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SOLUBILITY STUDIES IN FORMAMIDE

II. SOLUBILITY PRODUCT OF SILVER IODATE AND STANDARD ELECTRODE POTENTIAL OF SILVER–SILVER IODATE ELECTRODE IN FORMAMIDE*

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ABSTRACT

The solubility and solubility product of silver iodate in formamide in sodium perchlorate solutions have been determined at 25, 30 and 35°C. The solubilities in pure formamide are found to be 2.169×10^{-4}, 2.488×10^{-4}, and 2.943×10^{-4} mole l^{-1}, respectively, at these temperatures, and the corresponding solubility products are 4.609×10^{-8}, 6.053×10^{-8}, and 8.448×10^{-8} mole^2 l^{-2}. The standard potential of the $Ag_{(s)}/AgIO_{3(s)}/IO_3^-$ electrode has been calculated and found to be 0.2562 V at 25°C. The mean activity coefficients of silver iodate at various rounded molarities of sodium perchlorate solutions, and the standard thermodynamic quantities for the process $AgIO_{3(s)} \rightarrow Ag^+(\text{solvated}) + IO_3^-(\text{solvated})$ have been calculated at these three temperatures.

INTRODUCTION

Quantitative data on solubility and solubility product of sparingly soluble salts in formamide, a solvent having a dielectric constant higher than that of water, are rather meagre. In the first part of this series[1], we reported the solubility, the solubility product and the heat of solution of silver oxalate in formamide over a range of temperatures. The present communication deals with similar studies made on silver iodate at 25, 30 and 35°C using formamide as the solvent. In course of these studies, besides obtaining the solubility and the other related data, the influence of ionic strength on the mean activity coefficients of silver iodate in solution has been examined. The solubility product of silver iodate at 25°C has been further combined with the standard potential of the Ag electrode in formamide to obtain the standard potential of $Ag_{(s)}/AgIO_{3(s)}/IO_3^-$ electrode in formamide at 25°C.

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* Ref. 1 is to be regarded as Part I of this series.

EXPERIMENTAL

Silver iodate and anhydrous sodium perchlorate were prepared according to the standard procedures given in literature[2,3]. Formamide (Riedel, pure) was further purified as described earlier[1].

The solutions of sodium perchlorate were prepared by dissolving appropriate and weighed amounts of the salt in known weights of formamide, and were then put into amber-coloured glass-stoppered bottles containing an excess of silver iodate. The stoppers were heavily paraffined and the bottles were then rotated in a water thermostat maintained at the appropriate temperature (to within ±0.01°) 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 (a typical run shown in Fig. 1) that a time period of seven to eight hours was sufficient to reach equilibrium, and the solubility hardly changed thereafter. The solute contents were analysed by the iodometric determination of the iodate 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 ±0.2%.

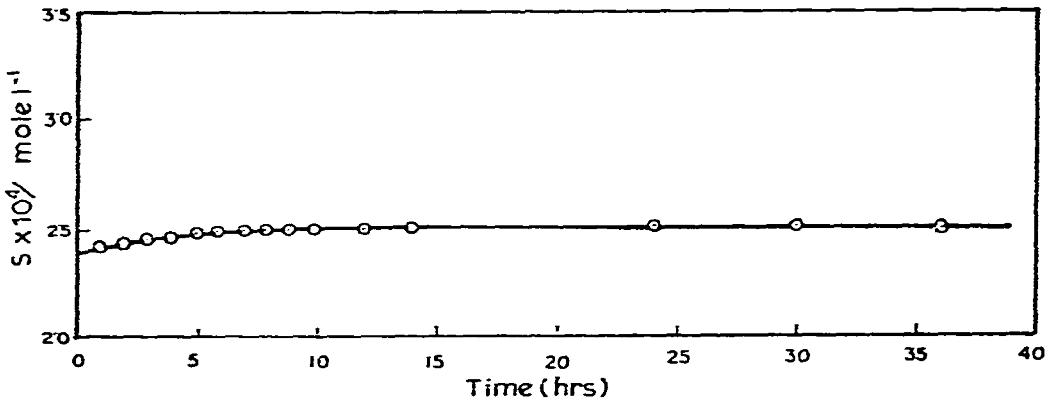

Fig. 1. Plot of *s* versus time (hours).

