SOLUBILITY STUDIES IN AQUEOUS MEDIA

II. SOLUBILITY PRODUCT OF SILVER THIOCYANATE AND STANDARD ELECTRODE POTENTIALS OF SILVER–SILVER THIOCYANATE ELECTRODE IN AQUEOUS MEDIA

U. N. DASH, J. MOHANTY AND K. N. PANDA

Department of Chemistry, G. M. College, Sambalpur, Orissa (India)

(Received 12 December 1975)

ABSTRACT

The solubility and solubility product of silver thiocyanate in water have been determined at the temperatures ranging from 15 to 35°C over 5°C intervals in the presence of sodium perchlorate. The solubility of silver thiocyanate ranges from 0.661×10^{-6} mol l^{-1} at 15°C to 1.563×10^{-6} mol l^{-1} at 35°C and the corresponding solubility product 0.437×10^{-12} mol^2 l^{-2} at 15°C to 2.443×10^{-12} mol^2 l^{-2} at 35°C. The variation of the solubility product, K_s with temperature has been expressed by the equation,

$$\log K_s = -86.6126 + 0.14389\,T + 9450.17/T$$

The standard potentials of the Ag(s)/AgCNS(s)/CNS$^-$ electrode have been calculated at these temperatures and the standard electrode potential has been expressed through the equation

$$E_r^\circ = 0.0873 - 1.14 \times 10^{-3}(t-25) + 3.644 \times 10^{-5}(t-25)^2$$

over the temperature range 15–35°C. The mean activity coefficients of silver thiocyanate at various rounded molarities of sodium perchlorate solutions, and the standard thermodynamic quantities for the process, AgCNS(s) → Ag$^+$(aq) + CNS$^-$(aq) have been calculated at these temperatures.

INTRODUCTION

In a previous communication[1], we reported the solubility, and the solubility product of silver permanganate in aqueous sodium perchlorate solutions over the temperature range 15–35°C. The present investigation deals with similar studies made on silver thiocyanate at the temperatures ranging from 15 to 35°C in aqueous sodium perchlorate solutions.

Several studies[2,3] on the solubility of silver thiocyanate in aqueous media have been reported either at a single temperature or more temperatures. But these are mostly determined from the standard potentials of the silver–silver thiocyanate

electrode and in some cases from the solubility measurements by the conductivity method or by the ordinary method without added electrolyte. This paper reports the determination of solubility of this salt in the presence of an added electrolyte, sodium perchlorate over the temperature range 15–35 °C. The influence of ionic strength on the mean activity coefficients of silver thiocyanate in solution has also been examined. From the values of the solubility products of silver thiocyanate at these temperatures, the standard potentials of the Ag(s)/AgCNS(s)/CNS⁻ electrode have been obtained in aqueous media.

EXPERIMENTAL

Silver thiocyanate was precipitated by mixing dilute solutions of silver nitrate and potassium thiocyanate (B.D.H., AnalaRs). The precipitate was washed repeatedly with conductivity water and finally dried in a vacuum desiccator over $CaCl_2$ for several weeks. The dried, almost colourless salt, gave on analysis by standard methods a purity of 99.7%. Sodium perchlorate and a stock solution of sodium perchlorate were prepared as described earlier[1].

The method for the determination of the solubility was essentially similar to that of our previous article[1]. The solute contents were analysed by the potentiometric determination of silver using a 1×10^{-6} N potassium chloride solution.

RESULTS AND DISCUSSION

The experimental results of the solubility measurements are recorded in Table 1. The first column gives the molarity, c, of sodium perchlorate, the second the solubility, s, of silver thiocyanate in mol l⁻¹; the third column lists the total salt concentration, $c + s$, which is the same as the ionic strength of the solution.

