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SOLUBILITY STUDIES IN FORMAMIDE
V. SOLUBILITY PRODUCT OF SILVER PERMANGANATE AND STANDARD ELECTRODE POTENTIALS OF SILVER–SILVER PERMANGANATE ELECTRODE IN FORMAMIDE

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ABSTRACT

The solubility and solubility product of silver permanganate in formamide in sodium perchlorate solutions have been determined at 25, 30 and 35°C. The solubilities in pure formamide are found to be 5.985×10^{-5}, 6.512×10^{-5}, and 7.114×10^{-5} mol l^{-1}, respectively, at these temperatures, and the corresponding solubility products are 3.583×10^{-9}, 4.240×10^{-9} and 5.060×10^{-9} mol^2 l^{-2}. The standard potentials of the $Ag(s)/AgMnO_4(s)/MnO_4^-$ electrode have been calculated and found to be 0.2055 V, 0.1964 V, and 0.1872 V at 25, 30, and 35°C, respectively. The mean activity coefficients of silver permanganate at various rounded molarities of sodium perchlorate solutions, and the standard thermodynamic quantities for the process $AgMnO_4(s) \rightarrow Ag^+(\text{solvated}) + MnO_4^-(\text{solvated})$ have been calculated at these three temperatures.

INTRODUCTION

In previous communications[1–4], we reported the solubility, and the solubility product of sparingly soluble silver salts in formamide over a range of temperatures. The present investigation deals with similar studies made on silver permanganate at 25, 30, and 35°C using formamide as the solvent. The influence of ionic strength on the mean activity coefficients of silver permanganate in solution has also been examined. From the values of the solubility products of silver permanganate at these temperatures, the standard potentials of the $Ag(s)/AgMnO_4(s)/MnO_4^-$ electrode have been obtained in formamide.

EXPERIMENTAL

Silver permanganate was prepared according to the method described earlier[5]. Anhydrous sodium perchlorate was prepared according to the standard procedure given in the literature[6]. Formamide (Riedel, pure) was further purified as described earlier[1].

The method of determination of solubility, the analysis of the solute contents and the accuracy of the analysis have been adequately described[2,5].

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,

TABLE 1

SUMMARY OF SOLUBILITY DATA FOR SILVER PERMANGANATE IN SODIUM PERCHLORATE SOLUTIONS IN FORMAMIDE AT 25, 30 AND 35°C

$c \times 10^2$ ($mol\ l^{-1}$)	$s \times 10^5$ ($mol\ l^{-1}$)	$(c+s) \times 10^2$ ($mol\ l^{-1}$)	$(c+s)^{\frac{1}{2}} \times 10^2$ ($mol\ l^{-1})^{\frac{1}{2}}$	$\frac{A(c+s)^{\frac{1}{2}} \times 10^2}{1+(c+s)^{\frac{1}{2}}}$	$-\log s$ ($mol\ l^{-1}$)	$-\log s^{\circ\prime}$ ($mol\ l^{-1}$)
Temperature: 25°C						
0.938	6.436	0.944	9.72	2.719	4.1914	4.2186
1.589	6.695	1.596	12.63	3.444	4.1742	4.2086
2.120	6.795	2.127	14.58	3.905	4.1678	4.2068
3.431	6.988	3.438	18.54	4.803	4.1556	4.2036
5.895	7.598	5.903	24.30	5.999	4.1192	4.1792
9.475	8.324	9.483	30.79	7.228	4.0797	4.1520
12.530	8.995	12.539	35.40	8.028	4.0460	4.1263
				$-\log s^\circ$ (extrapolated)		4.2253
				B' (l mol^{-1})		−0.7724
Temperature: 30°C						
0.785	6.945	0.792	8.90	2.517	4.1583	4.1837
1.256	7.150	1.263	11.24	3.113	4.1457	4.1768
2.658	7.425	2.665	16.32	4.324	4.1293	4.1725
4.582	7.950	4.590	21.42	5.437	4.0996	4.1540
6.684	8.243	6.692	25.87	6.330	4.0839	4.1472
8.985	8.772	8.994	29.99	7.108	4.0569	4.1280
14.680	10.050	14.690	38.32	8.535	3.9980	4.0834
				$-\log s^\circ$ (extrapolated)		4.1888
				B' (l mol^{-1})		−0.7067
Temperature: 35°C						
1.438	7.766	1.446	12.02	3.318	4.1098	4.1430
2.650	8.301	2.658	16.30	4.331	4.0809	4.1242
3.693	8.401	3.701	19.24	4.989	4.0757	4.1256
7.890	9.317	7.899	28.10	6.781	4.0307	4.0985
10.380	9.900	10.390	32.23	7.536	4.0044	4.0798
12.560	10.660	12.571	35.45	8.085	3.9722	4.0530
13.830	10.840	13.841	37.20	8.379	3.9648	4.0486
				$-\log s^\circ$ (extrapolated)		4.1505
				B' (l mol^{-1})		−0.7293

