Chelate Formation between Chromate Ions and Disodium-1, 8-dihydroxy Naphthalene-3, 6-disulphonate

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Disodium-1, 8-dihydroxy naphthalene-3, 6-disulphonate, commonly known as chromotropic acid (sodium salt), has found application in colorimetric analysis.[1] It has been reported to yield coloured complexes with vanadium, titanium, mercury, silver, uranium and ferric ions. It has also been found to yield coloured reactions with various other metals.[2,3] More detailed work on the application of this reagent in the estimation of titanium has been done by Sommer and his co-workers. Sommer and Okâĉ[4] discussed the functional analytical groups for titanium. The spectrophotometric determination of titanium using this reagent has been described by Sommer,[5] and Sommer and Benisêk[6] made a polarographic study of the reaction between titanium and chromotropic acid. Sommer[7,8] then extended the work, working out the details of the reaction and determining the composition and the stability constant. He also discussed the structure. The titanium-chromotropic acid system was also described by Shnaiderman[9] and Babko[10].

Heller and Schwarzenbach[11] studied the chelate formed between trivalent iron and chromotropic acid. They were of the opinion that a six-membered ring is formed and that iron is chelated between the two phenolic oxygens. The formation of manganese(II),

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[1] The B. D. H. Book of Organic Reagents, Poole, p. 33 (1949).

[2] K. C. Mathur and A. K. Dey, *Z. anal. Chem.*, **154**, 347 (1957).

[3] L. Sommer, ibid., **163**, 412 (1958).

[4] L. Sommer and A. Okâĉ, *Chem. Listy.*, **50**, 1746 (1956).

[5] L. Sommer, ibid., **51**, 875 (1957).

[6] L. Sommer and L. Benisêk, ibid., **50**, 1215 (1956).

[7] L. Sommer, Intl. Conf. Coordination Chem, Rome (1957).

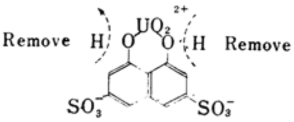
[8] L. Sommer, *Chem. Listy.*, **50**, 1729 (1956); Symp. Chem. Coordination Compounds, Agra (1959).

[9] S. Ya. Shnaiderman, *Z. neorg. Khim.*, **2**, 2122 (1957).

[10] A. K. Babko and O. I. Popva, ibid., **2**, 138 (1957).

[11] E. Heller and G. Schwarzenbach, *Helv. Chem. Acta*, **34**, 1869 (1959).

lead and copper chelates has also been described.[12] Mathur and Dey[2] had earlier reported the formation of a red-coloured chelate between uranium and chromotropic acid. Also, Ware[13] had earlier suggested the use of chromotropic acid for the colorimetric determination of uranium, but no details have been recorded. Mukerji and Dey[14,15] have, however, described in detail the colorimetric determination of uranium with this reagent and studied the interference of foreign ions. They also determined the composition of the chelate by conductometric methods and found it to be 1 : 1. Banerji and Dey[16] studied the uranium - chromotropic acid chelate and determined the composition, the stability, the formation constant and the free energy of formation of the chelate. This work confirmed the earlier views that a 1 : 1 chelate is formed; therefore, the following structure for the chelate was proposed:



Uranium - Chromotropic acid chelate

The chelation involved the phenolic oxygens, as had been suggested by the earlier workers.

In the course of these investigations, a detailed study was made of the reaction of chromotropic acid with different metal ions. Details of this are presented in Table I. It may be observed therein that the chromate ion develops a very beautiful red colour with chromotropic acid; this chelate was, therefore, investigated with regard to its composition, stability, formation constant and free energy of formation by the spectrophotometric method. The composition, as investigated by the conductometric method, has also been described.

Experimental

Materials.—Potassium chromate of BDH Analar quality was dissolved in distilled water. A concentrated stock solution of 0.01 M was then prepared. Acid was added to prevent any possible hydrolysis. Standard solutions were prepared from this solution by dilution.

BDH reagent-grade disodium-1, 8-dihydroxy naphthalene-3, 6-disulphonate, commonly known as chromotropic acid (abbreviated as CAD), was used. A 0.01 M stock solution was prepared. Suitable standard solutions were prepared from this solution by dilution.

In all cases freshly-prepared solutions were used. Extremely dilute solutions were used for these studies so that the contraction in volume, if any, would be negligible.

The absorbance measurements were made on a Hilger Uvispek spectrophotometer using glass cells one centimeter thick. The individual solutions and mixtures were kept for 30 min. before absorbance measurements were made in order for them to attain equilibrium. All observations were made in the 2—3 pH range on a Phillips pH meter (GM 4494).

