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DETERMINATION OF THE THERMODYNAMIC PARAMETERS OF HEXAOXOIODATE(VII) HYDRATES OF THE TYPE $M_2HIO_6 \cdot nH_2O$, WHERE M^{II} = Ni, Cu, Zn AND Cd, BY SOLUBILITY MEASUREMENTS IN WATER AT VARIOUS TEMPERATURES

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ABSTRACT

The solubilities of metal hexaoxoiodate(VII) hydrates of the type $M_2HIO_6 \cdot nH_2O$ (M^{II} = Ni, Cu, Zn, Cd; $n = 3$, 2, 1.25, 1.25) in water have been measured at several temperatures with the aid of 4-(2′-thiazolylazo)-resorcinol (TAR) reagent using a Beckman DU-2 spectrophotometer. Mean activity coefficients are determined. The thermodynamic parameters of these salts, e.g., ΔH^0, ΔG^0 and ΔS^0, have been computed. A retrograde solubility phenomenon has been observed over the temperature range 298.5–328 K.

INTRODUCTION

The current status of thermodynamic data on periodates is far from satisfactory, though several ternary phase studies involving periodates have been published [1–7]. The investigation described in the present paper is part of a continuing programme at this laboratory of the systematic three-component phase study of some new periodates [8–10] and the evaluation of high-quality thermodynamic data for the same. The solubility and the related thermodynamic parameters of the periodates of the type $M_2HIO_6 \cdot nH_2O$ (M^{II} = Ni, Cu, Zn, Cd), are presented in this report at various temperatures.

EXPERIMENTAL

The metal hexaoxoiodate(VII) hydrates were prepared by mixing equimolar dilute solutions of reagent grade periodic acid and metal acetate as previously described [8,10]. The results of the chemical analysis (Table 1) in combination with X-ray diffraction and infrared spectroscopy results led to the following general formula for these compounds: $M_2HIO_6 \cdot nH_2O$ (M^{II} = Ni, Cu, Zn, Cd; $n = 3$, 2, 1.25, 1.25).

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TABLE 1

Analytical results

Compound	Metal (%)		Iodine (%)		Water (%)	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$Ni_2HIO_6 \cdot 3H_2O$	29.70	29.54	32.10	32.01	13.66	13.29
$Cu_2HIO_6 \cdot 2H_2O$	32.84	32.72	32.79	32.57	9.30	9.20
$Zn_2HIO_6 \cdot 1.25H_2O$	34.67	34.56	33.65	34.00	5.97	6.00
$Cd_2HIO_6 \cdot 1.25H_2O$	47.69	47.50	26.94	27.25	4.78	4.80

Initially, two distinctly different approaches, namely, supersaturation and slow attainment of equilibrium, were used to reach solubility equilibrium. However, the decreasing trend of solubility with increasing temperature necessitated the use of the latter technique. The temperature was controlled to ±0.01 K, which introduced an error of ~ 0.1–0.4% over the temperature

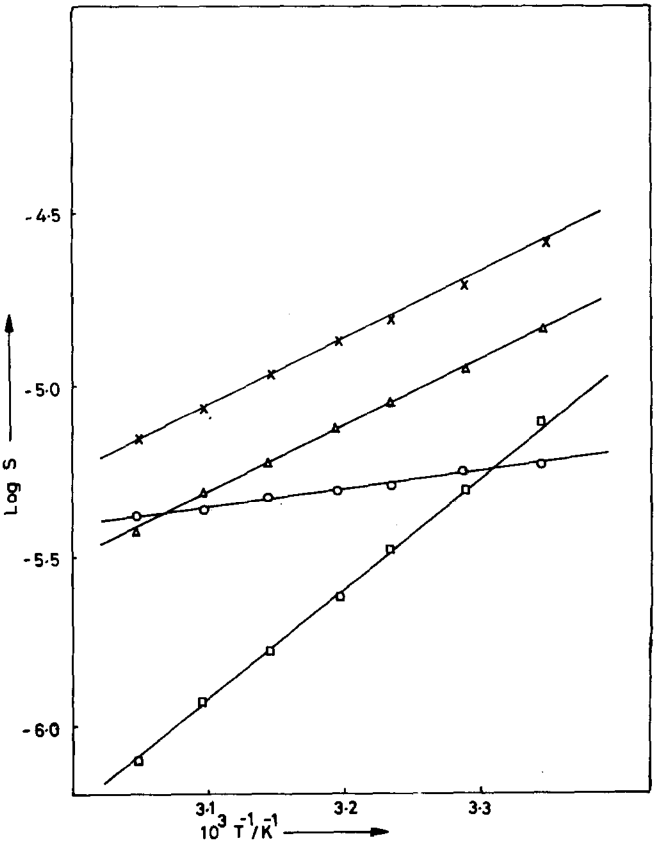

Fig. 1. Variation of solubility with temperature of $Ni_2HIO_6 \cdot 3H_2O$ (×), $Cu_2HIO_6 \cdot 2H_2O$ (□), $Zn_2HIO_6 \cdot 1.25H_2O$ (○) and $Cd_2HIO_6 \cdot 1.25H_2O$ (△).

