Behavior of Chromotropic Acid as a Colloidal Electrolyte in Aqueous Solution

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A number of organic reagents have been used in these laboratories as complexants, and during the study of composition and stability of their metal chelates spectrophotometrically, it was observed that they deviated from stoichiometry when the solutions employed were not dilute. This was found to be due to the behavior of the reagents as colloidal electrolytes. In concentrated solutions, such reagents display colloidal behavior, but when extremely dilute they show the characteristics of true solutions. The reagents so far investigated from this point of view in these laboratories are ammonium aurintricarboxylate,[1] sodium alizarin-3-sulfonate,[2] *p*-nitrobenzene azochromotropic acid,[3] 7-iodo-8-hydroxy-quinoline-5-sulfonic acid,[4] sulfodichlorohydroxydimethylfuchsondicarboxylic acid,[5] sodium 2-naphthol-3, 6-disulfonic acid,[6] and 1-(*o*-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid.[7]

Chromotropic acid has widely been studied and it is observed that it forms colored chelates with many metals. As a part of a detailed study on the composition and stability of the metal chelates of chromotropic acid, its behavior as a colloidal electrolyte has been investigated and the results are communicated in this paper.

Experimental

Instruments. — Electrical conductance of the reagent in solution was measured with a Leeds and Northrup Kohlrausch Slidewire with an audiofrequency oscillator in the circuit, operated by 220/50 cycles a. c. mains, and using a dip type measuring cell having a cell constant 0.5875.

Materials.—Solutions of the reagent was prepared by dissolving chromotropic salt (B. D. H.) in conductivity water.

1) A. K. Mukherji and A. K. Dey, *J. Colloid Sci.*, **13**, 99 (1958).
2) A. K. Mukherji and A. K. Dery, *Kolloidzschr.*, **158**, 147 (1958).
3) S. C. Srivastava, R. L. Seth and A. K. Dey, *J. Ind. Chem. Soc.*, in course of publication.
4) S. C. Srivastava, R. L. Seth and A. K. Dey, *Kolloidzschr.*, **183**, 73 (1962).
5) S. C. Srivastava, R. L. Seth and A. K. Dey, *J. Colloid Sci.*, **17**, 86 (1962).
6) S. N. Sinha, S. C. Srivastava and A. K. Dey, ibid., **17**, 601 (1962).
7) S. P. Sangal and A. K. Dey, *J. Sci. Ind. Res.*, **21B**, 600 (1962).

Results and Discussion

The electrical conductance of solutions of chromotropic salt was determined at different dilutions at 25°C, and the curve obtained by plotting the square root of the concentration of reagent solution against molar conductance (Fig. 1, Table I) is not linear and resembles that of colloidal electrolytes as recorded by McBain.[8] It would have been a straight line if the system behaved as a true electrolyte and the Debye-Hückel equation would have been applicable.

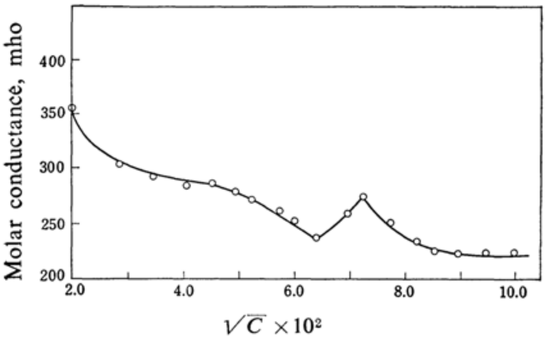

Fig. 1. Variation of molar conductance with concentration.

TABLE I. VARIATION OF MOLAR CONDUCTANCE WITH CONCENTRATION

Concentration of chromotropic acid, M	$\sqrt{C} \times 10^2$	Molar conductance mho
0.0004	2.00	357
0.0008	2.83	304
0.0012	3.46	292
0.0016	4.00	282
0.0020	4.47	287
0.0024	4.89	278
0.0028	5.27	274
0.0032	5.65	265
0.0036	6.00	268
0.0040	6.32	265
0.0044	6.64	239
0.0048	6.99	258
0.0052	7.21	261
0.0056	7.41	271
0.0060	7.74	253
0.0068	8.24	236
0.0072	8.47	250
0.0080	8.94	250
0.0092	9.50	250
0.0100	10.00	250

The specific conductance of the aqueous solution of chromotropic acid was also determined at different temperatures (Table II).