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 iodate 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 in formamide, the solubility, *s*, of silver iodate at any salt concentration *c* may be written as

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

TABLE I

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

$c \times 10^2$ mole l^{-1}	$s \times 10^4$ mole l^{-1}	$(c+s) \times 10^2$ mole l^{-1}	$(c+s)^{\frac{1}{2}} \times 10^2$ (mole $l^{-1})^{\frac{1}{2}}$	$\frac{A(c+s)^{\frac{1}{2}} \times 10^2}{1+(c+s)^{\frac{1}{2}}}$	$-\log s$ mole l^{-1}	$-\log s^{\circ\prime}$ mole l^{-1}
Temperature: 25 °C						
1.592	2.360	1.616	12.72	3.462	3.6271	3.6617
1.836	2.371	1.860	13.63	3.684	3.6251	3.6619
3.200	2.388	3.224	17.96	4.671	3.6219	3.6686
5.912	2.471	5.937	24.36	6.013	3.6071	3.6672
6.089	2.490	6.114	24.73	6.087	3.6038	3.6647
9.568	2.585	9.594	30.97	7.257	3.5875	3.6601
14.040	2.692	14.067	37.51	8.373	3.5699	3.6536
					$-\log s^\circ$ (extrapolated)	3.6683
					B' (litre/mole)	−0.0899
Temperature: 30 °C						
0.893	2.500	0.918	9.58	2.683	3.6021	3.6289
1.665	2.690	1.692	13.01	3.546	3.5704	3.6059
2.980	2.788	3.008	17.34	4.554	3.5547	3.6002
3.134	2.862	3.163	17.78	4.649	3.5433	3.5898
4.964	2.944	4.993	22.35	5.623	3.5311	3.5873
9.918	3.133	9.949	31.54	7.389	3.5041	3.5780
14.240	3.383	14.274	37.78	8.443	3.4707	3.5551
					$-\log s^\circ$ (extrapolated)	3.6090
					B' (litre/mole)	−0.3331
Temperature: 35 °C						
1.029	3.142	1.060	10.29	2.884	3.5028	3.5316
1.183	3.153	1.215	11.03	3.069	3.5013	3.5320
2.629	3.208	2.661	16.31	4.334	3.4938	3.5371
5.254	3.347	5.288	22.99	5.777	3.4754	3.5382
6.726	3.416	6.760	25.99	6.375	3.4664	3.5302
8.196	3.492	8.231	28.69	6.889	3.4569	3.5258
9.668	3.545	9.703	31.15	7.336	3.4504	3.5238
17.470	3.784	17.508	41.84	9.118	3.4220	3.5132
					$-\log s^\circ$ (extrapolated)	3.5366
					B' (litre/mole)	−0.1393

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

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

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

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

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 the 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 place[4]

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

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

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

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

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. 2. Here the left-hand side of eqn (4) which for brevity is represented by the expression $\log s^{\circ\prime}$ has been plotted against the total salt concentration, $(c+s)$. For this purpose, the values of A used were as reported by Agarwal and Nayak[5]. 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.

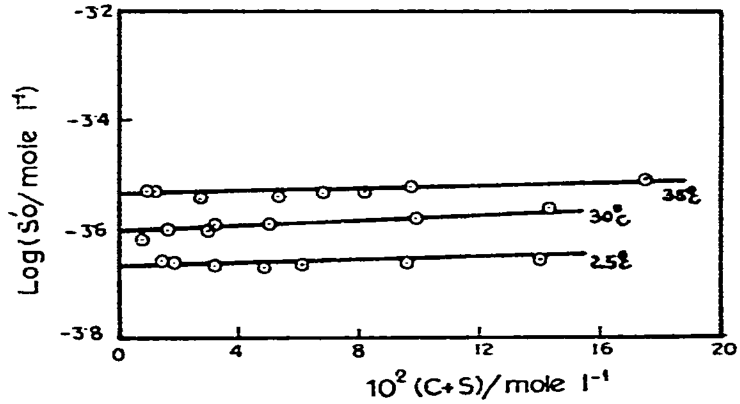

Fig. 2. Plot of $\log s^{\circ\prime}$ versus total salt concentration.

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 approriate 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 iodate 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.