TABLE 2

Solubility data for the compound $Ni_2HIO_6 \cdot 3H_2O$ [a]

T (K)	$s \times 10^6$ (mol l^{-1})	$I_m \times 10^6$	$\gamma_\pm$	$K_{sp} \times 10^{14}$ (mol^2 l^{-2})
298.5	26.41 ± 0.08	316.82	0.846	4.463 ± 0.037
304	19.59 ± 0.77	235.06	0.865	1.953 ± 0.208
309	15.76 ± 0.23	189.07	0.877	1.058 ± 0.043
313	13.12 ± 0.11	157.39	0.886	0.630 ± 0.013
318	10.65 ± 0.11	127.75	0.896	0.348 ± 0.016
323	8.52 ± 0.08	102.27	0.907	0.184 ± 0.005
328	7.07 ± 0.09	84.83	0.912	0.108 ± 0.004

[a] The molar mass of compound $Ni_2HIO_6 \cdot 3H_2O$ was taken to be 395.33 g mol^{-1}. From a graph of log s vs. $1/T$, $s_{298\ K} = 27.1 \times 10^{-6}$ mol l^{-1}. From a graph of pK_s vs. $1/T$, $K_{sp\ 298\ K} = 4.954 \times 10^{-14}$ mol^2 l^{-2}.

range 298.5–328 K. To ensure attainment of equilibrium, aliquots of the sample were withdrawn intermittently and analysed for metal content with a highly sensitive spectrophotometric reagent, 4-(2′-thiazolylazo)-resorcinol (TAR) [11–15], at appropriate pH and wavelength values, with the aid of a Beckman DU-2 spectrophotometer. The concentration of metal ion and, hence, that of the salt was calculated from the respective standard curves of metal ions obtained before each solubility measurement. A minimum of ten determinations was made for each solubility and the standard deviations were evaluated.

The ionic strength, I_m, of the solution was computed assuming the complete dissociation of the salt in water and activity coefficients, $\gamma_\pm$, were calculated from the Debye–Hückel limiting law equation applicable to very

TABLE 3

Solubility data for the compound $Cu_2HIO_6 \cdot 2H_2O$ [a]

T (K)	$s \times 10^6$ (mol l^{-1})	$I_m \times 10^6$	$\gamma_\pm$	$K_{sp} \times 10^{16}$ (mol^2 l^{-2})
298.5	7.47 ± 0.13	89.69	0.915	12.830 ± 0.001
304	4.82 ± 0.16	57.90	0.931	3.600 ± 0.032
309	3.27 ± 0.12	39.65	0.942	1.220 ± 0.103
313	2.42 ± 0.16	29.27	0.949	0.496 ± 0.010
318	1.65 ± 0.08	19.83	0.957	0.161 ± 0.002
323	1.18 ± 0.11	14.16	0.963	0.060 ± 0.002
328	0.79 ± 0.12	9.44	0.970	0.019 ± 0.001

[a] The molar mass of the compound $Cu_2HIO_6 \cdot 2H_2O$ was taken to be 386.99 g mol^{-1}. From a graph of log s vs. $1/T$, $s_{298\ K} = 7.94 \times 10^{-6}$ mol l^{-1}. From a graph of pK_s vs. $1/T$, $K_{sp\ 298\ K} = 1.585 \times 10^{-15}$ mol^2 l^{-2}.

