

SOLUBILITY STUDIES IN FORMAMIDE

III. SOLUBILITY PRODUCT OF SILVER BROMATE AND STANDARD ELECTRODE POTENTIAL OF SILVER-SILVER BROMATE ELECTRODE IN FORMAMIDE

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ABSTRACT

The solubility and solubility product of silver bromate in formamide in sodium perchlorate solutions have been determined at 25, 30 and 35°C. At these temperatures, the solubilities in pure formamide are found to be 1.837×10^{-2} , 1.967×10^{-2} , and $2.092 \times 10^{-2} \text{ mol l}^{-1}$, respectively, and the corresponding solubility products are 3.375×10^{-4} , 3.869×10^{-4} , and $4.377 \times 10^{-4} \text{ mol}^2 \text{ l}^{-2}$. The standard potentials of the $\text{Ag(s)}/\text{AgBrO}_3\text{(s)}/\text{BrO}_3^-$ electrode have been calculated and found to be 0.4997, 0.4948, and 0.4892 V, at 25, 30, and 35°C, respectively. The mean activity coefficients of silver bromate at various rounded molarities of sodium perchlorate solutions, and the standard thermodynamic quantities for the process $\text{AgBrO}_3\text{(s)} \rightarrow \text{Ag}^+$ (solvated) + BrO_3^- (solvated) have been calculated at these three temperatures and compared with those for the process $\text{AgIO}_3\text{(s)} \rightarrow \text{Ag}^+$ (solvated) + IO_3^- (solvated) in formamide.

INTRODUCTION

In continuation of the study on the solubility of sparingly soluble salts in formamide^{1,2}, the solubility, the solubility product and the heat of solution of silver oxalate and silver iodate have been reported in formamide over a range of temperatures. The present communication deals with similar studies made on silver bromate at 25, 30, and 35°C using formamide as the solvent. The influence of ionic strength on the mean activity coefficients of silver bromate in solution has also been examined. The solubility products of silver bromate at these temperatures have been further combined with the standard potentials of the Ag-electrode in formamide to obtain the standard potentials of the $\text{Ag(s)}/\text{AgBrO}_3\text{(s)}/\text{BrO}_3^-$ electrode in formamide at these temperatures.

EXPERIMENTAL

Silver bromate and anhydrous sodium perchlorate were prepared according to the standard procedures given in the literature^{3,4}. Formamide (Riedel, pure) was further purified as described earlier¹.

The solubility was determined by the method described earlier². The solute contents were analysed by the iodometric determination of the bromate using a 0.01 M sodium thiosulphate solution and a calibrated microburette. The sodium thiosulphate solutions were standardised against potassium dichromate. The titrations were accurate to $\pm 0.2\%$.

RESULTS AND DISCUSSION

The experimental results of the solubility measurements are recorded in Table I. The first column gives the molarity, c , of sodium perchlorate, the second the solubility, s , of silver bromate 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 calculations of the solubility is similar to our previous paper², assuming that the salts employed are completely dissociated in formamide, the solubility, s , of silver bromate at any salt concentration c may be written as

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

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

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

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

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

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

However, in the absence of any definite knowledge about ion size parameter in formamide, the application of eqn (3) creates some difficulties. Consequently, as a measure of good approximation, the following equation may be used in its place⁵

