THE THERMOKINETICS OF THE FORMATION REACTIONS OF CERIUM(III) *n*-DODECYLBENZENE SULFONATE AND CERIUM(III) STEARATE

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Abstract

The thermokinetics of the formation reactions of cerium(III) *n*-dodecylbenzene sulfonate and cerium(III) stearate are studied by using a microcalorimeter. On the basis of experimental and calculated results, three thermodynamics parameters (the activation enthalpies, the activation entropies, the activation free energies), the rate constant, three kinetic parameters (the activation energies, the pre-exponential constant and the reaction order) and the enthalpies of the reaction of preparing cerium(III) *n*-dodecylbenzene sulfonate in the temperature range of 20–35°C and cerium(III) stearate in the temperature range of 44.6–62.8°C are obtained. The results showed that the title reactions easily took place in the studied temperature.

Keywords: cerium(III) *n*-dodecylbenzene sulfonate, cerium(III) stearate, formation, thermokinetics

Introduction

Cerium(III) *n*-dodecylbenzene sulfonate (CDBS) has utility particularly as some graft polymerization initiators [1]. Its synthesis and chemical structure have been reported [2]. The cerium(III) stearate's (CSA) synthesis, IR and fusing point have also been reported [3, 4]. However, the formation thermokinetics of CDBS and CSA have not been reported. In this paper, the fundamental parameters for two reactions of preparing CDBS and CSA, including the reaction rate constant (k), the activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy $\Delta H_{\neq}^{0}$, the activation entropy $\Delta S_{\neq}^{0}$, the activation free energies ($\Delta G_{\neq}^{0}$) and the enthalpies (ΔH_0) obtained by means of a microcalorimeter, were studied. These parameters will provide a scientific basis for technological processing of preparing CDBS and CSA.

Experimental

Materials

The sodium *n*-dodecylbenzene sulfonate (A), which was of chemical purity, was re-crystallized in non-aqueous alcohol in order to get rid of some inorganic salts. The potassium stearate (B) had chemical purity. The ceric(III) nitrate was of analysis purity. They were dissolved in distilled water. The molarities of solution A and B were 0.21 (A) and 0.12 mol l^{-1} (B), respectively. The molarities of ceric(III) nitrate were 0.21 (C) and 0.12 mol l^{-1} (D). In our experimental, the molar ratio of both solution. A to solution C and solution B to solution D were 3:1.
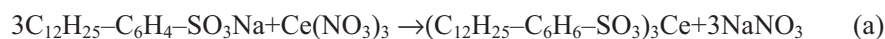
Experimental equipment and conditions

The thermokinetics of the formation of CDBS were measured by using a microcalorimeter, type RD-496 II, China with the sensitivity of 66.5 μV mW^{-1}. The thermokinetics of the formation of CSA were measured by using a microcalorimeter, type F, Calvet from Setaram, France with the sensitivity of 66.5 μV W^{-1} and a paper speed of 2.5 mm min^{-1}. All the microcalorimeters were equipped with two 15 ml vessels and calibrated after each experiment. The precision of enthalpy measured is 2%. The measurements of the formation reaction were carried out at 20, 25 and 35°C for CDBS and at 44.6, 50.7, 55.7 and 62.8°C for CSA. The device used for the study of the title reactions is shown in Fig. 1. The IR spectra for CDBS and CSA were determined by the Nicolot of USA, Model 60 SXR FT-IR spectrophotometer. The qualitative and quantitative analyses of cerium of CDBS and CSA were determined by using ICP-AES, Model of JY-38-Plus, France.