s, of silver permanganate in mol l^{-1}, averaged in each case, from three closely agreeing results; 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 papers[2,3,5], assuming that the salts employed are completely dissociated in formamide, the solubility, s, of silver permanganate 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 permanganate, 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 expressed by

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

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

Unfortunately, at present, there seems to be no adequate method for determining the ion size parameter in formamide. The following equation has been used, as in the previous papers[1,2,5], in place of eqn (3),

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

where B'' replaces the empirical constant B' in eqn (3).

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

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

By plotting the left-hand side of eqn (4), which for brevity is represented by the expression $\log s^{\circ\prime}$ 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 required for such a calculation at different temperatures were obtained from the literature[7]. In Fig. 1 the values of $\log s^{\circ\prime}$ have been plotted against the total salt concentration,

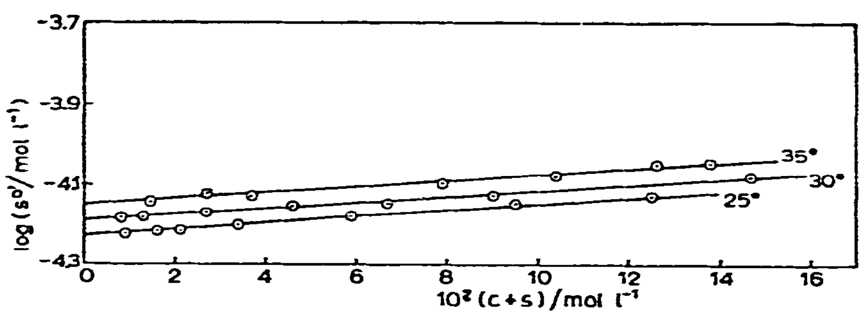

Fig. 1. Plot of log s°' versus total salt concentration.

$(c+s)$, 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.

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 (3a). For this purpose, eqn (4) may be written in the form

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

Using the appropriate value of c and the known values of s°, 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

TABLE 2

SUMMARY OF ACTIVITY COEFFICIENTS FOR SILVER PERMANGANATE IN SODIUM PERCHLORATE SOLUTIONS IN FORMAMIDE AT 25, 30 AND 35°C

$c \times 10^2$ (mol l^{-1})	$s \times 10^5$ (mol l^{-1})	$f_\pm$ from eqn (1)	$f_\pm$ from eqn (3a)	$f_\pm$ from eqn (6)
Temperature: 25°C				
0	5.985	0.9945	0.9945	0.9945
1	6.465	0.9208	0.9208	0.9315
2	6.735	0.8839	0.8839	0.9046
3	6.971	0.8539	0.8539	0.8847
4	7.193	0.8275	0.8275	0.8680
5	7.404	0.8039	0.8039	0.8537
10	8.429	0.7062	0.7062	0.7997
15	9.471	0.6285	0.6285	0.7603
Temperature: 30°C				
0	6.512	0.9942	0.9942	0.9942
1	7.021	0.9221	0.9221	0.9313
2	7.305	0.8863	0.8863	0.9044
3	7.551	0.8574	0.8574	0.8843
4	7.778	0.8324	0.8324	0.8676
5	7.997	0.8097	0.8097	0.8533
10	9.036	0.7164	0.7164	0.7991
15	10.070	0.6427	0.6427	0.7598
Temperature: 35°C				
0	7.114	0.9940	0.9940	0.9940
1	7.676	0.9212	0.9212	0.9311
2	7.989	0.8851	0.8851	0.9040
3	8.262	0.8559	0.8559	0.8839
4	8.517	0.8303	0.8303	0.8672
5	8.760	0.8072	0.8072	0.8527
10	9.926	0.7124	0.7124	0.7986
15	11.100	0.6371	0.6371	0.7590

the same equation. Using the 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 permanganate in formamide 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 (3a). The values of s and $f_{\pm}$ obtained through this procedure are recorded in Table 2.

