The Colloidal Behaviour of Ammonium Purpurate (Murexide) in an Aqueous Solution

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(Received June 22, 1964)

Ammonium purpurate (murexide), which has the following structure:

has been used extensively in the complexometric titrations of calcium. Sangal and Dey[1] used the reagent as a chelatochrome indicator in thorium-ethylenediaminetetraacetic acid titrations also. Murexide gives coloured chelates with scandium and rare earths. During the investigations of the composition and stability of these chelates, it was found that, when the solutions of the reagent used were not very dilute, deviations in the composition from true stoichiometry were observed. Similar deviations had been observed earlier by Mukherji and Dey[2] during their studies of the metal chelates of aluminium; by Srivastava, Seth and Dey during their studies of the metal chelates of sulphodichlorohydroxydimethylfuchson dicarboxylate,[3] *p*-nitrobenzene-azochromotropic acid,[4] and 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron),[5] and by Sangal and Dey during their studies of metal chelates of Thoron[6] with different metal ions. It appears, therefore, that murexide, like the above reagents, behaves as a colloidal electrolyte and does nos obey Beer's law in concentrated solutions.

The present communication records the results of our studies of the colloidal behaviour of murexide in an aqueous solution.

Experimental

Electrical conductance measurements were carried with a Leeds and Northrup Kohlrausch slide wire with an audiofrequency oscillator in the circuit, operated by a 220 V./50 cycl. a. c. mains and using a measuring cell of the dip type, with a cell constant of 0.5875.

All solutions were freshly prepared in conductivity water using a B. D. H. sample of murexide.

1) S. P. Sangal and A. K. Dey, *Talanta*, in press.
2) A. K. Mukherji and A. K. Dey, *J. Colloid Sci.*, **13**, 99 (1958).
3) S. C. Srivastava, P. L. Seth and A. K. Dey, ibid., **17**, 86 (1963).
4) S. C. Srivastava, R. L. Seth and A. K. Dey, *J. Indian Chem. Soc.*, in press.
5) S. C. Srivastava, R. L. Seth and A. K. Dey, *Kolloid.-Z.*, **181**, 137 (1962).
6) S. P. Sangal and A. K. Dey, *J. Sci. Ind. Research (India)*, **21B**, 600 (1962).

Results and Discussion

The electrical conductance of a series of solutions of murexide was measured at different dilutions at 25C°. A graph was then plotted between the square root of the concentration and the molar conductance (Fig. 1). The curve thus obtained was found to be similar to the curves of the colloidal electrolytes as recorded by McBain.[7] If the solution of Murexide had behaved like true electrolytes, the curve would have been linear and the Debye-Hückel equation would have been applicable.

The specific conductance of murexide was also determined at six temperatures, and by the extrapolation of the curves obtained by plotting the specific conductance against the temperature (Fig. 2), the temperature of the zero conductance was found to be −20°C. This observation confirms the findings of Mushran and Prakash,[8] who described, during their studies on colloidal systems, how although generally the temperature of the zero conductance of true electrolytes lies near −40°C, in the colloidal systems this temperature ranges between −15°C and −35°C.

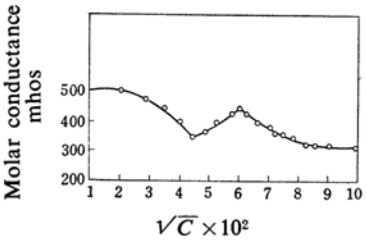

Fig. 1. Variation of molar conductance with concentration.

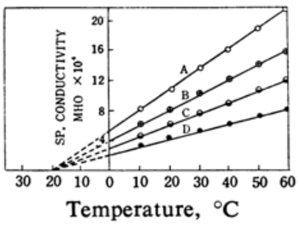

Fig. 2. Variation of specific conductance of murexide with temperature.
Curve A: Concn. of murexide 0.02 M
Curve B: Concn. of murexide 0.01 M
Curve C: Concn. of murexide 0.005 M
Curve D: Concn. of murexide 0.003 M

7) J. W. McBain, "Colloid Science," D. C. Heath and Co., Boston (1950).
8) S. P. Mushran and S. Prakash, *J. Phys. Chem.*, **50**, 251 (1946).

The temperature coefficients per 1°C per hundred of the conductance at 35°C have also been calculated; the results are as follows:

TABLE I. THE TEMPERATURE COEFFICIENT OF THE CONDUCTANCE

Cocn. M	Specific conductance at 35°C (from graph) mhos $\times 10^4$	Temperature coefficient per 1°C	Temperature coefficient per hundred of the conductance
0.003	5.8	0.050	0.86
0.005	8.4	0.100	1.19
0.010	11.2	0.150	1.34
0.020	15.2	0.250	1.65

These results also serve to establish the colloidal nature of murexide in concentrated solutions, as Shivapuri and Prakash[9] reported that usually the temperature coefficient per degree centigrade per hundred of the conductance at 35°C in a colloidal system is found to be below 2.0.

Thus, it may be concluded that murexide behaves as a colloidal electrolyte in concentrated solutions. For physico-chemical measurements, it is advisable, therefore, to work with very dilute solutions of the reagent for only then will the reagent behave as a true solution, as has also been suggested by Dey.[10]

Summary

By electrical conductance studies it has been found that ammonium purpurate behaves as a colloidal electrolyte and does not obey Beer's law in concentrated solutions. The curve between the square root of the concentration and the molar conductance is not linear and resembles that of a colloidal electrolyte. The temperature of zero conductance has also been determined to be −20°C. The temperature coefficient per degree centigrade per hundred of the conductance at 35°C ranges between 0.86 and 1.65.

The author is thankful to Dr. A. K. Dey for his suggestions and to the Council of Scientific and Industrial Research for the award of a fellowship.

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9) T. N. Shivapuri and S. Prakash, *Current Sci.* (*India*), **18**, 403 (1949).
10) A. K. Dey, *J. Colloid Sci.*, **3**, 473 (1948).