Studies on the Colloidal Nature of 2-(p-sulphophenylazo)-1.8-dihydroxy naphthalene 3.6-disulphonic acid (SPADNS) in Aqueous Solution

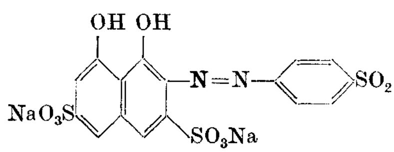
By SATENDRA P. SANGAL

With 2 Figures

Summary

The nature of 2-(p-sulphophenylazo)-1.8 dihydroxy naphthalene 3.6-disulphonic acid (SPADNS) (in aqueous solution) as a colloidal electrolyte has been determined by the electrical conducuance studies. The curve obtained by plotting the square root of concentration and the molar conductance was not linear and resembled that of colloidal electrolytes. The temperature of zero conductance as determined by extrapolation is −22.5 °C. The temperature coefficient per degree centigrade per hundred of the conductance at 35 °C is between 1.5 and 1.7.

2-(p-sulphophenylazo)-1.8-dihydroxy naphthalene 3.6-disulphonic acid commonly known as SPADNS, has been in use as a metallochromic indicator in complexometric titrations due to its tendency to form coloured chelates in solution with a number of of metal ions. It is represented by the following structure:



We have made detailed studies on the composition and stability of various metal chelates involving this reagent.

During the studies, it was observed that composition of the chelate deviated from true stoichiometry, when the solutions of the reagent used were not very dilute. However, the composition corresponded to true stoichiometric ratios, when very dilute solutions were employed. Similar deviations were reported earlier by MUKHERJI and DEY during their studies with the metal chelates of ammonium aurin tricarboxylate[1]) and sodium alizarin 3-sul-

[1]) A. K. MUKHERJI and A. K. DEY, J. Colloid Sci. 13, 99 (1958).

fonate[2]). SRIVASTAVA, SETH and DEY also reported these deviations on their studies with the metal chelates of p-nitrobenzene azochromotropic acid[3]), 7-iodo 8-hydroxy quinoline 5-sulphonic acid[4]) and sulphodichloro hydroxy dimethyl fuchson dicarboxylic acid[5]). Similar results were reported by SINHA and DEY and SANGAL and DEY with sodium-2 naphthol-3.6-disulphonic acid[6]) and 1 (arsonophenylazo) 2 naphthol 3.6 disulphonic acid[7]). Thus it seems likely that a solution of SPADNS too, behaves as a colloidal electrolyte and does not obey BEER s law in concentrated solutions, as is also the case with a number of dyes.

It was, therefore, thought interesting to investigate the colloidal nature of SPADNS by electrical conductance measurements and the present communication describes the results of these studies.

Experimental

Instruments. The measurements of electrical conductance were performed with a Leeds and Northrup Kohlrausch Slidewire with an audio-frequency oscillator in the circuit, operated by a 220 volt/50 cycles a. c. mains and using a dip type measuring cell having a cell constant 0.5875.

Materials. The solutions were always freshly prepared in conductivity water using SPADNS (B. D. H.) and kept immeresed in a thermostat before and during measurements.

Results and discussions

The electrical conductance of solutions of SPADNS was determined at different dilutions at a temperature of 30 °C., and a graph was plotted between the square root of concentration and molar conductance. (Tab. 1, fig. 1).

The specific conductance of SPADNS solutions was also determined at seven different temperatures. The values are given in Table 2 (fig. 2).

The temperature of zero conductance was extrapolated from the curves in fig. 2, and it is observed therefrom that this temperature in the case of SPADNS lies at − 22.5 °C.

The temperature coefficient per degree centigrade per hundred of the conductance at 35 °C has also been calculated from fig. 2. The values are recorded in table 3.

---

[2]) A. K. MUKHERJI and A. K. DEY, Kolloid Z. **158**, 147 (1958).
[3]) S. C. SRIVASTAVA, R. L. SETH and A. K. DEY, J. Ind. Chem. Soc. **39** (1962).
[4]) S. C. SRIVASTAVA, R. L. SETH and A. K. DEY, Kolloid Z. **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, J. Colloid Sci. **17**, 601 (1962).
[7]) S. P. SANGAL and A. K. DEY, J. Sci. Industr. Res. **21**B, 600 (1962).