The method of calculating the solubility is the same as in our previous paper[1], assuming that the salts employed are completely dissociated, the solubility, s, of silver thiocyanate at any salt concentration, c, may be written as

$$sf_{\pm} = s^{\circ} \tag{1}$$

where $f_{\pm}$ is the mean activity coefficient of silver thiocyanate, and s° its hypothetical solubility at zero ionic strength. Equation (1) may be written

$$\log s^{\circ} = \log s + \log f_{\pm} \tag{2}$$

As usual by following the Debye–Hückel theory, the mean activity coefficient may be more accurately expressed by

$$\log f_{\pm} = -A \frac{(c+s)^{1/2}}{1 + Ba^{\circ}(c+s)^{1/2}} + B'(c+s) \tag{3}$$

where A, B, and B' are the usual constants of the equation and a° is the ion size parameter.

TABLE 1

SUMMARY OF SOLUBILITY DATA FOR SILVER THIOCYANATE IN
AQUEOUS SODIUM PERCHLORATE SOLUTIONS AT
DIFFERENT TEMPERATURES

$c \times 10^2$ (mol l^{-1})	$s \times 10^6$ (mol l^{-1})	$(c \div s) \times 10^2$ (mol l^{-1})	$(c \div s)^{\frac{1}{2}} \times 10^2$ (mol l^{-1})$^{\frac{1}{2}}$	$\dfrac{A(c \div s)^{\frac{1}{2}} \times 10^2}{1 + a^\circ B(c \div s)^{\frac{1}{2}}}$	$-\log s$ (mol l^{-1})	$-\log s^{\circ}$ (mol l^{-1})
Temperature: 15°C						
0.250	0.757	0.2501	5.00	2.290	6.1209	6.1438
0.500	1.035	0.5001	7.07	3.121	5.9851	6.0163
1.000	1.265	1.0001	10.00	4.205	5.8979	5.9400
1.500	1.749	1.5002	12.25	4.963	5.7572	5.8068
2.250	2.846	2.2503	15.00	5.824	5.5458	5.6040
				$-\log s^{\circ}$ (extrapolated)		6.1835
				B' (l mol^{-1})		-25.5791
Temperature: 20°C						
0.250	0.975	0.2501	5.00	2.307	6.0112	6.0343
0.750	1.393	0.7501	8.66	3.745	5.8561	5.8936
1.250	1.951	1.2502	11.18	4.645	5.7098	5.7563
2.000	3.107	2.0003	14.15	5.606	5.5077	5.5638
2.500	4.814	2.5005	15.81	6.113	5.3175	5.3786
				$-\log s^{\circ}$ (extrapolated)		6.1183
				B' (l mol^{-1})		-29.1080
Temperature: 25°C						
0.250	1.285	0.2501	5.00	2.327	5.8911	5.9144
0.500	1.368	0.5001	7.07	3.173	5.8640	5.8957
0.750	1.689	0.7502	8.66	3.783	5.7724	5.8102
1.000	1.998	1.0002	10.00	4.273	5.6994	5.7421
1.500	3.102	1.5003	12.25	5.043	5.5083	5.5587
1.750	3.486	1.7504	13.23	5.365	5.4576	5.5113
2.250	4.666	2.2505	15.01	5.921	5.3310	5.3901
				$-\log s^{\circ}$ (extrapolated)		6.0123
				B' (l mol^{-1})		-28.2554
Temperature: 30°C						
0.250	1.513	0.2502	5.00	2.348	5.8201	5.8436
0.750	2.080	0.7502	8.66	3.815	5.6819	5.7201
1.000	2.661	1.0003	10.00	4.308	5.5573	5.6191
1.500	3.691	1.5004	12.25	5.084	5.4329	5.4837
1.750	4.006	1.7504	13.23	5.409	5.3973	5.4514
2.500	6.594	2.5007	15.81	6.215	5.1809	5.2431
				$-\log s^{\circ}$ (extrapolated)		5.9049
				B' (l mol^{-1})		-26.686
Temperature: 35°C						
0.500	2.249	0.5002	7.07	3.229	5.6481	5.6804
0.750	2.758	0.7503	8.66	3.851	5.5594	5.5979
1.250	3.446	1.2504	11.18	4.766	5.4626	5.5103
2.000	5.790	2.0006	14.15	5.753	5.2373	5.2948
2.250	6.853	2.2507	15.01	6.022	5.1641	5.2243
				$-\log s^{\circ}$ (extrapolated)		5.8068
				B' (l mol^{-1})		-25.5689