The composition of the chromate - chromotropic acid obtained from absorbance studies has also been investigated by adopting the conductometric method; the results thus obtained support those obtained by spectrophotometric methods. The electrical conductivity studies were made on a Serfass conductivity bridge.

Optimum Conditions.—The optimum conditions for the formation of the chelate were determined, and then these conditions were maintained throughout the studies.

The Order of the Addition of Reagents.—Studies were made of the addition of the chelating agent to the metal solution and vice versa. It was found that there was no change, whether the metal was added to the reagent and vice versa. To maintain uniformity, however, the chelating agent was added to the metal solution.

The Effects of Time.—Time effects were also studied; it was found that the chelate maintained its stability for more than twenty-four hours and, as such, was in keeping with the investigations here.

Acid Added to Prevent Hydrolysis.—Acid was added wherever neccessary to prevent hydrolysis.

Colour Formation with Inorganic Ions.—For studying the colorimetric reactions with various metal ions, a 0.05 M solution of chromotropic acid was prepared in distilled water. Solutions of various metallic salts using analytical-grade reagents was made of a 0.1 M concentration in distilled water, acid being added in several cases to prevent hydrolysis.

In several test tubes 1 ml. of solutions were placed; then two drops of the reagent solution were added to each and the colour noted visually. This colour was then compared with an equal amount of the reagent diluted to the same extent. The results have been recorded in Table I.

The Nature of the Complexes Formed.—The method described by Vosburg and Cooper[17] was employed to determine the nature of the complexes formed in solution. Mixtures containing different proportions of chromium - chromotropic acid (1 : 1, 1 : 2, 1 : 3, and 1 : 4) were prepared, and the absorbances of the solutions at different wavelenghts were measured. The exact compositions have been tabulated in Table II.

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[12] A. E. Martell and M. Calvin, "Chemistry of Metal chelate compounds," Prentice Hall, N. Y. (1952), p. 503.

[13] E. Ware, U. S. Atomic Energy Commission Rep. MDDC (1945).

[14] A. K. Mukerji and A. K. Dey, *J. Ind. Chem. Soc.*, **35**, 113 (1958).

[15] A. K. Mukerji and A. K. Dey, *J. Inorg. Nucl. Chem.*, **6**, 314 (1958).

[16] S. K. Banerji and A. K. Dey, *Nature*, **197**, 1002 (1963).

[17] W. C. Vosburg and Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941); **64**, 1630 (1947).

TABLE I

	Salt	Coloration	Remark
1	Reagent	Light brown	
2	Li CH_3COO	Light brown	No particular change
3	$Mg(NO_3)_2$	Light brown	No particular change
4	$BaCl_2$	Light brown	No particular change
5	$Bi(NO_3)_3$	Light brown	No particular change
6	$SrCl_2$	Light brown	No particular change
7	$Zr(SO_4)_2$	Light brown	No particular change
8	$MnCl_2$	Light brown	Buff-colored precipitate in an alkaline medium
9	$PdCl_2$	Light brown	No particular change
10	$CoSO_4$	Light brown	Black precipitate in an alkaline medium
11	Na_3AsO_4	Light brown	No particular change
12	$Be(NO_3)_2$	Light brown	No particular change
13	$AgNO_3$	Light brown	No particular change
14	$CdSO_4$	Light brown	White precipitate in an alkaline medium
15	K_2CrO_4	Red	Red colour in an acid medium Very sensitive
16	$Pb(NO_3)_2$	Light brown	No particular change
17	$ZnSO_4$	Light brown	No particular change
18	$NiSO_4$	Light brown	No particular change
19	$Al(NO_3)_3$	Light brown	No particular change
20	$CuSO_4$	Light brown	No particular change
21	$Ca(C_2H_3O_2)_2$	Light brown	No particular change
22	K_2WO_4	Light brown	No particular change

TABLE II

	Final concn. of $K_2CrO_4\times10^4$	Final concn. of $CAD\times10^4$	Ratio Cr(VI) : CAD
A	0.00	1.0	0 : 1
B	1.00	1.0	1 : 1
C	0.50	1.0	1 : 2
D	0.33	1.0	1 : 3
E	0.25	1.0	1 : 4