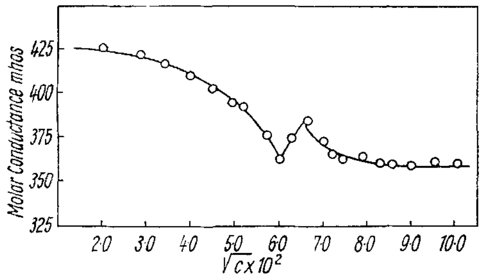


Fig. 1. Variation of Molar Conductance with concentration

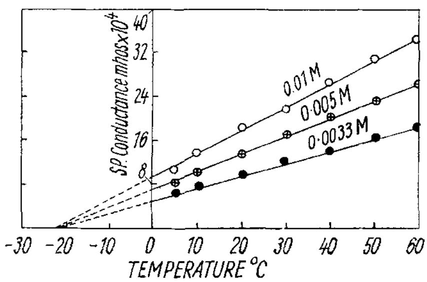


Fig. 2. Variation of specific conductance of chromotropic acid solution with temperature

Table 1
Variation of Molar conductance with concentration

Concentration of SPADNS (M)	$\sqrt{C} \times 10^2$	Molar Conductance mhos
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	233
0.0072	8.47	250
0.0080	8.94	250
0.0092	9.50	250
0.0100	10.00	250

Table 2
Variation of specific conductance with temperature

Concentration of SPADNS (M)	Specific conductance mhos · 10^4 5°	10°	20°	30°	40°	50°	60°
0.003	7.0	8.0	9.9	11.7	14.1	16.4	18.8
0.005	18.0	10.5	14.0	17.6	21.9	23.5	26.4
0.010	10.0	14.1	18.8	21.7	27.6	31.1	35.2

Table 3
Temperature coefficient of conductance

Concentration of SPADNS (M)	Sp. Conductance at 35 °C (from graph) mhos · 10^4	Temperature Coefficient per degee centigrade	Temperature coefficient per hundred of the conductance
0.003	13.00	0.200	1.5
0.005	18.50	0.300	1.6
0.010	24.00	0.400	1.7

The curve between (concentration)$^{\frac{1}{2}}$ and molar conductance is not linear and resembles that of colloidal electrolytes as recorded by McBAIN[8]). It should have been a straight line, if the system behaved as a true electrolyte and the DEBYE-HÜCKEL equation would have been applicable. Further, it has been found that the temperature of zero conductance of the reagent lies at — 22.5 °C and the temperature coefficient per degree centigrade per hundred of the conductance at 35 °C ranges between 1.5 and 1.7. These results conclusively establish the colloidal characteristics of the reagent. It would be interesting to recall that MUSHRAN and PRAKASH[9]) as a result of their work on a number of colloidal systems found that, in general, the temperature of zero conductance of true electrolytes lies at — 40 °C, whereas, in the case of colloidal systems, this temperature ranges between — 15 °C and — 35 °C. Similar observations were recorded by SHIVAPURI and PRAKASH[10]) who sought to establish the colloidal nature of some acidic and basic dyes. It was further emphasised by PRAKASH and co-workers that the temperature coefficient perdegree centigrade per hundred of the conductance at 35 °C, in colloidal systems and colloidal electrolytes is mostly found to be below 2.0.

Hence it has been concluded that SPADNS exhibits the behaviour of a colloidal electrolyte, on the basis of the above results. It is probable that in determining the composition of chelate compounds the colloidal characteristics of the chelating agent too, plays a significant role, due to which often nonstoichiometric ratios are arrived at. Therefore, for physico chemical studies it is advisable to work with extremely dilute solutions, when the chelating agent would behave as a true solution[11]).

The author is thankful to Dr. ARUN K. DEY for his valuable advice and to the Council of Scientific and Industrial Research, New Delhi, for the financial aid.

[8]) J. W. McBAIN, Colloid Science (D. C. Heath and Co., Boston) 1950.
[9]) S. P. MUSHRAN and S. PRAKASH, J. Phys. Chem. **50**, 251 (1946).
[10]) T. N. SHIVAPURI, and S. PRAKASH, Curr. Sci. 18, 403 (1949).
[11]) A. K. DEY, J. Colloid Sci. **3**, 473 (1948).

Allahabad (India), Chemical Laboratories, University of Allahabad.

Bei der Redaktion eingegangen am 11. Juni 1963.