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SOLUBILITY PRODUCT AND RELATED THERMODYNAMIC QUANTITIES OF SILVER AND BARIUM CHROMATES IN FORMAMIDE

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ABSTRACT

The values of ΔG^0, ΔH^0, and ΔS^0 for the dissolution process, $M_2(CrO_4)_x$ + solvent $\rightarrow$ 2 M^{x+} (solvated) + $xCrO_4^{2-}$ (solvated), where M is Ag or Ba, and x is 1 or 2, have been determined in formamide from solubility studies. The negative value of ΔS^0 indicates that there is more order in the dissolved state than in the undissolved state.

INTRODUCTION

In continuation of our study [1—6] on the solubility of some sparingly soluble silver salts in formamide, we now report the solubility products of silver and barium chromates in this solvent in the presence of perchloric acid and sodium perchlorate or potassium chloride solutions at 25, 30, and 35°C. The standard thermodynamic quantities associated with the dissolution process have also been determined.

EXPERIMENTAL

Silver chromate was precipitated by mixing dilute solutions of silver nitrate and potassium chromate, and this precipitated silver chromate was repeatedly washed with hot conductivity water. The product consisted of small dark green crystals which were dried at 130°C for 3 days. This was analysed for silver content gravimetrically by precipitating silver as silver chloride, the oxidising power was determined iodometrically.

Barium chromate was prepared by careful precipitation from barium chloride and potassium chromate solutions. The precipitate was washed several times with conductivity water and dried at 120°C for at least 4 h. The barium content was estimated with standard EDTA solution by the usual method. The chromate content was estimated iodometrically. The results of the analyses were in good agreement with theory.

Anhydrous sodium perchlorate was prepared by the method described earlier [2]. Formamide (BDH, L.R.) was purified using the same method reported in our previous study [1]. Anhydrous perchloric acid was obtained by distilling a G.R. sample of perchloric acid over silver oxide under reduced pressure, and collecting the middle fraction of the distillate which was further distilled under reduced pressure. Potassium chloride (G.R.) was dried at 100°C for 2 h. All other chemicals were either G.R. or A.R. samples.

The solutions of perchloric acid and sodium perchlorate or potassium chloride were prepared by dissolving appropriate and weighed amounts of the acid and salt in known weights of formamide at ice-cold temperature [4]. The method of solubility measurements was similar to that described earlier [2]. The solute contents were analysed by the iodometric determination of the chromate using a standard sodium thiosulphate solution (about 0.001 M) by the usual method. The $Na_2S_2O_3$ consumed corresponded to the amount of chromate and bichromate taken together, present in solution and so it corresponded to the amount of Ag or Ba in the corresponding solubility determination.

RESULTS AND DISCUSSION

A summary of solubility data is presented in Table 1 for silver and barium chromates at 25, 30, and 35°C. Assuming silver chromate and barium chromate in solution to be completely dissociated, in the presence of $HClO_4$ the following equations hold good

$$\underset{m}{n[M^{x+}]} = [CrO_4^{2-}] + \underset{m_1}{[HCrO_4^-]} \qquad (1)$$

$$[HClO_4]_T = [HCrO_4^-] + [H^+] \qquad (2)$$

So

$$[HCrO_4^-] = m_1 = [HClO_4]_T - [H^+]$$

and

$$[CrO_4^{2-}] = nm - m_1$$

The ionic strength of the solution

$$\begin{aligned}\mu &= \tfrac{1}{2}nx^2[M^{x+}] + 2[CrO_4^{2-}] + \tfrac{1}{2}[HCrO_4^-] + \tfrac{1}{2}[H^+] + \tfrac{1}{2}[ClO_4^-] + \tfrac{1}{2}[K^+] + \tfrac{1}{2}[Cl^-] \\ &= \tfrac{1}{2}nx^2[M^{x+}] + 2[CrO_4^{2-}] + [HClO_4]_T + [KCl]_T \\ &= \left(\frac{nx^2}{2} + 2n\right)[M^{x+}] - 2[HCrO_4^-] + [HClO_4]_T + [KCl]_T \qquad (3)\end{aligned}$$

where M is Ag or Ba, x is 1 or 2, and n is 2 or 1, respectively. In eqn. (3), $[HClO_4]_T$ and $[KCl]_T$ are the stoichiometric molalities of $HClO_4$ and KCl (in the case of silver chromate $NaClO_4$ was taken) and are known from the amounts added to the solution. $[M^{x+}]$ is known as explained earlier. The value of $[HCrO_4^-]$ was obtained from the second ionization constant, K_{2a} of H_2CrO_4 and $f_{CrO_4^{2-}}$ reported earlier in formamide [7], as follows

$$K_{2a} = \frac{[H^+][CrO_4^{2-}]}{[HCrO_4^-]} \cdot \frac{f_{H^+}f_{CrO_4^{2-}}}{f_{HCrO_4^-}} \qquad (4)$$

