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SOLUBILITY STUDIES IN AQUEOUS MEDIA

I. SOLUBILITY PRODUCT OF SILVER PERMANGANATE AND STANDARD ELECTRODE POTENTIALS OF SILVER–SILVER PERMANGANATE ELECTRODE IN AQUEOUS MEDIA

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ABSTRACT

The solubility and solubility product of silver permanganate in water have been determined at the temperatures ranging from 15 to 35°C over 5°C intervals in the presence of an added electrolyte, sodium perchlorate. The solubility of silver permanganate ranges from 0.966×10^{-5} mol l^{-1} at 15°C to 1.420×10^{-5} mol l^{-1} at 35°C and the corresponding solubility product 0.933×10^{-10} mol^2 l^{-2} at 15°C to 2.017×10^{-10} mol^2 l^{-2} at 35°C. The standard potentials of the $Ag(s)/AgMnO_4(s)/MnO_4^-$ electrode have been calculated at these temperatures. The mean activity coefficients of silver permanganate at various rounded molarities of sodium perchlorate solutions, and the standard thermodynamic quantities for the process $AgMnO_4(s) \rightarrow Ag^+(aq) + MnO_4^-(aq)$ have been calculated at these temperatures.

INTRODUCTION

Several studies on the solubility of sparingly soluble salts of silver in aqueous media have been made either in presence of or without the added electrolyte. A similar study on the solubility of the sparingly soluble salt, silver permanganate, in aqueous sodium perchlorate solutions, over the temperature range 15–35°C, is the subject of the present communication. Previous investigation of solubility of silver permanganate in water is known[1], although it does not seem to have been carried out under optimal conditions. This paper reports a more accurate determination of the solubility of this salt. In course of these studies, besides obtaining solubility and other related data, the influence of ionic strength on the mean activity coefficients of silver permanganate in solution has also been examined. The solubility product of silver permanganate at different temperatures has been further combined with the standard potentials of the Ag-electrode in water to obtain the standard potentials of the $Ag(s)/AgMnO_4(s)/MnO_4^-$ electrode in water at these temperatures.

EXPERIMENTAL

Silver permanganate was prepared by mixing dilute solutions of silver nitrate and potassium permanganate (B.D.H., AnalaRs). The crystals were washed repeatedly with conductivity water and finally dried in a vacuum desiccator over $CaCl_2$ for several weeks. The dried, almost black crystals, gave on analysis by standard methods a purity of 99.6%.

Sodium perchlorate was prepared according to the standard procedure given in literature[2]. A stock solution of sodium perchlorate was prepared by dissolving a weighed quantity of sodium perchlorate in triply distilled water.

The solutions of sodium perchlorate of required molarities were prepared from the stock solution by dilution, and were then put into amber-coloured glass-stoppered bottles containing an excess of silver permanganate. The stoppers were heavily paraffined and the bottles were then rotated in a water thermostat maintained at the appropriate temperature (to within ±0.03 °C) for several weeks, till equilibration, after which the solute content of the saturated solution in each of the bottles was analysed. It was found by means of a few trial runs that a time period of four weeks was sufficient to reach equilibrium. The solute contents were analysed by the permanganametric determination of the permanganate using a 0.01 M sodium oxalate solution and a calibrated microburette. The titrations were accurate to ±0.2%.

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 permanganate in moles per litre, 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.

Assuming that the salts employed are completely dissociated, the solubility, s, of silver permanganate at any salt concentration c may be written as

$$sf_{\pm} = s^{\circ} \qquad (1)$$

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

$$\log s^{\circ} = \log s + \log f_{\pm} \qquad (2)$$

Following the Debye–Hückel theory, the mean activity coefficient may be more accurately expressed by

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

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 PERMANGANATE IN AQUEOUS SODIUM PERCHLORATE SOLUTIONS AT DIFFERENT TEMPERATURES