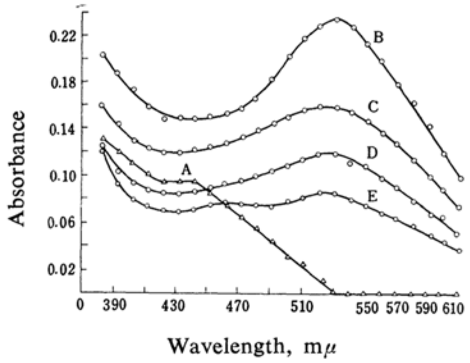

Fig. 1. Absorption spectra studies of mixtures of chromate and disodium-1, 8-dihydroxy naphthalene-3, 6-disulphonate.
Curve A : reagent 1.0×10^{-3} M
Curve B : $c=1.0\times10^{-4}$ M, $p=1$
Curve C : $c=0.5\times10^{-4}$ M, $p=2$
Curve D : $c=0.33\times10^{-4}$ M, $p=3$
Curve E : $c=0.25\times10^{-4}$ M, $p=4$

The results obtained from the absorbance studies have been graphically represented in Fig. 1. It may be seen there that the absorption maxima lies

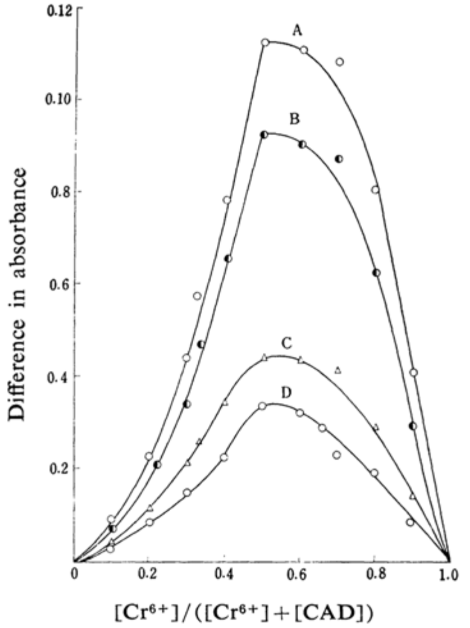

Fig. 2. Determination of the composition from absorption spectra studies at 500 mμ.
Curve A : $c=13.3\times10^{-4}$ M, $p=1$
Curve B : $c=10\times10^{-4}$ M, $p=1$
Curve C : $c=5.0\times10^{-4}$ M, $p=1$
Curve D : $c=3.3\times10^{-4}$ M, $p=1$

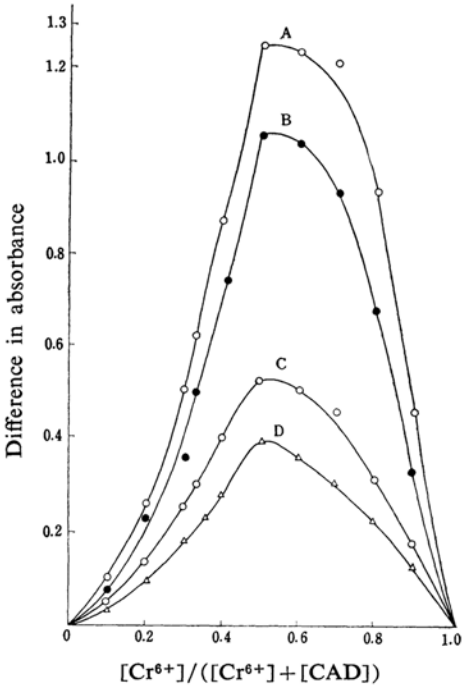

Fig. 3. Determination of the composition from absorption spectra studies at 530 mμ. Concentrations same as Fig. 2.

at 530 mμ, which also indicates that only one complex is formed under the conditions of study.

The Stoichiometry of the Compounds.—Job's[18] method of continuous variation has been adopted for the determination of the composition of the coloured complex formed. The total volume in each case was kept at 50 ml. The pH values of the solutions were kept between 2 and 3. The absorption spectra of the Cr_2O_7-chelating agent and the mixtures were measured at two different wavelengths, 500 and 530 mμ. Measurements using equimolecular and non-equimolecular solutions, in large numbers, were taken. The results obtained have been represented in Figs. 2—5.