Fig. 1 Device used for the study of the formation reaction; 1 – calorimetric cell; 2 – adding tube containing sodium *n*-dodecylbenzene sulfonate solution or potassium nitrate; 3 – adding tube containing ceric(III) nitrate solution; 4 – silicone rubber cover; 5 – glass rod (on depressing the rod, the bottom of tube 2 is broken. The two solutions are mixed in the tube 1 and 2)

Results and discussion

The IR spectra of CDBS in Fig. 2 show the S–O absorption appeared at 1229, 1133, 1048 and 690 cm^{-1}. The IR spectra of CSA in Fig. 2 didn't show any C=O absorption, but C–O absorption appeared at 1529 and 1467 cm^{-1}. The mass percent of the cerium in CDBS and CSA was 13.01 and 14.16%, respectively. Whereas the two reactions could be represented as follows:

$$3C_{12}H_{25}\text{–}C_6H_4\text{–}SO_3Na + Ce(NO_3)_3 \rightarrow (C_{12}H_{25}\text{–}C_6H_6\text{–}SO_3)_3Ce + 3NaNO_3 \qquad (a)$$

$$3C_{17}H_{35}COOK + Ce(NO_3)_3 \rightarrow (C_{17}H_{35}COO)_3Ce + 3KNO_3 \qquad (b)$$

The typical thermokinetic (TK) curves of the formation reaction of CDBS and CSA were shown in Fig. 3. The original data obtained from the TK curves were shown in Tables 1 and 2. These experimental data were put into Eq. (1) obtained by
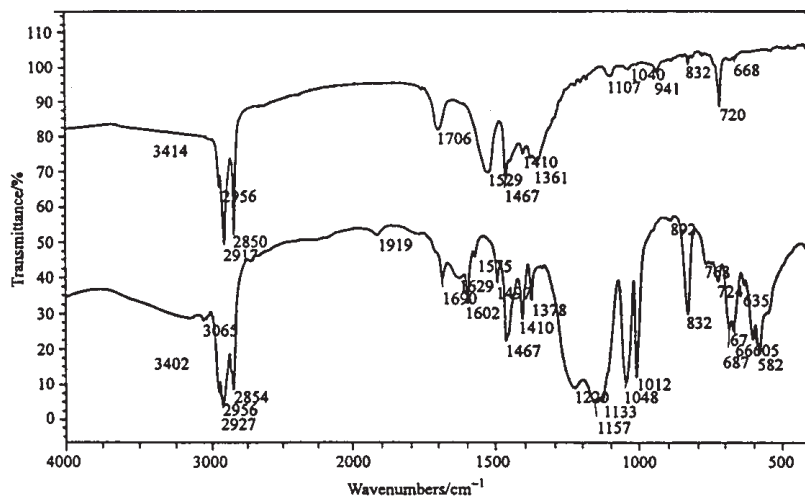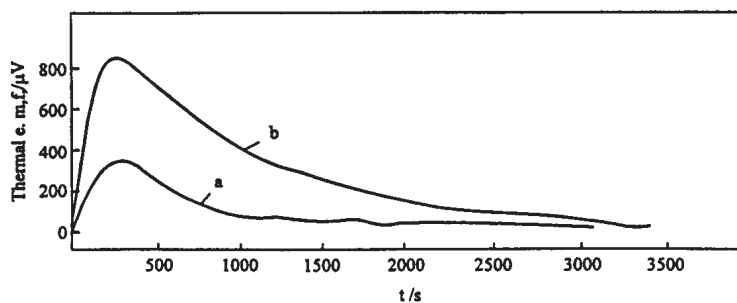

Fig. 2 IR spectra of a – CDBS and b – CSA

Fig. 3 Typical thermokinetic curves of the reactions (a) and (b)

Table 1 Thermokinetic data of the reacion (a)