$c \times 10^2$ ($mol\ l^{-1}$)	$s \times 10^5$ ($mol\ l^{-1}$)	$(c+s) \times 10^2$ ($mol\ l^{-1}$)	$(c+s)^{\frac{1}{2}} \times 10^2$ ($mol\ l^{-1})^{\frac{1}{2}}$	$\dfrac{A(c+s)^{\frac{1}{2}} \times 10^2}{1+(c+s)^{\frac{1}{2}}}$	$-\log s$ ($mol\ l^{-1}$)	$-\log s^{\circ\prime}$ ($mol\ l^{-1}$)
Temperature: 15°C						
0.250	1.209	0.251	5.01	2.386	4.9176	4.9415
0.500	1.388	0.501	7.08	3.306	4.8576	4.8907
0.750	1.582	0.752	8.67	3.991	4.8007	4.8406
1.000	1.899	1.002	10.01	4.552	4.7214	4.7669
1.500	2.441	1.502	12.26	5.459	4.6124	4.6670
1.750	2.702	1.753	13.24	5.851	4.5683	4.6268
2.500	4.747	2.505	15.82	6.839	4.3236	4.3920
				$-\log s^{\circ}$ (extrapolated)		5.0168
				B' (l mol^{-1})		−23.97
Temperature: 20°C						
0.250	1.290	0.251	5.01	2.407	4.8894	4.9135
0.500	1.455	0.501	7.08	3.334	4.8372	4.8705
0.750	1.676	0.752	8.67	4.025	4.7757	4.8160
1.000	2.216	1.002	10.01	4.591	4.6544	4.7003
1.750	3.481	1.754	13.24	5.900	4.4582	4.5172
				$-\log s^{\circ}$ (extrapolated)		4.9946
				B' (l mol^{-1})		−27.13
Temperature: 25°C						
0.250	1.443	0.251	5.01	2.429	4.8407	4.8650
0.500	1.567	0.502	7.08	3.367	4.8049	4.8386
0.750	1.999	0.752	8.67	4.061	4.6992	4.7398
1.000	2.289	1.002	10.01	4.633	4.6404	4.6867
1.500	3.402	1.503	12.26	5.555	4.4682	4.5237
1.750	3.798	1.754	13.24	5.954	4.4205	4.4800
2.250	4.942	2.255	15.02	6.648	4.3061	4.3726
2.500	5.811	2.506	15.82	6.960	4.2358	4.3054
				$-\log s^{\circ}$ (extrapolated)		4.9555
				B' (l mol^{-1})		−25.63
Temperature: 30°C						
0.250	1.563	0.252	5.02	2.457	4.8059	4.8305
0.500	1.788	0.502	7.08	3.399	4.7475	4.7815
0.750	2.178	0.752	8.67	4.101	4.6620	4.7030
1.250	2.968	1.253	11.19	5.177	4.5276	4.5794
1.500	3.588	1.504	12.27	5.611	4.4451	4.5012
1.750	4.133	1.754	13.24	6.012	4.3837	4.4438
2.250	6.068	2.256	15.02	6.713	4.2169	4.2840
				$-\log s^{\circ}$ (extrapolated)		4.9101
				B' (l mol^{-1})		−27.40

(Table 1 continued on p. 192)

TABLE 1 (*continued*)

$c \times 10^2$ $(mol\ l^{-1})$	$s \times 10^5$ $(mol\ l^{-1})$	$(c+s) \times 10^2$ $(mol\ l^{-1})$	$(c+s)^{1/2} \times 10^2$ $(mol\ l^{-1})^{1/2}$	$\frac{A(c+s)^{1/2} \times 10^2}{1+(c+s)^{1/2}}$	$-\log s$ $(mol\ l^{-1})$	$-\log s^{\circ\prime}$ $(mol\ l^{-1})$
Temperature: 35 °C						
0.250	1.695	0.252	5.02	2.480	4.7708	4.7956
0.750	2.402	0.752	8.67	4.140	4.6194	4.6608
1.000	2.842	1.003	10.01	4.724	4.5464	4.5936
1.250	3.383	1.253	11.19	5.223	4.4708	4.5230
1.750	4.362	1.754	13.24	6.070	4.3603	4.4210
2.000	5.563	2.006	14.16	6.434	4.2547	4.3190
2.250	6.748	2.257	15.03	6.778	4.1708	4.2386
				$-\log s^\circ$ (extrapolated)		4.8669
				B'' (l mol^{-1})		−27.23

However, not having any definite knowledge about the ion size parameter in aqueous media, the application of eqn (3) gives rise to some difficulties. Consequently, as a measure of good approximation, the following equation may be used in its place[3].

