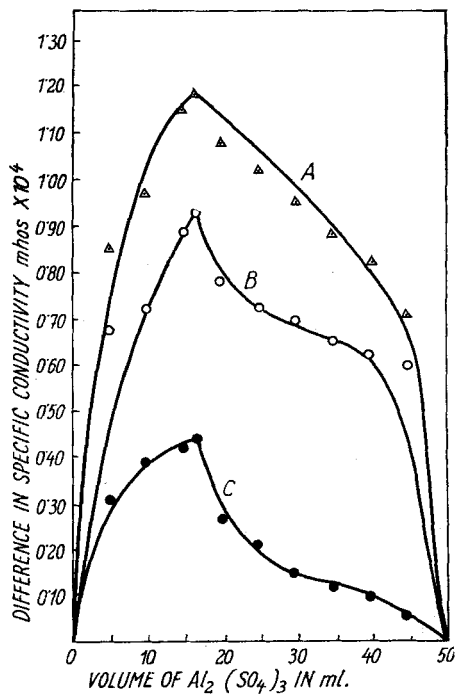
Fig. 4. Determination of the composition
from electrical conductance studies of equi-
molecular solutions (p = 1).
Curve A, c = 6.66 · 10⁻⁴ M;
Curve B, c = 5.00 · 10⁻⁴ M;
Curve C, c = 3.33 · 10⁻⁴ M
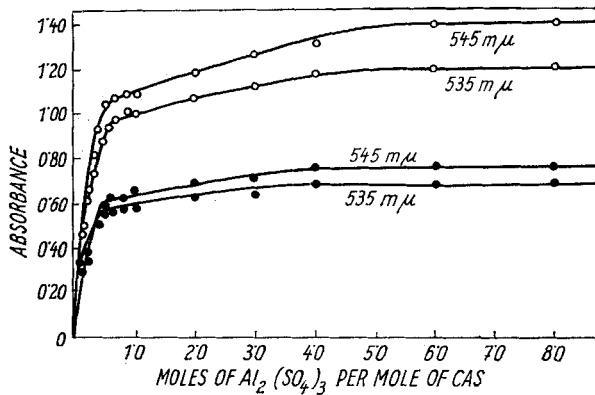

Fig. 5. Determination of the composition from absorbance
studies by the mole ratio method, pH 4.0 = 0.2, μ 0.2 (KCl),
concentration of CAS.
● 3.33 · 10⁻⁵ M; ○ 5.00 · 10⁻⁵ M

pH 3.05 and 6.60, indicating thereby that the chelate is stable within this pH range. The colour intensity also remains the same between pH 4.5 and 6.0.

Sensitivity of the reaction. According to Sandell's expression, the sensitivity is 0.00067 γ/cm^2 at 545 mμ. The practical sensitivity based on an absorbance of 0.010 unit is 0.0067 γ/cm^2.
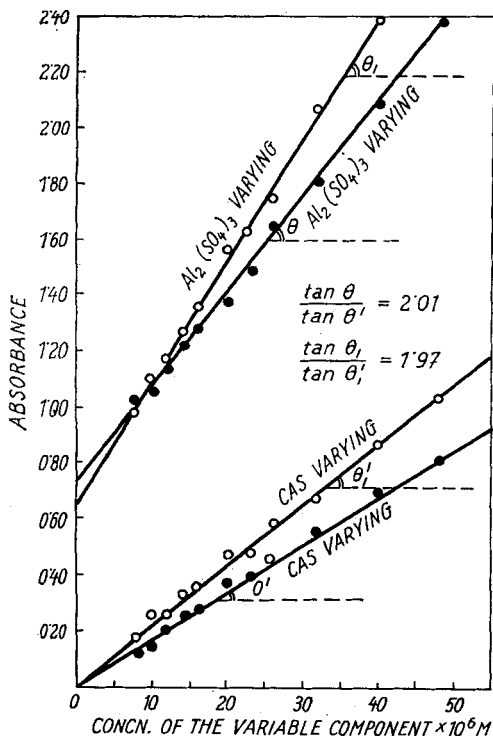

Fig. 6. Determination of the composition from absorbance studies by the slope ratio method. pH 4.0 $\pm$ 0.2, concentration of the excess component 1.6 · 10^{-4} M, ● 635 mμ, ○ 545 mμ
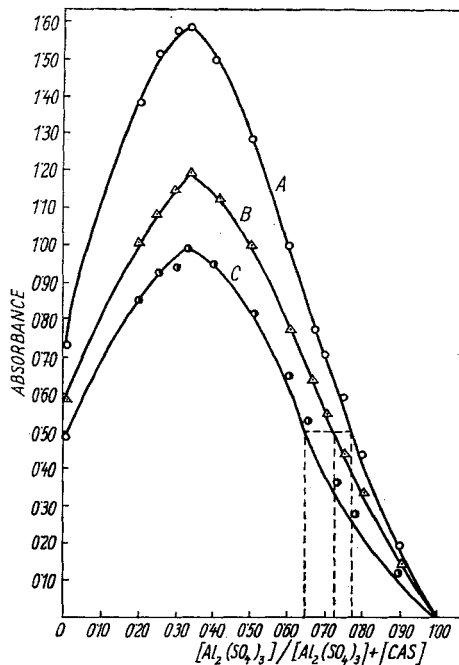
Fig. 7. Determination of the stability constant from absorbance data at 545 mμ. Concentration, pH and μ the same as in Fig. 2

Effect of diverse ions. The effect of a large number of cations and anions on the system has been studied and the tolerance limits determined in each case. The metal ions that react with Chrome Azurol S in an acidic medium exclusive of aluminium are copper, beryllium, zirconium, thorium, uranium, iron and palladium. These ions and also carbonate, borate, fluoride, oxalate and tartrate, interfere in the determination of aluminium at all concentrations.

Suggested procedure for the colorimetric determination of aluminium. For the determination of aluminium using Chrome Azurol S as a reagent, the following procedure may be suggested. The interfering substances as mentioned above should be removed from the sample by the usual methods. The pure solution of aluminium ions thus obtained
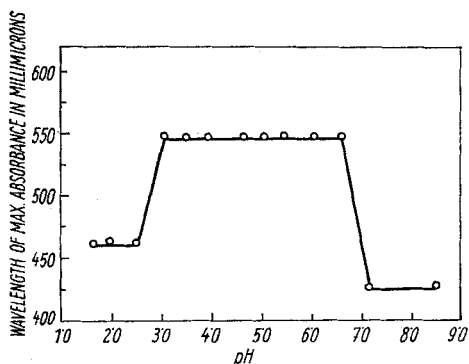

Fig. 8. Variation in the region of maximum absorption of the chelate with change in hydrogen-ion concentration.
$c = 2.5 \cdot 10^{-5}$ M; $p = 2.0$

should be diluted suitably and treated with a freshly prepared solution of Chrome Azurol S. The reagent should be present in about 8—10 fold molar excess. The pH should be maintained at 4.0 ± 0.2. The absorbance may be measured with a spectrophotometer and compared with a standard calibration curve to give the amount of aluminium.

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