Assuming $f_{H^+} = f_{HCrO_4^-}$ up to $\mu = 0.1$ and introducing eqns. (1) and (2) in eqn. (4), the following equation is obtained

$$K_{2a} = f_{CrO_4^{2-}} \left\{ \frac{([HClO_4]_T - [HCrO_4^-])(n[M^{x+}] - [HCrO_4^-])}{[HCrO_4^-]} \right\}$$

$$K_{2a} = f_{CrO_4^{2-}} \left\{ \frac{(m' - m_1)(nm - m_1)}{m_1} \right\}$$

where $[HClO_4]_T = m'$. Solving the above quadratic equation, we get m_1. From eqn. (1), we now find $[CrO_4^{2-}]$ from our measurements. The ionic strength μ was computed from eqn. (3). These values are shown in Table 1 for different temperatures.

The solubility product, K_s is obtained as

$$K_s = a^n_{M^{x+}} \cdot a_{CrO_4^{2-}} = [M^{x+}]^n [CrO_4^{2-}] f^n_{M^{x+}} \cdot f_{CrO_4^{2-}} \tag{5}$$

Using the Debye—Huckel—Bronsted equation [1]

$$\log f_{\pm} = -AZ_+Z_- \sqrt{\mu} + \beta\mu \tag{6}$$

we obtain

$$\log K_s = n \log[M^{x+}] + \log[CrO_4^{2-}] - (n + 1)\, 2A \sqrt{\mu} + (n + 1)\beta\mu$$

so

$$n \log[M^{x+}] + \log[CrO_4^{2-}] - (n + 1)\, 2A \sqrt{\mu} = \log K_s - \beta\mu \tag{7}$$

A plot of the left-hand side against μ gives a straight line in each case, the intercept of which on the ordinate gives $\log K_s$. Using the method of least squares, the values of $\log K_s$ and slopes of the curves, β are obtained, these values are recorded in Table 1.

The ΔH^0 values of the dissolution processes have been calculated from the slopes of the plot of $-\log K_s$ against $1/T$, assuming it to be independent of temperature. The ΔG^0, ΔH^0, and ΔS^0 values at 25°C are shown in Table 2 along with those available in water [8]. The values of K_s for both Ag_2CrO_4 and $BaCrO_4$ obtained in formamide, and reported in water [8,9] are also included in Table 2. It is found from these results that silver chromate and barium chromate are more soluble in formamide than in water. This is consistent with the solubility of other silver salts determined in formamide [1—3,5,6]. The values of ΔG^0 do not change much on passing from water to formamide whereas there are appreciable changes in ΔH^0 and ΔS^0 values. This indicates that the dissolution process is less energy consuming in formamide than in water. The values of ΔS^0 in both formamide and water are expected to be negative, but in formamide these values (in the case of Ag_2CrO_4) appear to be more negative, pointing to the fact that the degree of re-orientation and partial immobilization of the formamide molecules by the Ag^+ and CrO_4^{2-} ions is greater in formamide than in water.

TABLE I

Summary of solubility data for silver and barium chromates in formamide at 25, 30, and 35°C