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

Where, because of the approximation involved, B'' now replaces the empirical constant B' in eqn (3).

Combining eqns (2) and (3a), we further obtain

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

The validity of eqn (3a) can be tested by plotting the left-hand side of eqn (4) based on experimental data against $(c+s)$, in which case a straight line should be obtained yielding an intercept equal to $\log s^\circ$ and a slope equal to $-B''$. Plots of such type using experimental data at different temperatures are shown in Fig. 1. Here the left-hand

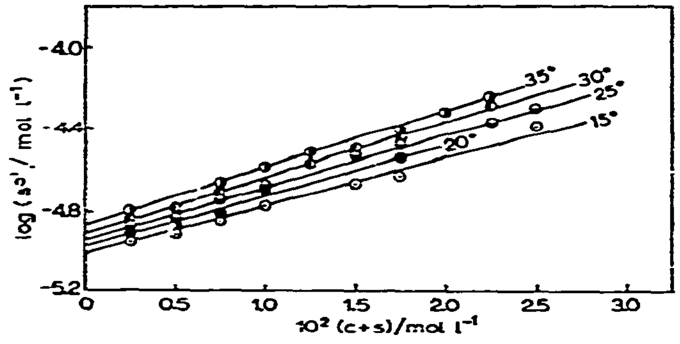

Fig. 1. Plot of log $s^{\circ\prime}$ versus salt concentration.

side of eqn (4) which for brevity is represented by the expression $\log s^{\circ\prime}$ has been plotted against the total salt concentration $(c+s)$. The values of A, needed for such calculation, were taken from the literature[4]. The close fit of $\log s^{\circ\prime}$ values with a straight-line plot at each temperature clearly suggests that eqn (3a) is indeed a good approximation for $\log f_{\pm}$. 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 procedure further allows the evaluation of both s and $f_{\pm}$ at rounded concentrations of the salt, i.e., sodium perchlorate. This can be achieved 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 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 permanganate 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 (3a). The values of s and $f_{\pm}$ obtained through this procedure are shown in Table 2.

As expected the $f_{\pm}$ values calculated with the help of eqn (1) agree well with those calculated from eqn (3a). In the last column of Table 2, the $f_{\pm}$ values computed by Debye–Hückel's limiting expression

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

are also shown. It will be observed 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, and in most cases the values are much higher than the experimental values.

The solubilities of silver permanganate in water in the absence of any added salt are found to be 0.966×10^{-5}, 1.051×10^{-5}, 1.152×10^{-5}, 1.282×10^{-5}, and 1.420×10^{-5} mol l^{-1} at 15, 20, 25, 30, and 35 °C, respectively. Hein and Daniel[1] have reported the solubility of silver permanganate in water at 20 °C, but their solubility value (0.04066 mol l^{-1}) at 20 °C differs appreciably from our value (1.051×10^{-5} mol l^{-1}) at this temperature. As the full experimental details of their work are lacking and the data are only available at a single temperature, we are not giving much significance to their reported value and consider the present set of solubility data more reliable.

TABLE 2

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

$c \times 10^2$ $(mol\ l^{-1})$	$s \times 10^5$ $(mol\ l^{-1})$	$f_\pm$ *from eqn (1)*	$f_\pm$ *from eqn (3a)*	$f_\pm$ *from eqn (6)*
Temperature: 15°C				
0	0.966	0.9959	0.9959	0.9963
1	1.858	0.5180	0.5180	0.8913
2	3.350	0.2871	0.2871	0.8496
3	5.994	0.1605	0.1605	0.8191
4	10.660	0.0902	0.0902	0.7939
5	18.950	0.0508	0.0508	0.7727
Temperature: 20°C				
0	1.051	0.9636	0.9636	0.9632
1	2.105	0.4810	0.4810	0.8902
2	4.090	0.2476	0.2476	0.8484
3	7.874	0.1286	0.1286	0.8175
4	15.090	0.0671	0.0671	0.7923
5	29.020	0.0349	0.0349	0.7705
Temperature: 25°C				
0	1.152	0.9616	0.9616	0.9610
1	2.226	0.4976	0.4976	0.8892
2	4.179	0.2651	0.2651	0.8470
3	8.971	0.1235	0.1235	0.8160
4	16.370	0.0677	0.0677	0.7907
5	33.650	0.0329	0.0329	0.7690
Temperature: 30°C				
0	1.282	0.9592	0.9592	0.9585
1	2.580	0.4767	0.4767	0.8882
2	5.047	0.2437	0.2437	0.8457
3	9.790	0.1256	0.1256	0.8143
4	18.910	0.0650	0.0650	0.7891
5	36.650	0.0336	0.0336	0.7668
Temperature: 35°C				
0	1.420	0.9568	0.9568	0.9561
1	2.841	0.4782	0.4782	0.8874
2	5.544	0.2451	0.2451	0.8443
3	10.710	0.1269	0.1269	0.7962
4	20.650	0.0658	0.0658	0.7870
5	39.920	0.0340	0.0340	0.7647