Combining eqns (2) and (3), the following equation is obtained

$$\log s - A \frac{(c+s)^{1/2}}{1+Ba^{\circ}(c+s)^{1/2}} = \log s^{\circ} - B'(c+s) \tag{4}$$

By plotting the left-hand side of eqn (4), which is represented by the expression $\log s^{\circ}$ against the total salt concentration, $(c+s)$, a straight line should be obtained yielding an intercept equal to $\log s^{\circ}$ and a slope equal to $-B'$. The left-hand side of eqn (4) is calculated from the experimental data. The values of A and B required for such a calculation at different temperatures were obtained from the literature[4]. The value of a°, the ion size parameter, is taken as 6 Å as obtained in the work of Vanderzee and Smith[2]. In Fig. 1 the values of $\log s^{\circ}$ have been plotted against the total salt concentration, $(c+s)$, at different temperatures. The values of $-\log s^{\circ}$ as obtained from the intercepts of these plots and those of B' as obtained from the slopes of these plots are shown in Table 1.
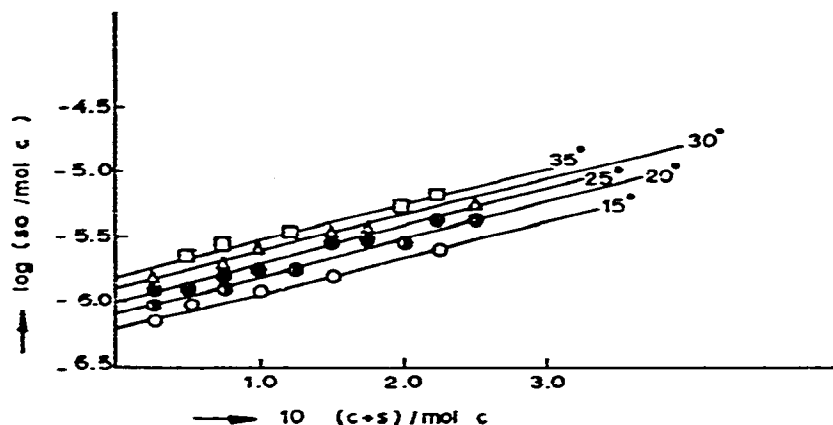

Fig. 1. Plot of $\log s^{\circ}{}'$ versus total salt concentration.

The values of s and $f_{\pm}$ at rounded concentrations of the salt, i.e., sodium perchlorate have been evaluated through a short series of approximations using eqns (4) and (3). For this purpose, eqn (4) may be written in the form

$$\log s = \log s^{\circ} + \frac{A(c+s)^{1/2}}{1+Ba^{\circ}(c+s)^{1/2}} - B'(c+s) \tag{5}$$

Using the appropriate value of c and the known values of s°, A, B, a°, and B' and substituting for s an arbitrary, but reasonable value as a trial measure, the right-hand side of eqn (5) is evaluated which yields a rough value for s occurring in the left-hand side of the same equation. Using this value of s in the right-hand side of eqn (5), a second and more accurate value of s is obtained. This process is repeated several times till the value of s does not change further on reiteration. This final value of s, therefore, represents the solubility of silver thiocyanate in water at the appropriate rounded

concentration of the added salt. Once the value of s is known, the mean activity coefficient may then be calculated using either eqn (1) or (3). The values of s and $f_\pm$ obtained through this procedure are recorded in Table 2.

