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MICROCALORIMETRIC STUDY OF THE OSCILLATING EXTRACTION SYSTEM

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Abstract

The power–time curves of the oscillating extraction system were determined at different temperatures for the extraction of hydrochloric acid and acetic acid with primary amine N_{1923} (R–CH(NH_2)–R^1), *R*, R^1 represent alkyl of C_{9-11} in chloroform using the titration microcalorimetric method. The apparent activation energy was calculated from the induction period (t_{in}), the first oscillation period ($t_{p.1}$) and the second oscillation period ($t_{p.2}$).

Keywords: acetic acid, hydrochloric acid, oscillating extraction system, primary amine N_{1923}, titration microcalorimetric method

Introduction

Since Belousov [1] first reported that the homogeneous system of citric acid oxidized by bromic acid in the presence of Ce^{3+} as catalyst could produce an oscillating reaction system, many researches have been engaged in oscillation research work [2–5].

In previous papers [6, 7], we reported the calorimetric curves of oscillating reaction systems at different temperatures and the study of oscillating biological system by microcalorimetric method.

In this paper, we found the oscillating extraction system. The power–time curves of oscillating extraction system were determined for the extraction of hydrochloric acid and acetic acid with primary amine N_{1923} in chloroform at different temperatures. Non-linear relationships of the induction period (t_{in}), the first oscillation ($t_{p.1}$), the second oscillation period ($t_{p.2}$) and temperature were established and the apparent activation energy was calculated.

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Experimental

Instrument

The 2277 thermal activity monitor was produced by Thermometric AB (Thermometric AB is a company in Stockholm, Sweden, working in the field of thermal measurements). The 2277 thermal activity monitor is an isothermally thermostated 23 L water bath holding up to four independent calorimetric units and operating at working temperatures between 10 to 90°C. With an external water circulator, its stability over 24 h is better than $\pm 10^{-4}$°C. This monitor is very sensitive, the detection limit is 0.15 μW and the baseline stability (over a period of 24 h) is 0.20 μW.

4 mL steel titration ampoule unit is an independent unit, which is used in this experiment. The titration ampoule unit has a stirrer, which is equipped with a motor rotating the stirrer shaft at the desired speed (usually between 60 to 120 rpm). A Kelf turbine is used for a 4 mL system filled with 2.5–3 mL of solution.

Materials

Primary amine (R–CH(NH_2)–R^1), R, R^1 represent alkyl of C_{9-11} (Institute of Shanghai Organic Chemistry, Chinese Academy of Sciences): content of primary amine is bigger than 99.8%, content of nitrogen is $3.61\cdot 10^{-3}$ mol g^{-1} and average molecular mass is 291.8.

Solution(1): 0.100 mol dm^{-3} hydrochloric acid (analytical grade).
Solution(2): 0.300 mol dm^{-3} acetic acid (analytical grade).
Solution(3): 0.500 mol dm^{-3} primary amine N_{1923} in chloroform (analytical grade).

Method

In the experiment, two 4 mL ampoule units were used. One of them contained the sample solution and the other the reference solution. The sample solution normally occupied position A and the reference occupied position B in the monitor.

The solutions (1), (2), (3) were maintained constant at given temperature. The sample solution of the extraction system contained: 1 mL solution (1) or (2) and 1 mL solution (3), the reference solution contained 1 mL solution (1) or (2) and 1 mL chloroform.

All measurements were carried out at constant given temperature and the amplifier of the monitor was set at 1000 μW. The stirrer shaft was set at the desired speed of 120 rpm for sample solution. The monitor began to record the power (μW)–time curve. When the recording pen returned to the baseline and became stabilized, the process of the oscillating extraction system was completed.

Instrumental thermal power was carried out with electrical standardization.

Results and discussion

Experimental results

All measurements were carried out at 298, 303, 308 and 313 K respectively. Every system was experimental thrice, average data of experimental curves was obtained.

The power–time curves of the extraction of 0.100 mol dm^{-3} hydrochloric acid with 0.500 mol dm^{-3} primary amine N_{1923} in chloroform were determined at different temperatures. These curves are shown in Fig. 1.