TABLE 2

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

$c \times 10^2$ mole l^{-1}	$s \times 10^4$ mole l^{-1}	$f_\pm$ *from eqn (1)*	$f_\pm$ *from eqn (3a)*	$f_\pm$ *from eqn (6)*
	Temperature: 25°C			
0	2.169	0.9893	0.9897	0.9897
1	2.295	0.9350	0.9353	0.9290
2	2.354	0.9118	0.9120	0.9044
3	2.398	0.8948	0.8955	0.8843
4	2.435	0.8810	0.8812	0.8678
5	2.468	0.8695	0.8696	0.8403
10	2.597	0.8263	0.8264	0.7749
15	2.698	0.7954	0.7958	0.7254
	Temperature: 30°C			
0	2.488	0.9887	0.9888	0.9888
1	2.647	0.9292	0.9294	0.9307
2	2.730	0.9010	0.9012	0.9038
3	2.798	0.8792	0.8796	0.8839
4	2.857	0.8610	0.8612	0.8674
5	2.912	0.8447	0.8448	0.8401
10	3.152	0.7804	0.7807	0.7752
15	3.365	0.7301	0.7311	0.7261
	Temperature: 35°C			
0	2.943	0.9877	0.9879	0.9879
1	3.114	0.9335	0.9335	0.9303
2	3.198	0.9090	0.9090	0.9036
3	3.261	0.8913	0.8913	0.8835
4	3.316	0.8764	0.8764	0.8670
5	3.365	0.8638	0.8638	0.8594
10	3.562	0.8161	0.8160	0.8114
15	3.721	0.7812	0.7811	0.7775
20	3.862	0.7527	0.7526	0.7515

The solubility and activity coefficient data presented in this paper 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 $AgIO_3$ 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. 2 seem to suggest that the error from this source is not at all significant.

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 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 experimental value.

The solubilities of $AgIO_3$ in formamide in the absence of any added salt are found to be 2.169×10^{-4}, 2.488×10^{-4}, and 2.943×10^{-4} mole 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 $AgIO_3$ in that solvent by Monk[6] (1.78×10^{-4} *M*), by Keefer and Reiber[7] (1.794×10^{-4} *M*), by Kolthoff and Lingane[8] (1.776×10^{-4} *M*), by Kohlrausch[9] (1.79×10^{-4} *M*) all at 25 °C and by Li and Tulo[2] (1.785×10^{-4}, 2.152×10^{-4} and 2.587×10^{-4} *M*, respectively) at 25, 30 and 35 °C. Thus silver iodate 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, $AgIO_{3(s)} \rightarrow Ag^+$ (solvated) $+ IO_3^-$ (solvated), by the relation, $\Delta G^\circ = -RT \ln K_s$. The values of K_s as well as ΔG° are shown in Table 3 together with similar data in water for the sake of comparison.

TABLE 3

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

Temp. °*C*	$K_s \times 10^8$ *mole*^{2} *l*$^{-2}$	ΔG° *kcal mole*$^{-1}$	ΔH° *kcal mole*$^{-1}$	ΔS° *cal deg*$^{-1}$ *mole*$^{-1}$	*Solution*
25	4.609	10.00	11.16	3.89	formamide
25	3.055	10.252	13.535	11.03	water
30	6.053	10.00	11.16	3.81	formamide
30	4.490	10.190	13.542	11.05	water
35	8.448	9.97	11.16	3.88	formamide
35	6.456	10.142	13.549	11.07	water

A plot of log K_s against $1/T$ yields a straight line and the heat of solution (ΔH°) of silver iodate calculated from the slope of this plot turns out to be 11.16 kcal mole^{-1}, which is somewhat less than that found in water (13.542 kcal at 30 °C). 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 to be 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.

The solubility product may further be used to compute the standard potential of silver–silver iodate electrode ($E^\circ_{\mathrm{Ag/AgIO_3}}$) through the relation

$$E^\circ_{\mathrm{Ag-AgIO_3}} = E^\circ_{\mathrm{Ag}} + \frac{RT}{F} \ln K_s$$

Unfortunately, the only value of E°_{Ag} reported in this solvent[10] is at 25 °C, the value being 0.6902 V. Using this, the standard potential of silver–silver iodate electrode is found to be 0.2562 V at 25 °C which may be compared with the values 0.3550 V, and 0.3551 V reported in water[2]. The lower value of $E^\circ_{\mathrm{Ag-AgIO_3}}$ found in formamide compared with water is in agreement with the general behaviour exhibited by other electrodes of this class, such as Ag–AgCl and Ag–AgBr electrodes[5,11].

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