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Calorimetric studies for the dissolution of orthoperiodate salt of the type: $M_2HIO_6{\cdot}nH_2O$ ($M = Cu^{2+}, Zn^{2+}, Cd^{2+}$)

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Abstract

The standard molar dissolution enthalpies of metallic orthoperiodates hydrates salts of the type, $M_2HIO_6{\cdot}nH_2O$ ($M = Cu^{2+}$, Zn^{2+}, Cd^{2+}; $n = 2, 1.25, 1.25$), in aqueous $3\,mol\,dm^{-3}$ HNO_3 have been measured by using an isoperibolic calorimeter at 298.2 K. The thermodynamic parameters of these compounds, e.g. $\Delta_{diss}G_m^\circ$ and $\Delta_{diss}S_m^\circ$, have been calculated or estimated. The related values published in the literature and that were obtained from solubility determinations using a spectrophotometer in the 298.5–328 K temperature range have been also revised by using a linear regression analysis.

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1. Introduction

The interest in the study of transition metallic iodates, periodates and orthoperiodates have been prompted because of the electrical and corrosion inhibition properties of these compounds and also by their practical analysis, etc. [1]. The thermal kinetic parameters of nickel orthoperiodate hydrates have been reported by Maneva et al. [2]. The thermodynamic parameters obtained from the solubility measurements of these compounds at different temperatures have been also reported [3,4]. Recently, the values for the standard molar formation enthalpies for several iodates and periodates at 298.2 K have been published [5].

In the present paper, the standard molar dissolution enthalpies of orthoperiodates of general formula, $M_2HIO_6{\cdot}nH_2O$ ($M = Cu^{2+}, Zn^{2+}, Cd^{2+}$; $n = 2, 1.25, 1.25$), are reported, as well as, the calculated values of $\Delta_{diss}G_m^\circ$ and $\Delta_{diss}S_m^\circ$ of the solution process. In addition, data from [3] that was obtained by solubility determinations in the 298.5–328 K temperature range have been revised by using a linear regression analysis.

2. Experimental

The metallic orthoperiodates hydrates were prepared by mixing equimolar dilute solutions of periodic acid and metallic acetate (a.r., Shanghai Reagent Factory) as previously described [6]. The compounds were characterized by chemical analysis by using an iodimetry coupled with a Nicolet 170SX FT-IR spectrophotometer (CsI plates) and a CDR-1 DTA generator.

The isoperibolic calorimeter used in this work was adapted to measure enthalpies of solid–solid and liquid–liquid reactions. The volume of the enthalpimetric vessel was $100\,cm^3$. The precision of the

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temperature values were measured to an accuracy of ±0.001 K and deviation to an accuracy of ±0.0001 K [7,8].

The accuracy of the calorimeter was tested by determining the standard molar dissolution enthalpies of KCl (SRM, Shanghai Reagent Factory) in double-distilled water at 298.2 K given a value of $17.569 \pm 0.017\,\mathrm{kJ\,mol^{-1}}$, which agrees with the values $17.564 \pm 0.042\,\mathrm{kJ\,mol^{-1}}$ [9] or $17.536 \pm 0.009\,\mathrm{kJ\,mol^{-1}}$ [10].

3. Results

3.1. Direct injection enthalpimetry

Since $Cu_2HIO_6{\cdot}2H_2O$, $Zn_2HIO_6{\cdot}1.25H_2O$ and $Cd_2HIO_6{\cdot}1.25H_2O$ hardly dissolve in water and usual organic solvents, they were at first finely ground by using an agate mortar followed by the dissolution in $100\,\mathrm{cm^3}$ of aqueous $3\,\mathrm{mol\,dm^{-3}}$ HNO_3 at 298.2 K. The measurement procedure is similar to that described in [3]. The results are presented in Table 1. In this table, thermodynamic parameters of the compounds, $\Delta_{\mathrm{diss}}G_m^\circ$ were calculated from the values of the solubility products, by using Eq. (1) [11]:

$$\Delta_{\mathrm{diss}}G_m^\circ = -RT\ln K_{\mathrm{sp}}^0 \tag{1}$$

and the values of $\Delta_{\mathrm{diss}}S_m^\circ$ were calculated by using Eq. (2):

$$\Delta_{\mathrm{diss}}S_m^\circ = -\frac{\Delta_{\mathrm{diss}}G_m^\circ - \Delta_{\mathrm{diss}}H_m^\circ}{T} \tag{2}$$

where $R = 8.314\,\mathrm{J\,mol^{-1}}$, $T = 298.2\,\mathrm{K}$, and K_{sp}^0 values were found out by using a least-squares treatment (see Eq. (3)).