TABLE 4

Solubility data for the compound $Zn_2HIO_6 \cdot 1.25H_2O$ [a]

T (K)	$s \times 10^6$ (mol l^{-1})	$I_m \times 10^6$	$\gamma_\pm$	$K_{sp} \times 10^{16}$ (mol^2 l^{-2})
298.5	5.89 ± 0.09	70.68	0.924	6.440 ± 0.274 [b]
304	5.51 ± 0.12	66.07	0.926	5.330 ± 0.345
309	5.12 ± 0.09	61.48	0.928	4.298 ± 0.212
313	4.89 ± 0.06	58.68	0.929	3.753 ± 0.135
318	4.59 ± 0.06	55.03	0.930	3.107 ± 0.118
323	4.36 ± 0.07	52.31	0.931	2.680 ± 0.114
328	4.13 ± 0.07	49.55	0.932	2.283 ± 0.102

[a] The molar mass of the compound $Zn_2HIO_6 \cdot 1.25H_2O$ was taken to be 377.17 g mol^{-1}. From a graph of log s vs. $1/T$, $s_{298\ K} = 5.9 \times 10^{-6}$ mol l^{-1}. From a graph of pK_s vs. $1/T$, $K_{s\ 298\ K} = 6.66 \times 10^{-16}$ mol^2 l^{-2}.

[b] The value of K_s reported earlier [19] was 1.31×10^{-19} mol^2 l^{-2}, possibly because of the difference in the extent of hydration of the parent compound.

dilute solutions [16]. The Debye–Hückel constants for the solvent were obtained from standard data [16] or from the dielectric constants of water at the respective temperatures [17].

In the present work the solubility products were obtained using the relationship [18]

$$K_s = (s_0\gamma_\pm)^{X+Y} X^X Y^Y = 4(s_0\gamma_\pm)^3$$

where $X = 2$ and $Y = 1$.

A graph of log s vs. T^{-1} was plotted (Fig. 1) where s is the solubility of the salt (mol l^{-1}). The enthalpy of the salt solution over the temperature range 298.5–328 K was evaluated using a least-squares treatment for the

TABLE 5

Solubility data for the compound $Cd_2HIO_6 \cdot 1.25H_2O$ [a]

T (K)	$s \times 10^6$ (mol l^{-1})	$I_m \times 10^6$	$\gamma_\pm$	$K_{sp} \times 10^{16}$ (mol^2 l^{-2})
298.5	14.59 ± 0.15	175.32	0.883	8.570 ± 0.248
304	11.07 ± 0.19	133.90	0.896	3.908 ± 0.184
309	8.86 ± 0.06	106.27	0.906	2.070 ± 0.040
313	7.30 ± 0.14	87.67	0.914	1.186 ± 0.060
318	5.86 ± 0.09	70.14	0.921	0.628 ± 0.029
323	4.80 ± 0.09	57.38	0.928	0.354 ± 0.021
328	3.81 ± 0.06	45.69	0.935	0.180 ± 0.007

[a] The molar mass of the compound $Cd_2HIO_6 \cdot 1.25H_2O$ was taken to be 471.23 g mol^{-1}. From a graph of log s vs. $1/T$, $s_{298\ K} = 14.79 \times 10^{-6}$ mol l^{-1}. From a graph of pK_s vs. $1/T$, $K_{s\ 298\ K} = 9.120 \times 10^{-16}$ mol^2 l^{-2}.

TABLE 6

Thermodynamic data for the compounds $M_2HIO_6 \cdot nH_2O$

Temp., T (K)	$Ni_2HIO_6 \cdot 3H_2O$		$Cu_2HIO_6 \cdot 2H_2O$		$Zn_2HIO_6 \cdot 1.25H_2O$		$Cd_2HIO_6 \cdot 1.25H_2O$	
	$\Delta G^0 \times 10^{-3}$ (J mol^{-1})	$\Delta S^0 \times 10^{-2}$ (J K^{-1} mol^{-1})	$\Delta G^0 \times 10^{-3}$ (J mol^{-1})	$\Delta S^0 \times 10^{-2}$ (J K^{-1} mol^{-1})	$\Delta G^0 \times 10^{-3}$ (J mol^{-1})	$\Delta S^0 \times 10^{-2}$ (J K^{-1} mol^{-1})	$\Delta G^0 \times 10^{-3}$ (J mol^{-1})	$\Delta S^0 \times 10^{-2}$ (J K^{-1} mol^{-1})
298.5	76.358	−3.775	85.103	−4.924	86.814	−3.241	80.391	−3.929
	±0.130	±0.004	±0.013	±0.001	±0.105	±0.004	±0.071	±0.002
304	79.797	−3.819	89.881	−4.992	88.893	−3.251	83.856	−3.972
	±0.272	±0.009	±0.021	±0.001	±0.118	±0.005	±0.117	±0.004
309	82.678	−3.851	94.148	−5.049	90.906	−3.263	86.868	−4.005
	±0.104	±0.112	±0.218	±0.007	±0.126	±0.004	±0.050	±0.002
313	85.094	−3.879	97.701	−5.098	92.437	−3.271	89.441	−4.036
	±0.054	±0.002	±0.004	±0.001	±0.092	±0.003	±0.134	±0.004
318	88.023	−3.910	102.236	−5.161	94.412	−3.281	92.554	−4.071
	±0.079	±0.003	±0.033	±0.001	±0.100	±0.003	±0.121	±0.004
323	91.119	−3.945	106.479	−5.212	96.295	−3.289	95.550	−4.100
	±0.075	±0.002	±0.071	±0.002	±0.113	±0.004	±0.159	±0.005
328	93.981	−3.972	111.533	−5.287	98.224	−3.297	98.868	−4.139
	±0.109	±0.003	±0.140	±0.004	±0.121	±0.004	±0.100	±0.003

