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DETERMINATION OF THE REACTION HEAT AND STUDIES OF THERMODYNAMIC FUNCTIONS
Hydrolytic polymerization of chromium(III) at relatively high concentrations by microcalorimetry

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Abstract

The hydrolytic polymerization of Cr^{3+} at relatively high concentrations was studied by microcalorimetry. The thermal curves were determined with a 2277 thermal activity monitor. From the curves, the identified reaction heats (ΔrH_m^σ), hydrolysis constants (K) and thermodynamic functions (ΔrG_m^σ,ΔrS_m^σ) were calculated at different temperatures.

Keywords: chromium(III), hydrolytic polymerization, reaction heat, thermodynamic functions

Introduction

Hall [1] and Anbang [2] have reported studies on the products $(Cr_2(OH)]^{5+}$, $[Cr_3(OH)_2]^{7+}$ of the hydrolytic polymerization of Cr^{3+}. Luo Qinhui and Dai Anbang [3, 4] have published the hydrolysis constants of this reaction.

The purpose of this work has been to determine the reaction heat (ΔrH_m^σ) of the mentioned reaction under similar experimental conditions and to calculate the hydrolysis constants (K^σ) and thermodynamic functions (ΔrG_m^σ,ΔrS_m^σ) of the hydrolysis process of Cr^{3+}.

Experimental

Equipment

The thermal curves of the hydrolytic polymerization of Cr^{3+} was measured with a 2277 thermal activity monitor (Sweden), which had a detection limit of 0.15 μW and a baseline stability of 0.2 μW/24 h.

Materials

0.2 mol dm^{-3} chromic nitrate and 0.5 mol dm^{-3} sodium nitrate were used as reaction system.

0.5 mol dm^{-3} sodium nitrate was used as reference system.

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Method

The thermal curves of the hydrolytic polymerization of Cr^{3+} were recorded using sealed ampoules, one containing a reference solution and the other the reaction sample. The sample normally occupied position A and the reference occupied position B in the monitor, each ampoule contrained 2 ml sample (or reference) and 2 ml of air.

All measurements were carried out at 313 K and the amplifier of the monitor was set at 30 μW.

Results and discussion

A typical curve of the hydrolytic polymerization of Cr^{3+} at 313 K is shown in Fig. 1.

Figure 1 consists of two exothermic peaks curve abc and curve cde. From this curve, the value of $\Delta rH_m^\sigma(1)$ of 9900 J mol^{-1} corresponding to the exothermic process (1) and of $\Delta rH_m^\sigma(2)$ of 21600 J mol^{-1} corresponding to the exothermic process (2) are obtained.

$$2Cr^{3+} + H_2O \overset{K^\circ_{(1)}}{\rightleftarrows} [Cr_2(OH)]^{5+} + H^+ \quad (1)$$

and

$$3[Cr_2(OH)]^{5+} + H_2O \overset{K^\circ_{(2)}}{\rightleftarrows} 2[Cr_3(OH)_2]^{7+} + H^+ \quad (2)$$

With the help of literature data: $\lg K^\sigma_{(1)} = -2.68$, $\lg K^\sigma_{(2)} = -3.84$, published by Lou Qinghue *et al.* and the dependences $\Delta rG_m^\sigma = -RT\ln K^\sigma$ and $\Delta rG_m^\sigma = \Delta rH_m^\sigma - T\,\Delta rS_m^\sigma$, the hydrolysis constants (K^σ) and thermodynamic functions (ΔrG_m^σ, ΔrS_m^σ) of the hydrolysis process were obtained at different temperatures (For data see Tables 1 and 2).

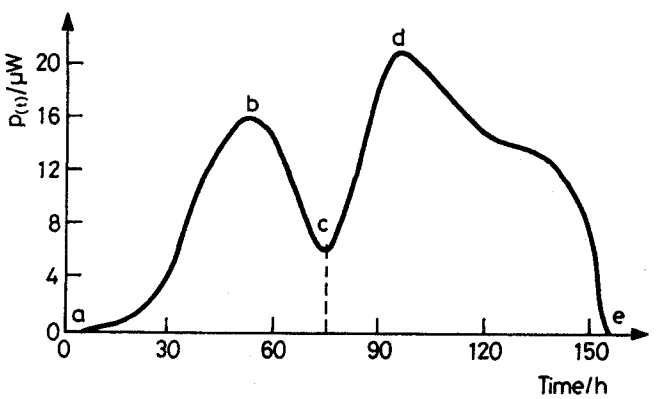

Fig. 1 Thermal curve of the hydrolytic polymerization of chromium(III) at 313K

Table 1 Hydrolysis constants and thermodynamic functions of process (1) at different temperatures

T/K	293	298	303	308	313	318	323
$\lg K^{\sigma}_{(1)}$	-2.79	-2.76	-2.73	-2.71	-2.68	-2.65	-2.63
$K^{\sigma}_{(1)}\times10^{3}$	1.61	1.73	1.84	1.96	2.09	2.22	2.35
$\Delta rG^{\sigma}_{m(1)}$/kJ mol^{-1}	15.66	15.76	15.84	15.96	16.06	16.16	16.26
$\Delta rS^{\sigma}_{m(2)}$/J K^{-1} mol^{-1}	-19.7	-19.7	-19.7	-19.7	-19.7	-19.7	-19.7

Table 2 Hydrolysis constants and thermodynamic functions of process (2) at different temperatures

T/K	293	298	303	308	313	318	323
$\lg K^{\sigma}_{(2)}$	-4.09	-4.02	-3.96	-3.90	-3.84	-3.78	-3.73
$K^{\sigma}_{(2)}\times10^{4}$	0.820	0.952	1.10	1.26	1.45	1.65	1.87
$\Delta rG^{\sigma}_{m(2)}$/kJ mol^{-1}	22.92	22.94	22.97	22.99	23.01	23.03	23.06
$\Delta rS^{\sigma}_{m(2)}$/J K^{-1} mol^{-1}	4.50	4.50	4.50	4.50	4.50	4.50	4.50

It can be seen in Tables 1 and 2 that the values of $K^{\sigma}_{(1)}$, $K^{\sigma}_{(2)}$, $\Delta rG^{\sigma}_{m(1)}$, $\Delta rG^{\sigma}_{m(2)}$, $\Delta rS^{\sigma}_{m(1)}$ and $\Delta rS^{\sigma}_{m(2)}$ all increase with temperature.

Conclusion

The recommended hydrolysis constants and thermodynamic functions of the hydrolysis process of Cr^{3+} at different temperatures are given in Tables 1 and 2.

References

1 H. T. Hall and H. Eyring, J. Amer. Chem. Soc., 72 (1950) 782.
2 Dai Anbang and Wn Youli, J. Taiking University, 2 (1957) 631.
3 Luo Qinghue, Ren Jianguo, Shen Mengchang and Dai Anbang, Chemical J. Chinese Universities, 4 (1983) 407.
4 Luo Qinghue, Ren Jianguo, Shen Mengchang and Dai Anbang, Scientia Sinica (B), 2 (1986) 137.