293.2 K			298.2 K			308.2 K		
t/s	$(\mathrm{d}H/\mathrm{d}t)_i \cdot 10^4/$ $\mathrm{J\ s^{-1}}$	$(H_t/H_0)_i$	t/s	$(\mathrm{d}H/\mathrm{d}t)_i \cdot 10^4/$ $\mathrm{J\ s^{-1}}$	$(H_t/H_0)_i$	t/s	$(\mathrm{d}H/\mathrm{d}t)_i \cdot 10^4/$ $\mathrm{J\ s^{-1}}$	$(H_t/H_0)_i$
260	0.978	0.261	270	1.555	0.248	260	2.059	0.326
420	0.703	0.384	420	1.233	0.380	400	1.736	0.473
580	0.689	0.483	570	0.979	0.481	540	1.285	0.591
750	0.558	0.564	720	0.778	0.559	680	0.943	0.682
910	0.461	0.630	880	0.674	0.629	820	0.743	0.750
1160	0.376	0.687	1040	0.551	0.689	960	0.590	0.802
1320	0.309	0.735	1190	0.492	0.742	1010	0.535	0.840
1490	0.250	0.777	1340	0.427	0.788	1250	0.403	0.879
1610	0.216	0.815	1490	0.355	0.830	1310	0.315	0.910
–	–	–	–	–	–	1450	0.233	0.929

Table 2 Thermokinetic data of the reaction (b)

317.8 K[*]			323.9 K			328.9 K			336.0 K		
t/s	$(\mathrm{d}H/\mathrm{d}t)_i\cdot10^3/$ J s^{-1}	$(H_t/H_0)_i$	t/s	$(\mathrm{d}H/\mathrm{d}t)_i\cdot10^3/$ J s^{-1}	$(H_t/H_0)_i$	t/s	$(\mathrm{d}H/\mathrm{d}t)_i\cdot10^3/$ J s^{-1}	$(H_t/H_0)_i$	t/s	$(\mathrm{d}H/\mathrm{d}t)_i\cdot10^3/$ J s^{-1}	$(H_t/H_0)_i$
260	5.04	0.274	320	9.07	0.505	370	8.98	0.591	350	13.26	0.575
360	4.14	0.389	520	6.06	0.668	570	4.66	0.775	550	7.22	0.755
460	3.41	0.496	720	3.77	0.789	770	2.62	0.868	750	3.75	0.864
560	2.73	0.595	920	1.96	0.897	970	1.48	0.919	950	1.95	0.925
660	2.17	0.672	1120	1.37	0.926	1170	0.86	0.952	1150	0.99	0.960
760	1.84	0.718	1320	0.95	0.948	1370	0.57	0.967	1350	0.51	0.978
860	1.55	0.768	1520	0.66	0.967	1570	0.39	0.977	1550	0.42	0.984
960	1.34	0.780	1720	0.53	0.972	1770	0.33	0.979	1750	0.31	0.987
1060	1.17	0.802	1920	0.42	0.977	1970	0.22	0.983	1950	0.21	0.989
–	–	–	2120	0.32	0.984	–	–	–	–	–	–

[*]The quality of reactant was the half of the other temperatures and the paper speed was 5 mm min^{-1}. H_0=188.0 kJ mol^{-1}

Table 3 The values of n, k, A, E, $\Delta G_{\neq}^0$, $\Delta H_{\neq}^0$ and $\Delta S_{\neq}^0$ of the reaction (a)

T/K	Eq. (1)			Eq. (2)			Eq. (3)	Eq. (4)		
	$k \cdot 10^4/$ s^{-1}	n	r^*	$E/$ kJ mol^{-1}	$\log A/$ s^{-1}	r^*	$\Delta G_{\neq}^0$ kJ mol^{-1}	$-\Delta H_{\neq}^0/$ kJ mol^{-1}	$-\Delta S_{\neq}^0/$ $\text{J mol}^{-1}\text{K}^{-1}$	r^*
293.2	0.83	1.086	0.995	38.2	2.74	0.978	94.67	35.71	200.6	0.976
298.2	1.26	0.987	0.992	–	–	–	95.29	–	–	–
308.2	1.83	0.956	0.997	–	–	–	97.62	–	–	–

