

*Short Communication*

**EXTRACTION OF Cr(III) WITH HEH[EHP] IN BENZENE OR CYCLOHEXANE, USING A PERFUSION/TITRATION MICROCALORIMETRIC METHOD**

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**Abstract**

The extraction of Cr<sup>3+</sup> with HEH[EHP] in benzene or cyclohexane was studied by using a perfusion/titration micro-calorimetric method. The heat produced in the reaction processes was determined via the power–time curve and the reaction heat at 298 K was identified. The extraction equilibrium constants and thermodynamic functions at different temperatures were calculated by using all of the reaction heats and extraction equilibrium constants.

**Keywords:** chromium(III), extraction, HEH[EHP], perfusion/titration micro-calorimetric monitor, reaction heat

**Introduction**

In previous papers [1–3], we have reported on the determination of the reaction heat of the hydrolytic polymerization of Cr<sup>3+</sup> and extraction of Cr<sup>3+</sup> with HEH[EHP] in benzene or cyclohexane. In the present work, under the same extraction experimental conditions, a perfusion/titration micro-calorimetric monitor was used to determine the power–time curve of extraction of Cr<sup>3+</sup> with HEH[EHP] in benzene or cyclohexane and the reaction heat was identified. In accordance with the Gibbs-Helmholtz equation and with  $\Delta_r G_m^\theta = -RT \ln K^\theta$  and  $\Delta_r G_m^\theta = \Delta_r H_m^\theta - T\Delta_r S_m^\theta$ , all of the reaction heats and extraction equilibrium constants determined in a previous paper were used

to calculate the extraction equilibrium constants and thermodynamic functions ( $\Delta_r G_m^\ominus$  and  $\Delta_r S_m^\ominus$ ) at different temperatures.

## Experimental

### *Instrument*

The 2277 thermal activity monitor (Sweden) involves isothermally thermostatic 23 l of water, holding up to four independent calorimetric units; 4 ml stainless steel perfusion/titration ampoule units are inserted in the thermostats. Perfusion/titration units come with two stirrer shafts, a hollow one for perfusion and the other plugged for titration. Perfusion/titration units are equipped with a stirrer and a stirrer motor, to rotate the stirrer shaft at the desired speed (usually between 60 and 120 rpm); a Kelf turbine is used as a 4 ml system to be filled with 2.5–3 ml of solution.

The instrument can be used in the range 10–80°C, the working range of the thermostat. It was maintained at a given temperature, constant at 298 K. This system is very sensitive: the detection limit is 0.15  $\mu$ W and the baseline stability (over a period of 24 h) is 0.2  $\mu$ W.

A glass electrode pH-meter was used (model HM-20S, TOA Electronics Ltd., Japan) with a range of pH=0.00–14.00.

### *Materials*

Solution (1):  $1.465 \cdot 10^{-3}$  mol dm<sup>-3</sup> Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>, pH=4.53 (in aqueous phase of extraction equilibrium); solution (1) was allowed to stand for 60 days.

Solution (2):  $1.538 \cdot 10^{-3}$  mol dm<sup>-3</sup> Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>, pH=4.50 (in aqueous phase of extraction equilibrium); solution (2) was allowed to stand for 60 days.

Solution (3): 0.15 mol dm<sup>-3</sup> HEH[EHP] in benzene.

Solution (4): 0.15 mol dm<sup>-3</sup> HEH[EHP] in cyclohexane.

### *Method*

In this experiment, a 4 ml stainless steel perfusion/titration ampoule microcalorimetric unit was used, which contained a reference solution and the reaction sample. The sample normally occupied position A and the reference occupied position B in the monitor. Each ampoule contained 3 ml of sample or reference.

The solution in the extraction system contained: 1.5 ml solution (1) and 1.5 ml solution (3) or 1.5 ml solution (2) and 1.5 ml solution (4); the reference solution contained: 1.5 ml solution (1) and 1.5 ml benzene or 1.5 ml solution (2) and 1.5 ml cyclohexane.

All measurements were carried out at 298 K and the amplifier of the monitor was set at 100  $\mu\text{W}$ . Before the monitor began to record the power-time curve, the operator rotated the stirrer shaft at the desired speed, 120 rpm.

## Results and discussion

The power-time curves of the extraction of  $\text{Cr}^{3+}$  with HEH[EHP] in benzene and cyclohexane were determined at 298 K (Figs 1 and 2). From the  $Pt$  and  $t$  data for the power-time curve, the reaction heats ( $\Delta_r H_m^\theta$ ) were obtained.

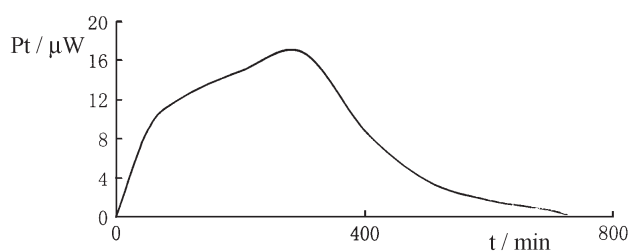


Fig. 1 Power-time curve of reaction (1)

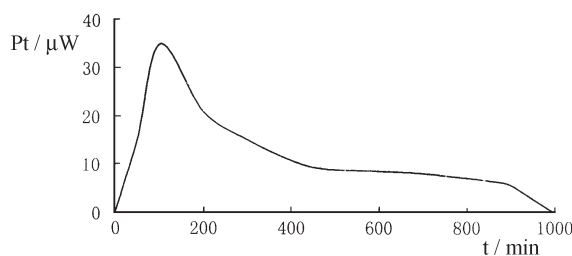


Fig. 2 Power-time curve of reaction (2)

For reaction (1): for extraction of  $\text{Cr}^{3+}$  with HEH[EHP] in benzene:  $\Delta_r H_{m(1)}^\theta = -169.28 \text{ kJ mol}^{-1}$ .

For reaction (2): for extraction of  $\text{Cr}^{3+}$  with HEH[EHP] in cyclohexane:  $\Delta_r H_{m(2)}^\theta = 312.09 \text{ kJ mol}^{-1}$ .

Under the same experimental conditions, the extraction equilibrium constants were  $\log K_{(1)}^\theta = -3.21$  and  $\log K_{(2)}^\theta = -2.91$ . On the basis of the equilibrium constant data in the literature [3], the determined reaction heat, the Gibbs-Helmholtz equation,  $\Delta_r G_m^\theta = -RT \ln K^\theta$  and  $\Delta_r G_m^\theta = \Delta_r H_m^\theta - T \Delta_r S_m^\theta$ , the extraction equilibrium constants ( $K^\theta$ ) and thermodynamic functions ( $\Delta_r G_m^\theta$  and  $\Delta_r S_m^\theta$ ) of the extraction process at different temperatures are shown in Tables 1 and 2.

The power-time curves reflect the solvent extraction process. The area under the curve represents the reaction heat. Reaction (1) is an exothermic reaction, whereas reaction (2) is an endothermic reaction. It can be seen in Table 1 that the values of  $K_{(1)}^\theta$  and



$\Delta_r G_{m(1)}^\theta$  both decrease with temperature, while Table 2 reveals that the values of  $K_{(2)}^\theta$  and  $\Delta_r G_{m(2)}^\theta$  both increase with temperature.

## Conclusions

The given curves provide much information concerning the extraction equilibrium constants ( $K^\theta$ ) and thermodynamic functions ( $\Delta_r G_m^\theta$  and  $\Delta_r S_m^\theta$ ) of the solvent extraction processes and ion-exchange. These data are very useful in studies of the thermokinetic properties of solvent extraction processes.

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## References

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