3.2. Enthalpies of dissolution previously determined

The $\Delta_{\mathrm{diss}}H_m^\circ$ values of the compounds $M_2HIO_6{\cdot}nH_2O$ in the 298.5–328 K temperature range were determined by using 4-(2-thiazolylazo)-resorciniol (TAR) reagent in water as a solvent and a Beckman DU-2 spectrophotometer have been reported in the literature [3]. They were −61.88 for copper, −9.93 for zinc and $-36.90\ \mathrm{kJ\,mol^{-1}}$ for cadmium orthoperiodate. Really the original data reported were: -6.188×10^{-4}, -0.993×10^{-4}, and $-3.690 \times 10^{-4}\,\mathrm{kJ\,mol^{-1}}$, possibly due to typographical errors. However, these parameters differed considerably from the values obtained in this paper (see Table 1). Thus, to solve this discrepancy we used a least-squares treatment of the solubility product data at different temperatures, reported in the literature [3]. The solubility (S), solubility products (K_{sp}), and then recalculated values for the enthalpies of dissolution are listed in Table 2.

Table 1
Dissolution enthalpy data for the compounds $M_2HIO_6{\cdot}nH_2O$ at 298.2 K ($R = 996.0\,\Omega$, $I = 19.6627\,\mathrm{mA}$)

No.	m (g)[a]	t_e (s)	Δ_rE/Δ_eE[b]	$\Delta_{\mathrm{diss}}H_m^\circ$ (kJ mol^{-1})[c]
$Cu_2HIO_6{\cdot}2H_2O$[d]				
1	0.2357	82.85	0.4174	−181.85
2	0.2360	80.04	0.4293	−180.47
3	0.2352	86.49	0.3976	−181.24
4	0.2354	87.31	0.3945	−181.38
5	0.2357	84.58	0.4087	−181.54
$Zn_2HIO_6{\cdot}1.25H_2O$[e]				
1	0.3840	42.21	0.2475	−32.86
2	0.3837	45.38	0.2256	−32.24
3	0.3842	45.70	0.2558	−32.92
4	0.3848	43.37	0.2427	−33.05
5	0.3850	43.54	0.2380	−32.51
$Cd_2HIO_6{\cdot}1.25H_2O$[f]				
1	0.2018	68.34	0.2200	−112.46
2	0.2020	69.07	0.2175	−112.27
3	0.2023	69.32	0.2171	−112.30
4	0.2030	69.40	0.2180	−112.51
5	0.2024	68.21	0.2209	−112.38

[a] The molar mass (M) of the compounds $M_2HIO_6{\cdot}nH_2O$ were, respectively taken to be 386.99, 377.17, 471.23 g mol^{-1} for copper, zinc and cadmium.

[b] Δ_rE (mV) and Δ_eE (mV) are the voltage change during the sample dissolution and the electrical calibration, respectively, and t_e is the time of electrical calibration.

[c] $\Delta_{\mathrm{diss}}H_m^\circ = (\Delta_rE/\Delta_eE)I^2Rt_e(M/m)$ where R is $8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

[d] $\Delta_{\mathrm{diss}}H_m^\circ = -181.30 \pm 0.22\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{diss}}G_m^\circ = 84.88\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{diss}}S_m^\circ = -892.62\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

[e] $\Delta_{\mathrm{diss}}H_m^\circ = -32.72 \pm 0.20\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{diss}}G_m^\circ = 86.69\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{diss}}S_m^\circ = -290.81\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

[f] $\Delta_{\mathrm{diss}}H_m^\circ = -112.38 \pm 0.05\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{diss}}G_m^\circ = 85.93\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{diss}}S_m^\circ = -665.02\,\mathrm{J\,mol^{-1}K^{-1}}$.

4. Discussion

According to the thermodynamic theory, the apparent solubility product at temperature T is related to the

