A STUDY OF THALLOUS-THIOCYANATE SYSTEM

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Introduction

This paper presents the results of a polarographic investigation of thallous thallium in potassium thiocyanate where the half-wave potential, diffusion coefficient, etc., have been determined and of the determination of the activity coefficients of thallous thiocyanate in potassium thiocyanate from solubility measurements.

Experimental

Reagents.—A stock solution of standard thallium nitrate was prepared from weighed amounts of E. Merck C.P. salt.

Thallous thiocyanate was prepared from thallous nitrate and B.D.H. AR potassium thiocyanate. The precipitate was washed well, dried at 110° C. and bottled.

A stock solution of 1·5 M potassium thiocyanate was prepared from B.D.H. AR salt and standardised by Volhard's method.[1] The solutions used were obtained by appropriate dilution of this stock solution.

Results and Discussion

Polarographic Study of Thallium in Potassium Thiocyanate.—Data for polarograms were obtained on a manual polarograph.[2] The potential applied at the electrode terminals and the current calculated in terms of the iR drop across a 10,000 ohms resistance were measured with a Leeds Northrup students' potentiometer using a Cambridge spot galvanometer as a null instrument. An H-type cell[3] was used in which a saturated calomel electrode served as a reference electrode. Thymol (2×10^{-4} per cent.) was used as a maximum suppressor. All measurements were made at $30 \cdot 0 \pm 0 \cdot 1°$ C. In all cases oxygen was removed by passing nitrogen through the solution for about 15 minutes.

The solubility of thallium in 0·1 M potassium thiocyanate was found from solubility measurements to be about 5 mM showing that this would be a suitable medium to study. The plot of $E_{d.e}$ *vs.* log $i/i_d\text{-}i$ in 0·1 M

thiocyanate gave a straight line having a slope of 0·061 V. Thus the number of electrons involved in the electrode reaction is one. The intercept on the X-axis led to a value of — 0·470 ± 0·005 V for the half-wave potential, its value in a non-complexing electrolyte such as 0·1 M potassium chloride being — 0·460 V.[4] It was observed that the half-wave potential remained unaffected with the change of concentration of thiocyanate (0·1 to 0·5 M); thus the reduction of thallium in this medium was that of a simple metal ion.

A diffusion current constant was calculated using the equations of Lingane[5] and Lingane and Loveridge[6] and the values were found to be 2·85 and 2·43 respectively. The value of the capillary constant $m^{2/3}t^{1/6}$ was determined as 2·03 mg.$^{2/3}$sec.$^{-1/2}$ at— 0·8 V vs. s.c.e. At — 0·8 V the diffusion current-concentration ratio was 5·80 ± 0·05 μ A per mM per litre between 0·25 and 2·0 mM thallium.

The diffusion coefficient for the thallous ion calculated from Ilkovic's equation[7] worked out as $2\cdot21\times10^{-5}$ cm.^{2}sec.$^{-1}$ which agreed well with the value $2\cdot00\times10^{-5}$ cm.^{2}sec.$^{-1}$ obtained from conductivity data.[8]

Studies on the Solubility of Thallous Thiocyanate.—The solubility of thallous thiocyanate in different concentrations of potassium thiocyanate was measured. The salt in sufficient excess was mechanically agitated with the solution in a 250 ml. pyrex bottle kept in a water-bath at 30·0 ± 0·1° C. till equilibrium was attained. The solution was filtered through Whatman No. 42 paper and thallium estimated by the chromate method.[9]

The polarographic investigation had revealed the absence of any complex formation between thallous ions and thiocyanate ions. This was confirmed since a plot of the concentration of thiocyanate against solubility of thallium did not indicate any minima.[10]

The solubility data were further used to calculate the activity coefficients and activity solubility product of thallous thiocyanate in potassium thiocyanate at 30° C.[11] The mean ionic molality m_+ of thallous thiocyanate calculated from the solubilities in presence of different concentrations of potassium thiocyanate was plotted against the square root of ionic strength (Fig. 1). A straight line was obtained which gave on extrapolation to infinite dilution the value of $K_S^{1/2}$ equivalent to $15\cdot25\times10^{-3}$. The activity coefficient $r_\pm$ of thallous thiocyanate was then calculated from the equation:

$$r_\pm = \frac{K_S^{\frac{1}{2}}}{m_\pm}$$

where K_S is the activity solubility product. The results are tabulated in Table I. The activity solubility product of thallous thiocyanate at 30° C. is $23\cdot1\times10^{-5}$.
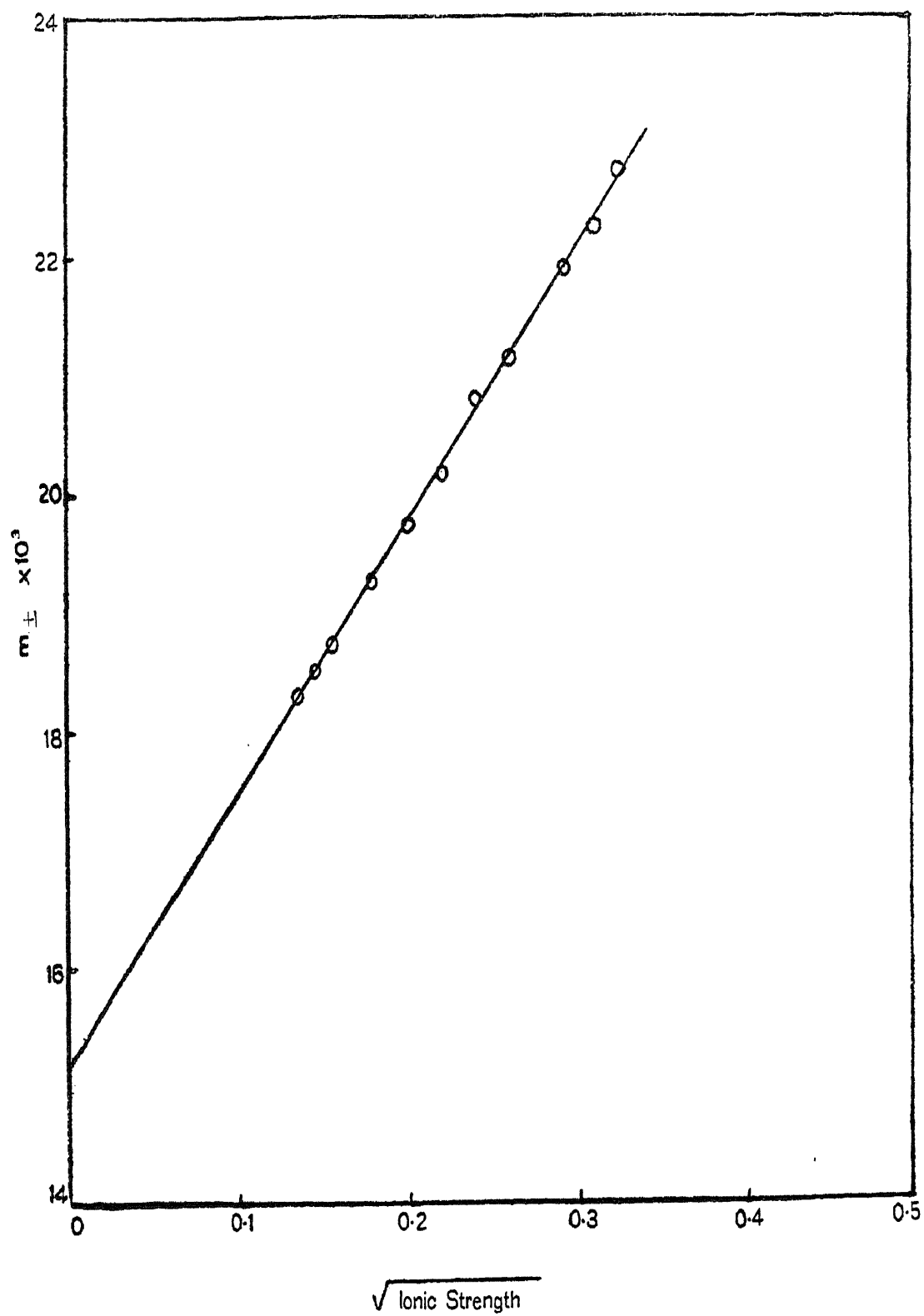
FIG. 1. Solubility of Thallous Thiocyanate in Potassium Thiocyanate. Plot of Mean Ionic Molality *vs.* The Square Root of the Ionic Strength.

TABLE I

Activity Coefficients of Thallous-Thiocyanate in Potassium Thiocyanate at 30° C.

Concentration of potassium thiocyanate in M	Activity Coefficient
0·0	0·825
0·005	0·815
0·01	0·805
0·02	0·784
0·03	0·765
0·04	0·749
0·05	0·727
0·06	0·703
0·08	0·690
0·09	0·679
0·10	0·666

SUMMARY

The reduction of thallium in thiocyanate involves a one-electron reduction. In 0·1 M KCNS, the $E_{\frac{1}{2}}$ is $-0\cdot470$ V *vs.* s.c.e. The diffusion coefficient and the diffusion current constant are determined. As the $E_{\frac{1}{2}}$ does not change with the concentration of thiocyanate the reduction is that of a simple metal ion. The activity coefficient for thallous thiocyanate in potassium thiocyanate and the activity solubility product are calculated from solubility measurements.

REFERENCES

1. Scott .. *Standard Methods of Chemical Analysis*, 5th Ed., **1**, D. Van Nostrand Co., Inc., 824.
2. Kolthoff, I. M. and Lingane, J. J. *Polarography*, **1**, Interscience Publishers, N.Y., 1952, 297.
3. ———— .. *Ibid.*, p. 354.

4. Lingane, J. J.   ..   *J.A.C.S.*, 1939, **61**, 2099.

5. ———————   ..   *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 583.

6. —— and   *J.A.C.S.*, 1950, **72**, 438.
   Loveridge, B. A.

7. Ilkovic, D.   ..   *Coll. Czec. Chem. Communs.*, 1934, **6**, 498.

8. Kolthoff, I. M. and   *Polarography*, Interscience Publishers, N.Y., 1952, **1**, 52.
   Lingane, J. J.

9. Scott   ..   *Standard Methods of Chemical Analysis*, 5th Ed., **1**, 944.
           D. Van Nostrand Co. Inc.

10. Reynolds, C. A. and   *J. Phys. Chem.*, 1952, **56**, 417.
    Argersinger Jr., W. T.

11. Glasstone, D.   ..   *Thermodynamics for Chemists*, 5th Ed., 1950, p. 398. D. Van
            Nostrand Co., Inc.