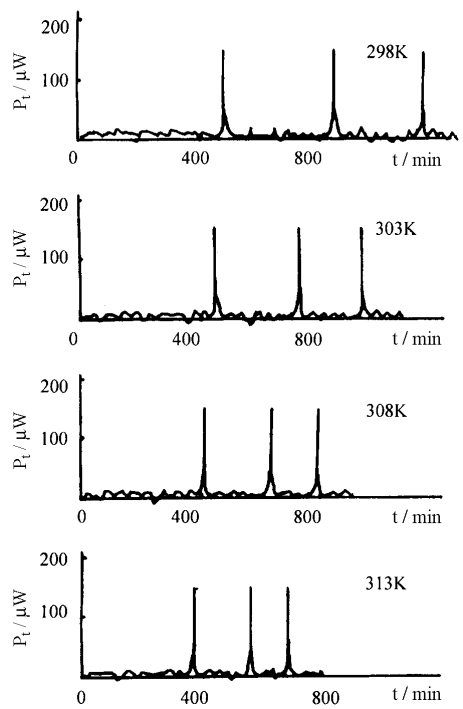

Fig. 1 Power–time curves of the extraction hydrochloric acid at different temperatures

The power–time curves of the extraction of 0.300 mol dm^{-3} acetic acid with 0.500 mol dm^{-3} primary amine N_{1923} in chloroform were determined at different temperatures. These curves are shown in Fig. 2.

In this paper, we only selected the induction period (t_{in}), first and second oscillation period ($t_{p.1}$ and $t_{p.2}$) and made a discussion.

According to a literature method [8], since $\ln 1/t = -E/(RT)+C$, the values of t_{in}, $t_{p.1}$ and $t_{p.2}$ were used to plot $\ln 1/t$ *vs.* $1/T$, the apparent activation energy were calculated.

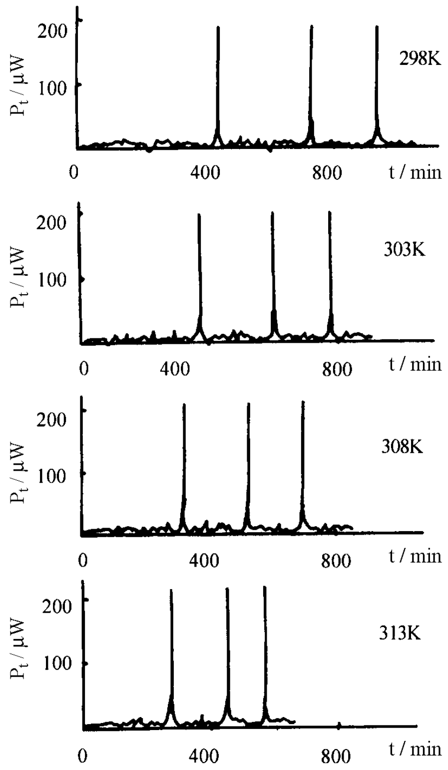

Fig. 2 Power–time curves of the extraction acetic acid at different temperatures

Effects of different temperatures on the extraction hydrochloric acid

We studied oscillating extraction system of extraction of 0.100 mol dm^{-3} hydrochloric acid with 0.500 mol dm^{-3} primary amine N_{1923} in chloroform. The values of t_{in}, $t_{p.1}$ and $t_{p.2}$ obtained from power–time curves and shown in Table 1.

Table 1 The values of t_{in}, $t_{p.1}$ and $t_{p.2}$ at different temperatures

Temperature, T/K	298	303	308	313
Induction period, t_{in}/min	485	450	420	390
First oscillation period, $t_{p.1}$/min	360	280	220	180
Second oscillation period, $t_{p.2}$/min	295	215	160	120

According to the literature method [8], the following equations were obtained.

$$\ln\frac{1}{t_{in}} = -1.6591 - \frac{1348.6}{T} \quad r = -0.9998 \quad E_{in} = 11.212 \text{ kJ mol}^{-1} \tag{1}$$

$$\ln\frac{1}{t_{p.1}}=8.6560-\frac{4331.4}{T} \quad r=-0.9993 \quad E_{p.1}=36.011 \text{ kJ mol}^{-1} \tag{2}$$

$$\ln\frac{1}{t_{p.2}}=13.0606-\frac{5585.9}{T} \quad r=-0.9999 \quad E_{p.2}=46.442 \text{ kJ mol}^{-1} \tag{3}$$

E represent apparent activation energy.