Table 2
Thermodynamic data recomputed for the compound $M_2HIO_6{\cdot}nH_2O$

T (K)	$S \times 10^{-4}$ (mol l^{-1})	$-\log K^0_{sp}$ (measured)	$-\log K^0_{sp}$ (predicted)	$\Delta_{diss}G^\circ_m$ (kJ mol^{-1})[a]	$-\Delta_{diss}S^\circ_m$ (J K^{-1} mol^{-1})[a]
$Cu_2HIO_6{\cdot}2H_2O$[b]					
298	–	–	14.8892	85.013	875.21
298.5	7.47	14.8918	14.8864	85.082	873.98
304	4.82	15.4437	15.4464	89.909	874.04
309	3.27	15.9136	15.9331	94.268	874.01
313	2.42	16.3090	16.9095	97.744	873.94
318	1.65	16.7932	16.7686	102.101	873.91
323	1.18	17.2218	17.2185	106.488	873.96
328	0.79	17.7212	17.7326	111.365	875.50
$Zn_2HIO_6{\cdot}1.25H_2O$[c]					
298	–	–	15.1928	86.688	388.20
298.5	5.89	15.1911	15.1869	86.800	387.93
304	5.51	15.2732	15.2793	88.934	387.93
309	5.12	15.3667	15.3596	89.405	389.48
313	4.89	15.4256	15.4217	91.240	389.11
318	4.59	15.5077	15.4974	92.877	389.37
323	4.36	15.5719	15.5716	96.303	387.93
328	4.13	15.6415	15.6428	98.241	387.92
298	–	–	15.0363	85.795	641.14
$Cd_2HIO_6{\cdot}1.25H_2O$[d]					
298.5	14.59	15.0670	15.0677	86.118	641.15
304	11.07	15.4080	15.4030	89.657	641.19
309	8.86	15.6840	15.6944	92.855	641.17
313	7.30	15.9259	15.9198	95.408	641.13
318	5.86	16.2020	16.1947	98.606	641.11
323	4.80	16.4510	16.4641	101.823	641.14
328	3.81	16.7448	16.7390	105.125	641.44

[a] $\Delta_{diss}G^\circ_m$ and $\Delta_{diss}S^\circ_m$ at each temperature are calculated from Eqs. (1) and (2), respectively.

[b] $\Delta_{diss}H^\circ_m = -175.80 \pm 0.02$ kJ mol^{-1} ($\Delta_{diss}H^\circ_m$ of the $M_2HIO_6{\cdot}nH_2O$ at 298 K are calculated by linear regression equations, from Eqs. (4), (5) or (6)).

[c] $\Delta_{diss}H^\circ_m = -28.30 \pm 0.01$ kJ mol^{-1} ($\Delta_{diss}H^\circ_m$ of the $M_2HIO_6{\cdot}nH_2O$ at 298 K are calculated by linear regression equations, from Eqs. (4), (5) or (6)).

[d] $\Delta_{diss}H^\circ_m = -105.27 \pm 0.01$ kJ mol^{-1} ($\Delta_{diss}H^\circ_m$ of the $M_2HIO_6{\cdot}nH_2O$ at 298 K are calculated by linear regression equations, from Eqs. (4), (5) or (6)).

molar dissolution enthalpy by Eq. (3):

$$\ln K^0_{sp} = -\frac{\Delta_{diss}H^\circ_m}{RT} + C \qquad (3)$$

The plot of $\ln K^0_{sp}$ versus the inverse of the temperature is not a linear function because $\ln K^0_{sp}$ is undetermined when T is zero. However, over a small temperature range, $-\log K^0_{sp}$ is a linear function of T^{-1}, with a slope (m) or so-called T^{-1} variable coefficient that is equal to: $m = -\Delta_{diss}H^\circ_m/2.303R$. Therefore, $\Delta_{diss}H^\circ_m$ can be calculated from the gradient of the plot.

Using MS Excel's Regression Tool was obtained three linear regression relationships between $-\ln K_{sp}$ and T^{-1} for the compounds, as shown below:

$$\ln K^0_{sp}\ (\text{copper}) = \frac{2114.06}{T} - 105.11 \qquad (4)$$

$$\ln K^0_{sp}\ (\text{zinc}) = \frac{3487.58}{T} - 46.46 \qquad (5)$$

$$\ln K^0_{sp}\ (\text{cadmium}) = \frac{12\,661.25}{T} - 77.12 \qquad (6)$$

where the square of correlation coefficients (R^2) for the three equations is the same: 0.9998. From these equations, it is found that the values for $\Delta_{diss}H^\circ_m$

are -175.80 ± 0.02 (Cu), -28.306 ± 0.01 (Zn) and $-105.27 \pm 0.01\,\mathrm{kJ\,mol^{-1}}$ (Cd). These values suit well with the values that were measured directly in this work. The small differences are probably due to intensive physico-chemical properties like the ionic strength and the activity coefficients in dilute aqueous solutions.

In conclusion, the dissolution of the metallic orthoperiodates hydrates is an exothermic process with $\Delta_{\mathrm{diss}}G_m^\circ > 0$ and $\Delta_{\mathrm{diss}}S_m^\circ > 0$. It follows therefore that the values of K_{sp} will decrease with the increase of the measurement temperature.

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