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

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

TABLE 1

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

$c \times 10^2$ (mol l ⁻¹)	$s \times 10^2$ (mol l ⁻¹)	$(c+s) \times 10^2$ (mol l ⁻¹)	$(c+s)^{\frac{1}{2}} \times 10^2$ (mol l ⁻¹) [†]	$\frac{A(c+s)^{\frac{1}{2}} \times 10^2}{1+(c+s)^{\frac{1}{2}}}$	$-\log s$ (mol l ⁻¹)	$-\log s^{\circ'}$ (mol l ⁻¹)
<i>Temperature: 25°C</i>						
0.759	1.862	2.621	16.19	4.277	1.7301	1.7729
2.735	1.890	4.625	21.50	5.433	1.7235	1.7778
3.543	1.905	5.448	23.34	5.811	1.7201	1.7782
4.645	1.940	6.585	25.65	6.266	1.7122	1.7749
6.352	1.950	8.302	28.81	6.868	1.7100	1.7787
8.539	1.955	10.494	32.39	7.509	1.7089	1.7840
9.315	1.960	11.275	33.58	7.716	1.7077	1.7849
10.420	1.965	12.385	35.20	7.991	1.7066	1.7865
					$-\log s^{\circ}$ (extrapolated)	1.7696
					B° (l mol ⁻¹)	+0.1575
<i>Temperature: 30°C</i>						
2.876	2.034	4.910	22.16	5.585	1.6916	1.7475
4.860	2.054	6.914	26.29	6.412	1.6873	1.7514
5.945	2.076	8.021	28.32	6.800	1.6827	1.7507
9.342	2.086	11.428	33.81	7.782	1.6806	1.7584
10.812	2.101	12.913	35.92	8.143	1.6776	1.7590
11.992	2.121	14.113	37.57	8.410	1.6734	1.7575
					$-\log s^{\circ}$ (extrapolated)	1.7413
					B° (l mol ⁻¹)	+0.1403
<i>Temperature: 35°C</i>						
1.470	2.136	3.606	18.99	4.932	1.6704	1.7197
2.625	2.152	4.781	21.86	5.543	1.6672	1.7226
3.225	2.165	5.390	23.21	5.824	1.6645	1.7227
5.226	2.170	7.396	27.19	6.607	1.6635	1.7296
6.180	2.178	8.358	28.91	6.929	1.6619	1.7312
7.185	2.211	9.396	30.66	7.249	1.6554	1.7279
9.766	2.220	11.986	34.62	7.950	1.6537	1.7332
					$-\log s^{\circ}$ (extrapolated)	1.7150
					B° (l mol ⁻¹)	+0.1571

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

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

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 $-B^{\circ}$. Plots of this type using experimental data at different temperatures are shown in Fig. 1. Here, the left-hand side of eqn (4) which for brevity is represented by the expression $\log s^{\circ'}$ has been plotted against the total salt concentration, $(c+s)$. For this purpose, the values of A used were as reported by Agarwal and Nayak¹². The close fit of $\log s^{\circ'}$ 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

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

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

TABLE 2

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

$c \times 10^2$ (mol l ⁻¹)	$s \times 10^2$ (mol l ⁻¹)	f_{\pm} from eqn (1)	f_{\pm} from eqn (3a)	f_{\pm} from eqn (6)
<i>Temperature: 25°C</i>				
0	1.837	0.9253	0.9253	0.9147
1	1.863	0.9122	0.9122	0.8971
2	1.882	0.9028	0.9028	0.8824
3	1.898	0.8956	0.8956	0.8708
4	1.914	0.8878	0.8878	0.8604
5	1.922	0.8847	0.8847	0.8513
10	1.952	0.8710	0.8710	0.7993
15	1.964	0.8654	0.8654	0.7949
20	1.967	0.8642	0.8642	0.7775
<i>Temperature: 30°C</i>				
0	1.967	0.9223	0.9223	0.9111
1	1.995	0.9093	0.9093	0.8930
2	2.016	0.8999	0.8999	0.8788
3	2.032	0.8925	0.8925	0.8670
4	2.046	0.8865	0.8865	0.8567
5	2.058	0.8816	0.8816	0.8474
10	2.095	0.8660	0.8660	0.8125
15	2.112	0.8590	0.8590	0.7879
20	2.119	0.8561	0.8561	0.7693
<i>Temperature: 35°C</i>				
0	2.092	0.9210	0.9210	0.9090
1	2.120	0.9088	0.9088	0.8919
2	2.142	0.8999	0.8999	0.8782
3	2.158	0.8932	0.8932	0.8668
4	2.172	0.8876	0.8876	0.8569
5	2.183	0.8831	0.8831	0.8482
10	2.217	0.8694	0.8694	0.8151
15	2.231	0.8638	0.8638	0.7921
20	2.235	0.8628	0.8628	0.7749

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 bromate 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 shown in Table 2.

As in the case of the solubility data of silver iodate², the solubility and activity coefficient data presented in this paper also are subject to the following source of error. Formamide is thermally unstable to some extent and ammonia is one of the decomposition products. It is possible that AgBrO_3 may react with the free ammonia to form the complex ion $\text{Ag}^+(\text{NH}_3)_2$ 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.