Effects of different temperatures on the extraction acetic acid

We studied oscillating extraction system of extraction of 0.300 mol dm^{-3} acetic acid with 0.500 mol dm^{-3} primary amine N_{1923} in chloroform. From power–time curves, the values of t_{in}, $t_{p.1}$ and $t_{p.2}$ were obtained and shown in Table 2.

Table 2 The values of t_{in}, $t_{p.1}$ and $t_{p.2}$ at different temperatures

Temperature, T/K	298	303	308	313
Induction period, t_{in}/min	440	385	350	300
First oscillation period, $t_{p.1}$/min	290	245	175	145
Second oscillation period, $t_{p.2}$/min	205	175	125	80

According to the same method, we established the following equations:

$$\ln\frac{1}{t_{in}}=1.6949-\frac{2319.6}{T} \quad r=-0.9957 \quad E_{in}=19.285 \text{ kJ mol}^{-1} \tag{4}$$

$$\ln\frac{1}{t_{p.1}}=9.4225-\frac{4504.8}{T} \quad r=-0.9910 \quad E_{p.1}=37.453 \text{ kJ mol}^{-1} \tag{5}$$

$$\ln\frac{1}{t_{p.2}}=14.3136-\frac{5875.3}{T} \quad r=-0.9766 \quad E_{p.2}=48.847 \text{ kJ mol}^{-1} \tag{6}$$

Conclusions

- We found oscillating extraction system from power–time curves of the extraction of acid with primary amine N_{1923} in chloroform at different temperatures. Compared with oscillating chemical system and oscillating biological system, the oscillating extraction system has the particular rule that the oscillation period changes with time.
- From power–time curves of oscillating extraction system, we can obtain the induction period (t_{in}), first oscillation period ($t_{p.1}$) and second oscillation period ($t_{p.2}$). From Tables 1 and 2, values of t_{in}, $t_{p.1}$ and $t_{p.2}$ decrease with increasing of temperature. In the same temperature, value of t_{in} is bigger than $t_{p.1}$, and $t_{p.1}$ is bigger than $t_{p.2}$.
- From values of apparent activation energy of the induction period, first oscillation period and the second oscillation period on the extraction hydrochloric acid and ace-

tic acid, we see values of apparent activation energy, induction period (E_{in})$<$first oscillation period ($E_{p.1}$)$<$second oscillation period ($E_{p.2}$).

These power–time curves of the oscillating extraction system provide much information concerning the oscillation period, the apparent activation energy and the order of oscillating extraction system. These data are very useful in studies of the properties of oscillating extraction system.

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References

1 B. P. Belousov, Sb. Ref. Radiat. Med., 145 (1959) 1958.
2 L. Hexing and X. Haihan, Acta Chimica Sinica, 49 (1991) 451.
3 Y. Chunlan and L. Zongxiao, Acta Physico-Chimica Sinica, 10 (1994) 871.
4 L. Zongxiao, Science Bulletin, 2 (1993) 191.
5 L. Hexing and N. Lihua, Communication Chimica Sinica, 10 (1996) 40.
6 S. Haitao, W. Xuezhi, L. Yongjun, N. Zhaodong and Z. Honglin, J. Therm. Anal. Cal., 58 (1999) 117.
7 Z. Honglin, Y. Xiufang, Y. Li, L. Fenghua, N. Zhaodong and S. Haitao, J. Therm. Anal. Cal., 65 (2001) 755.
8 G. Zhili, L. Junli, H. Degang, S. Shigang and W. Anzhou, Acta Physico-Chimica Sinica, 2 (1993) 218.