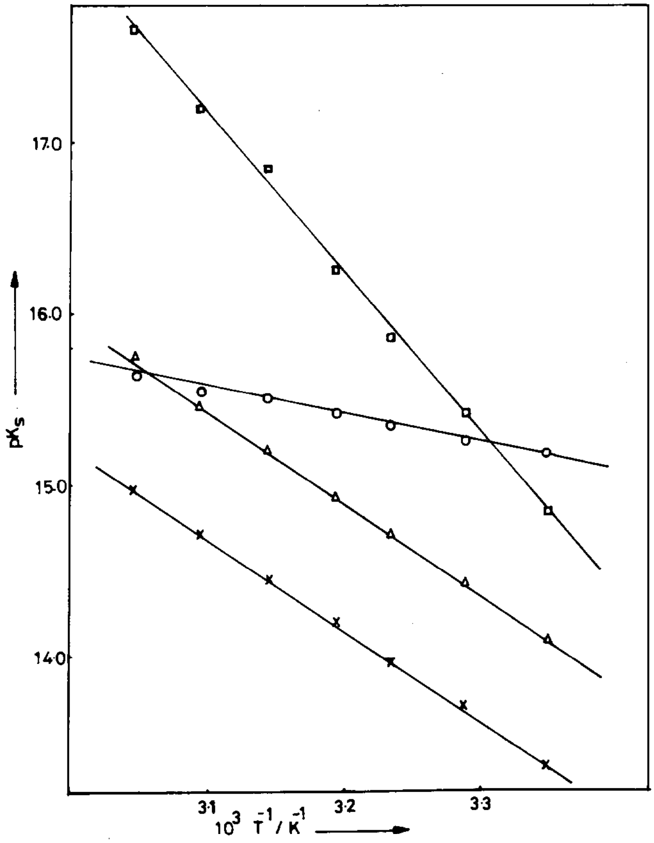

Fig. 2. Variation of solubility product with temperature of $Ni_2HIO_6 \cdot 3H_2O$ (×), $Cu_2HIO_6 \cdot 2H_2O$ (□), $Zn_2HIO_6 \cdot 1.25H_2O$ (○) and $Cd_2HIO_6 \cdot 1.25H_2O$ (△).

solubility data in Tables 2–5. The intercept on the Y-axis gives the solubility at 298 K. Interpolation of the graph of pK_s ($-\log K_s$) vs. T^{-1} (Fig. 2) gives the solubility product at 298 K.

The Gibbs free energy was evaluated from the relationship

$$\Delta G^0 = -RT \ln K_s$$

and the ΔS^0 values were computed using the relationship

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

DISCUSSION

It is interesting to note that the solubility data presented in Tables 2–5 are excellent illustrations of retrograde solubility.

The exothermicity of the reaction

$$M_2HIO_6 \cdot nH_2O_{(s)} \rightarrow 2M^{2+}_{(aq)} + HIO^{4-}_{6(aq)} + nH_2O$$

is reflected well in the regularly decreasing solubility product with increasing temperatures.

The interesting feature of these results is the constancy of the enthalpy of solution over the temperature range studied as exhibited in Fig. 1. Since only a marginal rise in $\gamma_{\pm}$ values with rising temperature is seen from Tables 2–5, ΔH has been replaced by ΔH^0, its value being -3.631×10^{-4}, -6.188×10^{-4}, -0.993×10^{-4} and -3.690×10^{-4} J mol^{-1} for the compounds of nickel, copper, zinc and cadmium, respectively.

Since dissociation corresponds to the relaxation of a constraint and the movement from widely spaced to closely spaced energy levels, the increase in the numerical values of entropy of the above reaction with increasing temperature is to be expected (Table 6).

In conclusion, the negative enthalpy values favour the products at low temperatures, whereas the negative entropy values favour reactants at high temperatures.

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