The solubility product is obtained by using the equation, $K_s = (s^\circ)^2$. The variation of K_s with temperature may be expressed through the equation

$$\log K_s = -37.3958 + 0.053788\,T + 3419.9/T \tag{7}$$

The standard free energy change ΔG°, for the dissolution process, $AgMnO_4(s) \rightarrow Ag^+(aq) + MnO_4^-(aq)$ is obtained by the relation, $\Delta G^\circ = -RT \ln K_s$. A plot of log K_s against $1/T$ (Fig. 2) yields a straight line, from the slope of which the heat of solution (ΔH°) of silver permanganate has been calculated. 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,

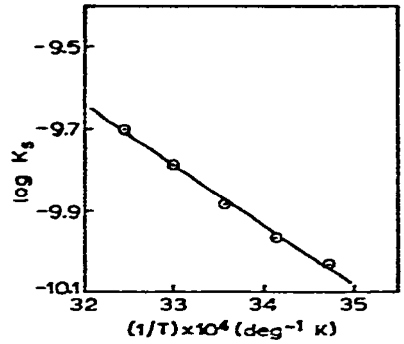

Fig. 2. Variation of log K_s with $1/T$.

$$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T$$

These standard thermodynamic quantities are shown in Table 3.

TABLE 3

STANDARD THERMODYNAMIC QUANTITIES OF SILVER PERMANGANATE IN WATER AT DIFFERENT TEMPERATURE

Temp. (°C)	$K_s \times 10^{10}$ ($mol^2\ l^{-2}$)	$\Delta G^{\circ} \times 10^{-3}$ (*J*)	$\Delta H^{\circ} \times 10^{-3}$ (*J*)	ΔS° ($J\ deg^{-1}$)
15	0.933	55.38	28.69	−85.72
20	1.104	55.93	28.69	−92.96
25	1.327	56.41	28.69	−93.03
30	1.644	56.82	28.69	−92.85
35	2.017	57.24	28.69	−92.68

The standard potentials of Ag–AgMnO$_4$ electrode have been calculated from the values of solubility product, K_s, and the standard electrode potential of silver by means of the equation

$$E^{\circ}_{Ag-AgMnO_4} = E^{\circ}_{Ag} + \frac{RT}{F} \ln K_s \qquad (8)$$

The standard electrode potential of silver in water needed for this purpose was obtained from the empirical equation available in the literature[4a]. The standard potentials of Ag–AgMnO$_4$ electrode thus calculated have been recorded in Table 4.

TABLE 4

STANDARD POTENTIALS OF Ag–AgMnO$_4$ ELECTRODE IN WATER AT DIFFERENT TEMPERATURES

Temp. (°C)	$E_{\text{Ag-AgMnO}_4}$ (V)	
	Obs.	*Calc. from eqn (9)*
15	0.2356	0.2349
20	0.2249	0.2253
25	0.2149	0.2155
30	0.2055	0.2056
35	0.1963	0.1956

The variation of E° of Ag–AgMnO$_4$ electrode with temperature may be expressed through the equation,

$$E_t^\circ = 0.21549 - 1.965\times10^{-3}(t-25) - 2.700\times10^{-6}(t-25)^2 \qquad (9)$$

The calculated values of E° are also presented in the same table along with the observed values.

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