TABLE 2

SUMMARY OF ACTIVITY COEFFICIENTS FOR SILVER THIOCYANATE IN AQUEOUS SODIUM PERCHLORATE SOLUTIONS AT DIFFERENT TEMPERATURES

$c \times 10^2$ (mol l^{-1})	$s \times 10^6$ (mol l^{-1})	$f_\pm$ from eqn (1)	$f_\pm$ from eqn (3)	$f_\pm$ from eqn (6)
Temperature: 15°C				
0	0.661	0.9911	0.9910	0.9910
1	1.300	0.5041	0.5040	0.8910
2	2.418	0.2710	0.2710	0.8494
3	4.451	0.1470	0.1472	0.8193
4	8.155	0.0803	0.0803	0.7941
5	14.900	0.0439	0.0439	0.7729
Temperature: 20°C				
0	0.769	0.9902	0.9902	0.9900
1	1.641	0.4641	0.4641	0.8902
2	3.309	0.2301	0.2302	0.8484
3	6.609	0.1153	0.1153	0.8177
4	13.130	0.0580	0.0580	0.7927
5	26.030	0.0292	0.0292	0.7711
Temperature: 25°C				
0	0.976	0.9963	0.9963	0.9963
1	2.054	0.4732	0.4732	0.8894
2	4.094	0.2374	0.2374	0.8472
3	7.962	0.1220	0.1221	0.8162
4	15.520	0.0626	0.0626	0.7911
5	30.160	0.0322	0.0322	0.7693
Temperature: 30°C				
0	1.247	0.9983	0.9986	0.9988
1	2.540	0.4901	0.4901	0.8884
2	4.849	0.2567	0.2567	0.8459
3	9.162	0.1358	0.1358	0.8147
4	17.220	0.0722	0.0722	0.7893
5	32.280	0.0385	0.0385	0.7676
Temperature: 35°C				
0	1.563	0.9987	0.9986	0.9986
1	3.161	0.4938	0.4938	0.8874
2	5.780	0.2700	0.2700	0.8445
3	10.640	0.1467	0.1467	0.8132
4	19.510	0.0800	0.0800	0.7874
5	35.630	0.0438	0.0438	0.7656

The values of $f_{\pm}$ calculated with the help of eqn (1) are in good agreement with those calculated from eqn (3). It is of interest to compare the $f_{\pm}$ values obtained by using the Debye–Hückel limiting expression

$$-\log f_{\pm} = A\mu^{1/2} \tag{6}$$

with those obtained from eqns (1) and (3). It is seen that the activity coefficient calculated from the limiting Debye–Hückel equation is accurate only upto a concentration of ca. 0.01 molar beyond which deviations occur from the experimental value, and in most cases the values are much higher than the experimental values.

The solubilities of AgCNS in water in the absence of any added salt are found to be 0.661×10^{-6}, 0.769×10^{-6}, 0.976×10^{-6}, 1.247×10^{-6}, and 1.563×10^{-6} mol l^{-1} at 15, 20, 25, 30, and 35°C, respectively. The solubility product is obtained by using the equation, $K_s = (s^c)^2$ and the values for the solubility product are found to be 0.437×10^{-12}, 0.592×10^{-12}, 0.952×10^{-12}, 1.555×10^{-12}, and 2.443×10^{-12} mol^2 l^{-2} at 15, 20, 25, 30, and 35°C, respectively. These results may be compared with the solubility product values in water as reported from the standard electrode potentials of the silver–silver thiocyanate electrode in that solvent by Lal and Prasad[3] $(0.269 \times 10^{-12}, 0.523 \times 10^{-12}, 1.003 \times 10^{-12}, 1.865 \times 10^{-12}$ and 3.406×10^{-12} mole^2 l^{-2}, respectively) at 15, 20, 25, 30, and 35°C, and by Vanderzee and Smith[2] (1.01×10^{-12} mol^2 l^{-2}) at 25°C. Our K_s values are found to be higher at 15 and 20°C and lower at 25, 30, and 35°C in comparison with the values reported by Lal and Prasad. These discrepancies are almost certainly due to the determination of the solubility in the presence of the added salt, sodium perchlorate and the high values at low temperatures show that the rate of dissolution of AgCNS in the presence of sodium perchlorate is higher at low temperatures than that at higher temperatures.