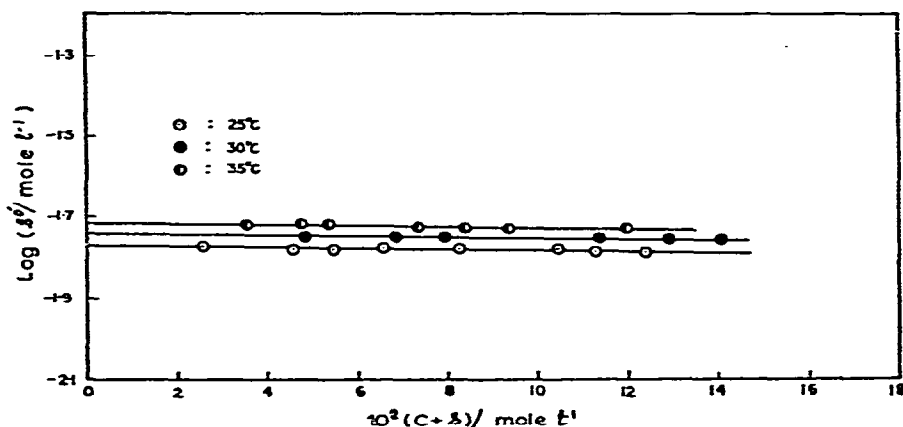


Fig. 1. Plot of $\log s''$ versus total salt concentration of silver bromate.

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

$$-\log f_{\pm} = A\sqrt{\mu} \quad (6)$$

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.

The solubilities of AgBrO_3 in formamide in the absence of any added salt are found to be 1.837×10^{-2} , 1.967×10^{-2} , and $2.092 \times 10^{-2} \text{ mol l}^{-1}$ at 25, 30, and 35°C, respectively. These results may be compared with the solubility values in water as reported from the solubility measurements of AgBrO_3 in that solvent by Owen⁶ ($6.812 \times 10^{-2} \text{ M}$), by Monk⁷ ($0.809 \times 10^{-2} \text{ M}$), by Latimer⁸ ($0.813 \times 10^{-2} \text{ M}$) all at

25°C, and by Reedy⁹ (0.827×10^{-2} , 0.962×10^{-2} , and 1.140×10^{-2} M, respectively) at 25, 30, and 35°C, and by Ramette and Dratz³ (0.809×10^{-2} and 1.122×10^{-2} M, respectively) at 25 and 35°C. Thus silver bromate is more soluble in formamide than in water at these temperatures.

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, $\text{AgBrO}_3(\text{s}) \rightarrow \text{Ag}^+$ (solvated) + BrO_3^- (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^{3,9}.

TABLE 3

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

Temp. (°C)	$K_s \times 10^4$ ($\text{mol}^2 \text{l}^{-2}$)	$\Delta G^\circ \times 10^{-3}$ (J)	$\Delta H^\circ \times 10^{-3}$ (J)	ΔS° (J deg ⁻¹)	Solution
25	3.375	19.80	34.07	47.87	formamide
25	0.684	24.40	48.96	82.43	water
30	3.869	19.80	34.07	47.15	formamide
30	0.926	23.40	48.96	84.39	water
35	4.377	19.81	34.07	46.31	formamide
35	1.259	23.56	48.96	82.47	water

A plot of $\log K_s$ against $1/T$ yields a straight line and the heat of solution (ΔH°) of silver bromate calculated from the slope of this plot turns out to be 34,070 J, which is somewhat less than that found in water³ (48,960 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

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

These values are also shown in Table 3 together with the corresponding values in water.

It is found from these results that ΔG° does not change much on passing from water to formamide whereas there are appreciable changes in ΔH° and ΔS° values. This indicates that the dissolution process is less energy-consuming and the dissolved state is less disordered in formamide than in water.