The figures indicate the difference between the absorbance of the mixture and that which would

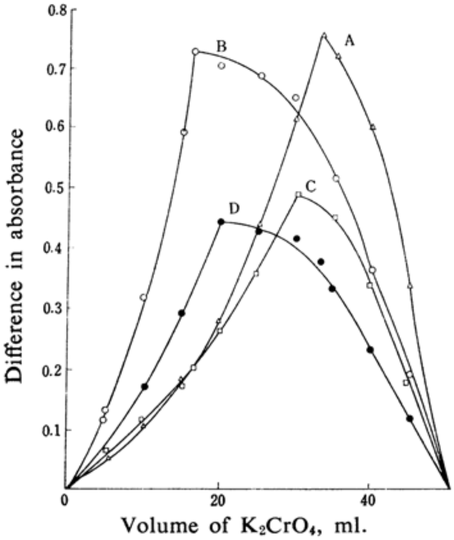

Fig. 4. Determination of the composition from absorption spectra studies at 500 mμ.
Curve A: $c=5.0\times10^{-4}$ M, $p=2$
Curve B: $c=10\times10^{-4}$ M, $p=0.5$
Curve C: $c=3.3\times10^{-4}$ M, $p=1.5$
Curve D: $c=5.0\times10^{-4}$ M, $p=0.66$

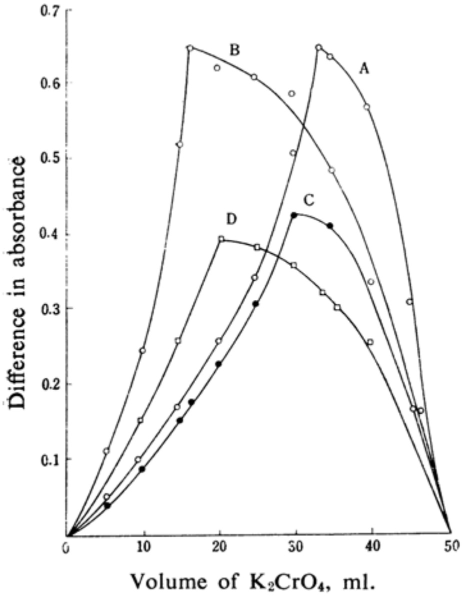

Fig. 5. Determination of the composition from absorption spectra studies at 530 mμ. Concentrations same as Fig. 4.

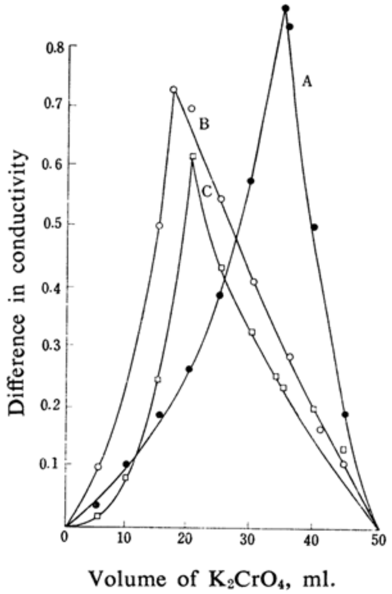

Fig. 6. Determination of the composition from conductivity studies.
Curve A: $c=10\times10^{-4}$ M, $p=1$
Curve B: $c=5.0\times10^{-4}$ M, $p=1$
Curve C: $c=3.3\times10^{-4}$ M, $p=1$

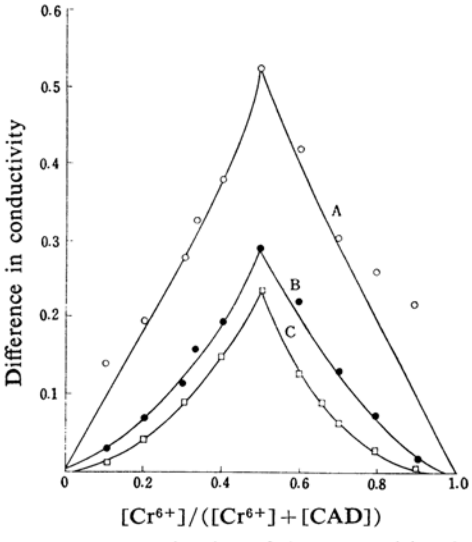

Fig. 7. Determination of the composition from conductivity studies.
Curve A: $c=5.0\times10^{-4}$ M, $p=2$
Curve B: $c=10\times10^{-4}$ M, $p=0.5$
Curve C: $c=5.0\times10^{-4}$ M, $p=0.66$

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[18] P. Job, *Compt. rend.*, **180**, 928 (1925).

be shown by the metal and the chelating agent if no chelation took place. This difference is plotted against the composition of the mixtures.

The Influence of pH on the Stability of the Chelate.—A detailed study was made of the effect of pH on the absorption maxima of the chelate to find out its stability; it was observed that the chelate is stable in the pH range 1—6. The observations were, therefore, made between pH 2 and 3, in which range the chelate is stable. It was also ascertained beforehand that the reagent did not change colour in this range of pH.