8) J. W. McBain, "Colloid Science," D. C. Heath and Co., Boston (1950).

TABLE II. VARIATION OF SPECIFIC CONDUCTANCE WITH TEMPERATURE

Concentration of chromotropic acid, M	Specific conductance mho $\times 10^4$						
	0°	10°	20°	30°	40°	50°	60°C
0.003	2.9	3.5	4.7	5.8	7.0	8.2	9.4
0.005	4.7	5.2	6.4	8.8	9.9	11.7	14.1
0.010	8.1	10.5	12.7	17.6	20.5	24.0	26.0

The curve obtained by plotting specific conductance against temperature (Fig. 2) was extrapolated to give the temperature of zero conductance which was found to be -20.0°C. The temperature coefficient per degree centigrade per hundred units of conductance at 35°C calculated from Fig. 2 is shown in Table III.

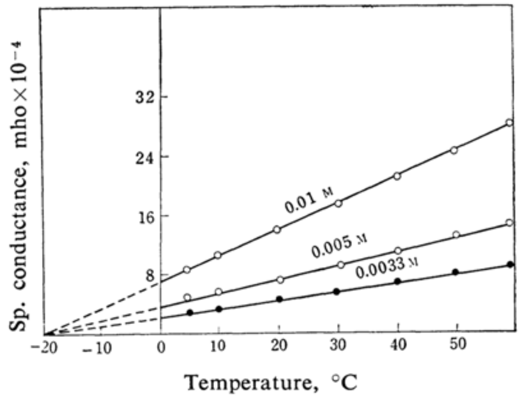

Fig. 2. Variation of specific conductance of chromotropic acid solution with temperature.

TABLE III. TEMPERATURE COEFFICIENT OF CONDUCTANCE

Concn. of chromotropic acid, M	Sp. cond. at 35°C (from graph) mho$\times 10^4$	Temp. coefficient per degree centigrade	Temp. coefficient per hundred of the conductance
0.003	6.5	0.10	1.5
0.005	10.0	0.16	1.6
0.010	19.5	0.33	1.7

The results conclusively establish the colloidal nature of the reagent. Mushran and Prakash[9] as a result of their investigations with a number of colloidal systems found that in general the temperature of zero conductance of true electrolytes lies near about -40°C, whereas, in the case of colloidal electrolytes this temperature ranges between -15 and -35°C. Shivapuri and Prakash[10] also corroborated these results from their study on the

9) S. P. Mushran and S. Prakash, *J. Phys. Chem.*, **50**, (1946).

10) T. N. Shivapuri and S. Prakash, *Curr., Sci.*, **18**, 403 (1949).

colloidal behavior of a number of dyes in aqueous solution. Also the temperature coefficient per degree centigrade per hundred units of conductance at 35°C in colloidal systems and colloidal electrolytes is mostly below 2.0.

Hence on the basis of the above results it is concluded that chromotropic acid behaves as a colloidal electrolyte. In the determination of the composition and stability of the chelates the colloidal characteristics of the chelating agent plays a significant part due to what non-stoichiometric ratios are often arrived at. Therefore, for physico-chemical studies it is advisable to work with extremely dilute solutions when the chelating agent behaves as a true solution.[11]

Summary

The nature of chromotropic acid as a colloidal electrolyte has been established from electrical conductance studies. The curve obtained by plotting the square root of concentration and molar conductance of the reagent solution is not linear and resembles that of a colloidal electrolyte. The temperature coefficient per degree centigrade per hundred units of conductance at 35°C is between 1.5 and 1.7. The temperature of zero conductance, determined by extrapolation, is −20.0°C.

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11) A. K. Dey, *J. Colloid Sci.*, 3, 473 (1948).