$10^2 m_X$ (mole kg^{-1})	$10^4 m_{MX^+}$ (mole kg^{-1})	$10^4 m_{HClO_4}$ (mole kg^{-1})	$10^4 m_{HCrO_4^-}$	$10^4 m_{CrO_4^{2-}}$	$(n+1)2 \times A\sqrt{\mu}$	$10^2\ \mu$	$-\log K_s$
X = NaClO$_4$, M = Ag							
Temp: 25°C							
2.777	1.682	0.139	0.128	3.236	0.3115	2.860	11.3499
4.089	1.802	0.141	0.131	3.473	0.3765	4.178	11.3242
4.098	1.824	0.143	0.133	3.481	0.3770	4.188	11.3133
4.253	1.858	0.145	0.135	3.582	0.3839	4.345	11.2916
6.674	1.888	0.149	0.138	3.638	0.4022	4.767	11.2891
5.504	1.908	0.149	0.139	3.677	0.4358	5.598	11.3091
6.726	2.056	0.151	0.141	3.971	0.4813	6.827	11.2562
						$-\log K_s$ (extrapolated)	11.4013
						Slope (kg mole^{-1})	+ 2.06
Temp: 30°C							
3.362	1.925	0.138	0.129	3.721	0.3435	3.457	11.2041
3.557	1.988	0.147	0.137	3.839	0.3533	3.655	11.1721
4.033	2.058	0.150	0.141	3.976	0.3757	4.134	11.1492
4.197	2.116	0.155	0.144	4.088	0.3833	4.301	11.1207
4.745	2.148	0.184	0.170	4.126	0.4070	4.851	11.1275
5.720	2.206	0.191	0.177	4.235	0.4462	5.828	11.1322
						$-\log K_s$ (extrapolated)	11.2669
						Slope (kg mole^{-1})	+ 2.65
Temp: 35°C							
1.872	2.085	0.129	0.121	4.049	0.2606	1.975	11.0148
2.959	2.212	0.131	0.124	4.300	0.3247	3.068	11.0016
3.057	2.286	0.134	0.126	4.446	0.3301	3.170	10.9639
3.169	2.308	0.148	0.140	4.476	0.3359	3.283	10.9586
3.226	2.324	0.156	0.147	4.501	0.3389	3.341	10.9532
3.350	2.382	0.164	0.154	4.610	0.3453	3.468	10.9276
4.101	2.498	0.179	0.167	4.829	0.3810	4.224	10.9021
						$-\log K_s$ (extrapolated)	11.1316
						Slope (kg mole^{-1})	+ 5.32

X = KCl, M = Ba

Temp: 25°C							
0.823	0.724	0.536	0.335	0.389	0.2260	0.817	8.7764
2.138	0.859	0.588	0.376	0.482	0.3615	2.166	8.7450
4.248	0.906	0.602	0.389	0.517	0.5080	4.278	8.8374
5.389	0.998	0.628	0.413	0.585	0.5719	5.423	8.8056
7.026	1.122	0.698	0.460	0.662	0.6528	7.064	8.7819
8.138	1.198	0.718	0.479	0.719	0.7024	8.179	8.7673
9.366	1.306	0.745	0.504	0.802	0.7534	9.411	8.7334
						$-\log K_s$ (extrapolated)	8.7921
						Slope (kg mole^{-1})	+0.261
Temp: 30°C							
0.785	0.788	0.508	0.332	0.456	0.2219	0.811	8.6664
1.836	0.860	0.558	0.363	0.497	0.3365	1.865	8.7056
3.486	0.994	0.598	0.398	0.596	0.4623	3.520	8.6897
6.786	1.186	0.638	0.439	0.747	0.6438	6.827	8.6964
8.348	1.268	0.686	0.471	0.797	0.7138	8.392	8.7092
						$-\log K_s$ (extrapolated)	8.6792
						Slope (kg mole^{-1})	−0.334
Temp: 35°C							
1.026	0.948	0.584	0.386	0.562	0.2543	1.058	8.5278
2.123	1.026	0.575	0.391	0.635	0.3631	2.158	8.5491
3.246	1.048	0.638	0.424	0.624	0.4478	3.282	8.6322
6.589	1.268	0.684	0.470	0.798	0.6367	6.633	8.6316
8.242	1.389	0.656	0.467	0.922	0.7118	8.291	8.6043
9.002	1.416	0.728	0.507	0.909	0.7413	9.051	8.6316
						$-\log K_s$ (extrapolated)	8.5448
						Slope (kg mole^{-1})	−1.009

TABLE 2

Solubility product and related thermodynamic quantities of silver and barium chromates in formamide [a] and water [b]

Temp. (°C)	K_s		ΔG^0 (kJ mole^{-1})		ΔH^0 (kcal mole^{-1})		ΔS^0 (J deg^{-1} mole^{-1})	
	a	b	a	b	a	b	a	b
$Ag_2CrO_4 \times 10^{12}$								
25	3.97	2.71	65.05 ± 0.21	65.99	46.95 ± 0.12	58.80	−60.75 ± 0.30	−25.00
30	5.41							
35	7.39	5.76						
$BaCrO_4 \times 10^{10}$								
25	16.14	1.6	50.16 ± 0.03	55.89	43.04 ± 0.06		−23.90 ± 0.02	
30	20.93							
35	28.52							

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