The variation of K_s with temperature may be expressed through the equation

$$\log K_s = -86.6126 + 0.14389\,T + 9450.17/T \tag{7}$$

The standard free energy change ΔG°, for the dissolution process, AgCNS(s) → Ag$^+$(aq) + CNS$^-$(aq) is obtained by the relation, $\Delta G^\circ = -RT \ln K_s$. A plot of $\log K_s$ against $1/T$ yields a straight line and the heat of solution (ΔH°) of silver

TABLE 3

STANDARD THERMODYNAMIC QUANTITIES OF
SILVER THIOCYANATE IN WATER AT DIFFERENT TEMPERATURES

Temp. ($^\circ C$)	$K_s \times 10^{12}$ (mol^2 l^{-2})	$\Delta G^\circ \times 10^{-3}$ (J)	$\Delta H^\circ \times 10^{-3}$ (J)	ΔS° (J deg^{-1})
15	0.437	68.15	37.79	−105.41
20	0.592	68.60	37.79	−105.15
25	0.952	68.58	37.79	−103.32
30	1.555	68.50	37.79	−101.35
35	2.443	68.47	37.79	−99.61

thiocyanate calculated from the slope of this plot turns out to be 37,790 J, which is less than that found from cell data (92,410 J) at 25°C by Lal and Prasad. If $\Delta H°$ is assumed to remain constant over the range of temperatures employed, which appears to be the case, the standard entropy change, $\Delta S°$ for the dissolution process may be evaluated from the relation, $\Delta S° = (\Delta H° - \Delta G°)/T$. These standard thermodynamic quantities are shown in Table 3.

The standard potentials of Ag–AgCNS electrode have been calculated from the values of the solubility product, K_s, and the standard electrode potential of silver[4a] by means of the equation

$$E°_{Ag-AgCNS} = E°_{Ag} + \frac{RT}{F} \ln K_s \tag{8}$$

The standard potentials of Ag–AgCNS electrode thus calculated have been presented in Table 4. The variation of $E°$ of Ag–AgCNS electrode with temperature may be expressed through the equation,

$$E°_t = 0.0873 - 1.14 \times 10^{-3}(t-25) + 3.644 \times 10^{-5}(t-25)^2 \tag{9}$$

The calculated values of $E°$ are also presented in the same table along with the observed values. Comparison of our $E°$ values with those determined from e.m.f. measurements by Vanderzee and Smith, and Lal and Prasad shows that our $E°$ values are in good agreement with their reported values suggesting that the solubility method may well be applicable for the determination of the standard electrode potentials of the silver–silver thiocyanate electrode.

TABLE 4

STANDARD POTENTIALS OF Ag–AgCNS ELECTRODE IN WATER AT DIFFERENT TEMPERATURES

Temp. (°C)	$E°_{Ag-AgCNS}$ (V)	
	Obs.	Calc. from eqn. (9)
15	0.1021	0.1023
20	0.0928	0.0932
25	0.0880	0.0873
30	0.0840	0.0818
35	0.0793	0.0795

REFERENCES

1 U. N. Dash and J. Mohanty, *Thermochim. Acta*, 12 (1975) 189.
2 C. E. Vanderzee and W. E. Smith, *J. Amer. Chem. Soc.*, 20 (1956) 721.
3 S. C. Lal and B. Prasad, *Indian J. Chem.*, 13 (1975) 372.
4 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 3rd ed., 1967, p. 165 and (a) p. 451.