As in the previous cases of the solubility data in formamide[1-3], the solubility and activity coefficient data presented in this paper also are subject to the similar source of error. Formamide is thermally unstable to some extent and ammonia is one of the decomposition products. It is possible that $AgMnO_4$ may react with the free ammonia to form the complex ion $Ag^{+}(NH_3)_2$ and thus increase the solubility. However, the smooth linear plots obtained in Fig. 1 seem to suggest that the error from this source is not at all significant.

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

$$-\log f_{\pm} = A\sqrt{\mu} \tag{6}$$

with those obtained from eqns (1) and (3a). It is seen that the activity coefficient calculated from the limiting Debye–Hückel equation is accurate only up to a concentration of ca. 0.01 molar beyond which deviations occur from the experimental value. The $f_{\pm}$ values computed from eqn (6) are presented in the last column of Table 2.

The solubilities of $AgMnO_4$ in formamide in the absence of any added salt are found to be 5.985×10^{-5}, 6.512×10^{-5}, and 7.114×10^{-5} mol l^{-1} at 25, 30, and 35 °C, respectively. These results may be compared with the solubility values in water[5], 1.152×10^{-5}, 1.282×10^{-5} and 1.420×10^{-5} mol l^{-1} at 25, 30 and 35 °C, respectively. Thus silver permanganate is more soluble in formamide than in water at these temperatures.

TABLE 3

STANDARD THERMODYNAMIC QUANTITIES OF SILVER PERMANGANATE IN FORMAMIDE AND WATER AT 25, 30 AND 35 °C

Temp. (°C)	$K_s \times 10^9$ (*mol*^{2} *l*$^{-2}$)	$\Delta G^\circ \times 10^{-3}$ (*J*)	$\Delta H^\circ \times 10^{-3}$ (*J*)	ΔS° (*J deg*$^{-1}$)	*Solution*
25	3.583	48.23	26.09	−74.30	formamide
25	0.133	56.41	28.69	−93.03	water
30	4.240	48.63	26.09	−74.40	formamide
30	0.164	56.82	28.69	−92.85	water
35	5.060	48.99	26.09	−74.33	formamide
35	0.202	57.24	28.69	−92.68	water

The solubility product, K_s is obtained by using the equation, $K_s = (s^\circ)^2$, and the standard free energy change, ΔG°, for the dissolution process, $AgMnO_4(s) \rightarrow Ag^+$ (solvated) $+ MnO_4^-$ (solvated), by the relation, $\Delta G^\circ = -RT \ln K_s$. The values of K_s as well as those of ΔG° are shown in Table 3 together with similar data in water for the sake of comparison[5].

From the slope of the plot of log K_s against $1/T$, the heat of solution (ΔH°) of silver permanganate has been calculated. The value of ΔH° is found to be 26090 J, which is somewhat less than that found in water[5] (28690 J). If ΔH° is assumed to remain constant over the range of temperatures employed, which appears to be the case, the standard entropy change, ΔS° for the dissolution process may be evaluated from the relation, $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$. These values are also shown in Table 3 together with the corresponding values in water.

The standard potentials of the silver–silver permanganate electrode ($E_{Ag/AgMnO_4}$) have been calculated from the values of the solubility product, K_s, and the standard electrode potential of silver (E°_{Ag}) by means of the equation

$$E^\circ_{Ag-AgMnO_4} = E^\circ_{Ag} + \frac{RT}{F} \ln K_s.$$

The standard electrode potential of silver in formamide required for this purpose was obtained from the previous studies[3]. The standard potentials of the silver–silver permanganate electrode are found to be 0.2055, 0.1964, and 0.1872 V, at 25, 30, and 35°C, respectively. The values of $E^\circ_{Ag-AgMnO_4}$ in formamide may be compared with the values in water[5] as reported from the solubility measurements of $AgMnO_4$ in that solvent (0.2149, 0.2055, and 0.1963 V, respectively) at 25, 30, and 35°C. The E° values are found to be lower in formamide than in water at these temperatures and are in agreement with the general behaviour exhibited by other electrodes of this class, such as Ag–$AgIO_3$, Ag–$AgBrO_3$, and Ag–AgOAc electrodes[3,8].

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