Table 4 gives the values of K_s and the standard thermodynamic quantities of silver bromate in both water and formamide and compares with those values of silver iodate evaluated in these solvents². From these results it is seen that the lower solubility of AgIO_3 in comparison with AgBrO_3 (i.e., the more positive free energy change) both in water and formamide is due to an enthalpy effect which is larger and thus

TABLE 4

COMPARISON OF SOLUBILITY DATA OF SILVER IODATE AND SILVER BROMATE IN FORMAMIDE AND WATER

Silver salt	K_s ($\text{mol}^2 \text{l}^{-2}$)	$\Delta G^\circ \times 10^{-3}$ (J)	$\Delta H^\circ \times 10^{-3}$ (J)	ΔS° (J deg $^{-1}$)	Solution
<i>Temperature: 25°C</i>					
Iodate $\times 10^8$	4.609	41.84	46.69	16.28	formamide
	3.055	42.88	56.65	46.15	water
Bromate $\times 10^4$	3.375	19.80	34.07	47.87	formamide
	0.684	24.40	48.96	82.43	water
<i>Temperature: 30°C</i>					
Iodate $\times 10^8$	6.053	41.84	46.69	15.94	formamide
	4.490	42.62	56.65	46.24	water
Bromate $\times 10^4$	3.869	19.80	34.07	47.15	formamide
	0.926	23.40	48.96	84.39	water
<i>Temperature: 35°C</i>					
Iodate $\times 10^8$	8.448	41.72	46.69	16.24	formamide
	6.456	42.42	56.69	46.31	water
Bromate $\times 10^4$	4.377	19.81	34.07	46.31	formamide
	1.259	23.56	48.96	82.47	water

overcomes an entropy effect which would favour higher solubility. This further indicates that the solvation energy for AgIO_3 is less than that of AgBrO_3 in both water and formamide and this causes the lower solubility of AgIO_3 relative to AgBrO_3 in both these solvents.

The standard potentials of silver-silver bromate electrode ($E_{\text{Ag}/\text{AgBrO}_3}^\circ$) have been calculated from the values of solubility product, K_s , and the standard electrode potential of silver (E_{Ag}°) by means of the equation

$$E_{\text{Ag}-\text{AgBrO}_3}^\circ = E_{\text{Ag}}^\circ + \frac{RT}{F} \ln K_s$$

The standard electrode potential of silver in formamide needed for this purpose was obtained from the values of solubility product, K_s , of silver oxalate¹ and the standard electrode potential of silver-silver oxalate ($E_{\text{Ag}-\text{Ag}_2\text{C}_2\text{O}_4}^\circ$) in formamide¹⁰. The E_{Ag}° values in formamide¹⁰ at 25, 30, and 35°C are found to be 0.7091, 0.7015 and 0.6954 V, respectively. Using these, the standard potentials of the silver-silver bromate electrode are found to be 0.4997, 0.4948, and 0.4892 V, respectively, at these temperatures. If, however, the value 0.6902 V as reported by Broadbank et al.¹¹ for

E_{Ag}° at 25°C is used, the standard potential of silver–silver bromate electrode turns out to be 0.4848 V, at this temperature, which is about 14.9 mV smaller than our value. The values of $E_{Ag-AgBrO_3}^{\circ}$ in formamide may be compared with the values in water as reported from the solubility measurements of $AgBrO_3$ in that solvent by Latimer⁸ (0.5500 V) at 25°C and by Reedy⁹ (0.5528, 0.5512, and 0.5506 V, respectively) at 25, 30 and 35°C.

The standard potentials of the Ag– $AgIO_3$ and Ag– $AgBrO_3$ electrodes are shown in Table 5 together with similar values in water at these temperatures for the

TABLE 5

STANDARD POTENTIALS OF SILVER–SILVER IODATE AND SILVER–SILVER BROMATE ELECTRODES IN FORMAMIDE AND WATER

Temp. (°C)	Formamide		Water	
	$E_{Ag-AgIO_3}^{\circ}$ (V)	$E_{Ag-AgBrO_3}^{\circ}$ (V)	$E_{Ag-AgIO_3}^{\circ}$ (V)	$E_{Ag-AgBrO_3}^{\circ}$ (V)
25	0.2711	0.4997	0.3551	0.5528
	0.2562	0.4848		0.5500
30	0.2659	0.4948	0.3525	0.5512
35	0.2621	0.4892	0.3499	0.5506

sake of comparison. 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–AgCl, Ag–AgBr and Ag–AgOAc electrodes^{12–15}. Further it is seen that the lower value of $E_{Ag-AgIO_3}^{\circ}$ both in water¹⁶ and formamide in comparison with E° of silver–silver bromate is due to the lower solubility of silver iodate in these solvents.

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