Conductivity Studies.—Electric conductivity studies were made at six different equimolecular and non-equimolecular concentrations. The solutions used were always freshly prepared. The results have been graphically represented in Figs. 6 and 7.

Conclusions

The composition of the chelate has been found to be 1 of the metal and 1 of the chelating agent, as may be seen from Table III, compiled from an examination of Figs. 2—5. The chelate can, therefore, be represented as Cr(CAD).

The results obtained from absorption measurement studies also receive confirmation from conductivity studies, as may be seen from Table IV.

For the purpose of determining the stability, calculations have been made of the formation constant from optical density data according to the method of calculation suggested by Dey[15] and worked out by Banerji and Dey[19-25] in several of their investigations. The method suggested by Dey has an advantage over the earlier method of Anderson et al.[26] wherein one of the reactants may be coloured.

By the above method the value of log K in the chromate-disodium-1,8-dihydroxy naphthalene-3,6-disulphonate systerm is 8.21±0.02 at 25°C.

TABLE III

Fig.	Curve	$c \times 10^4$ M	p	Wavelength of the observation mμ	Peak occurs at (vol. of K_2CrO_4) ml.	Composition of chelate Cr : CAD
2	A	13.3	1.0	500	25.0	1 : 1
2	B	10.0	1.0	500	25.0	1 : 1
2	C	5.0	1.0	500	25.0	1 : 1
2	D	3.3	1.0	500	25.0	1 : 1
3	A	13.3	1.0	530	25.0	1 : 1
3	B	10.0	1.0	530	25.0	1 : 1
3	C	5.0	1.0	530	25.0	1 : 1
3	D	3.3	1.0	530	25.0	1 : 1
4	A	5.0	2.0	500	33.5	1 : 1
4	B	10.0	0.5	500	16.5	1 : 1
4	C	3.3	1.5	500	30.0	1 : 1
4	D	5.0	0.66	500	20.0	1 : 1
5	A	5.0	2.0	530	33.5	1 : 1
5	B	10.0	0.5	530	16.5	1 : 1
5	C	3.3	1.5	530	30.0	1 : 1
5	D	5.0	0.66	530	20.0	1 : 1

TABLE IV

Fig.	Curve	$c \times 10^4$ M	p	Peak occurs at (Vol. of K_2CrO_4) ml.	Composition of the chelate Cr : CAD
6	A	10.0	1.0	25.0	1 : 1
6	B	5.0	1.0	25.0	1 : 1
6	C	3.3	1.0	25.0	1 : 1
7	A	5.0	2.0	33.5	1 : 1
7	B	10.0	0.5	16.5	1 : 1
7	C	5.0	0.66	20.0	1 : 1

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19) S. K. Banerji and A. K. Dey, Proc. XVII Intl. Cong. Pure Appl. Chem. Munich., 1072 A (1959).

20) S. K. Banerji and A. K. Dey, *Z. anorg. u. allagem. Chem.*, **309**, 226 (1961).

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25) S. K. Banerji, *Z. anorg. u. allgem. Chem.*, **315**, 229 (1962).

26) R. C. Anderson and S. E. Turner, *J. Am. Chem. Soc.*, **71**, 912 (1949).

The free energy of the formation, ΔF°, of the chelate has been calculated with the help of the relation:

$$\Delta F^\circ = -RT\ln K$$

where R is the gas constant, T is the absolute temperature, and K is the formation constant. The free energy of the chelate investigated here is:

$$-5.42 \pm 0.11 \text{ kcal. at } 25^\circ\text{C}$$

Judging from the results described here, the composition of the chelate corresponds to Cr(CAD).

Summary

The formation of a coloured chelate with a λ_{max} at 530 mμ between chromate ion and chromotropic acid (sodium salt)-disodium-1, 8-dihydroxy naphthalene-3, 6-disulphonate has been reported. The composition of the chelate has been studied by the method of continuous variation, using absorption spectra measurements, with a Hilger Uvispek spectrophotometer; it has been found to be Cr(CAD), (Disodium-1, 8-dihydroxy naphthalene-3, 6-disulphonate). The chelate has been found to be stable in the pH range 2—5 and so the investigations have been carried out in this range of pH. The chelate formed is deep red in colour and is very sensitive, being formed even at great dilutions.

The stability has been calculated by a method described earlier; the value of $\log K$ is 8.21 ± 0.02, and the value of the free energy of formation, ΔF°, has been found to be -5.42 ± 0.11 at 25°C.

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