*r – The correlation coefficient

Table 4 The values of n, k, A, E, $\Delta G_{\neq}^0$, $\Delta H_{\neq}^0$ and $\Delta S_{\neq}^0$ of the reaction (b)

T/K	Eq. (1)			Eq. (2)			Eq. (3)	Eq. (4)		
	$k \cdot 10^4/$ s^{-1}	n	r^*	$E/$ J mol^{-1}	$\log A/$ s^{-1}	r^*	$\Delta G_{\neq}^0$ kJ mol^{-1}	$-\Delta H_{\neq}^0/$ kJ mol^{-1}	$-\Delta S_{\neq}^0/$ $\text{J mol}^{-1}\text{K}^{-1}$	r^*
317.8	1.94	1.09	0.998	42.73	4.30	0.992	94.50	39.88	191.2	0.991
323.9	2.40	0.98	0.999	–	–	–	95.80	–	–	–
328.9	3.40	1.13	0.998	–	–	–	96.36	–	–	–
356.0	4.52	1.09	0.998	–	–	–	97.71	–	–	–

*r – The correlation coefficient

the equation of the reaction of the *n*th order and the relation [5] between the energy change of a reacting system and the extent of reaction by linear least-squares method.

$$\ln\left(\frac{1}{H_0}\frac{dH}{dt}\right)=\ln k+n\ln\left(\frac{H_t}{H_0}\right) \tag{1}$$

where H_0 is the total reaction heat (corresponding to the global area under the TK curve); H_t is the reaction heat in a certain time (corresponding to the partial area under the curve); dH_t/dt is the exothermic rate at time t; k is the rate constant of prepared reaction; n is the reaction order.

The values of k and n obtained by Eq. (1), the values of E and A obtained by Eq. (2), the value of $\Delta G_{\neq}^0$ obtained by Eq. (3) and the values of $\Delta H_{\neq}^0$ and $\Delta S_{\neq}^0$ obtained by Eq. (4) are all listed in Tables 3 and 4.

$$\ln k=\ln A-\frac{E}{RT} \tag{2}$$

$$\Delta G_{\neq}^0=RT\ln\frac{RT}{Nhk} \tag{3}$$

and

$$\ln\frac{k}{T}=-\frac{\Delta H_{\neq}^0}{RT}+\frac{\Delta S_{\neq}^0}{R}+\ln\frac{k_B}{h} \tag{4}$$

where A is the pre-exponential constant; E is the apparent activation energy; R is the gas constant; T is the absolute temperature; $\Delta G_{\neq}^0$ is the activation free-energy; N is the Avogadro number; h is Planck's constant; $\Delta H_{\neq}^0$ is the activation enthalpy; $\Delta S_{\neq}^0$ is the activation entropy; k_B is the Boltzmann constant.

The results in Tables 3 and 4 clearly indicate that the higher the temperature of the two reactions, the faster the rate of reaction and the title reactions were of the first order. The values of E and A for the formation reaction of CDBS were 38.2 kJ mol^{-1} and $579.54\cdot10^{2.74}$ s^{-1}, respectively. The values of E and A for the formation reaction of CSA were 42.7 kJ mol^{-1} and 104.30 s^{-1}, respectively. The values of $\Delta H_{\neq}^0$ and $\Delta S_{\neq}^0$ for the formation reaction of CDBS were −35.71 kJ mol^{-1} and −200.6 J mol^{-1} K^{-1}, respectively. The values of $\Delta H_{\neq}^0$ and $\Delta S_{\neq}^0$ for the formation reaction CSA were −39.88 kJ mol^{-1} and −191.2 J mol^{-1} K^{-1}, respectively. The values of k, E and A of two title reactions were very low and $\Delta S_{\neq}^0$ were high. These facts showed that the title reactions easily took place in the temperature range of 20–35 and 44.6–62.8°C.

Conclusions

1. On the basis of experimental and calculated results, the reaction rate of the formation of CDBS and CSA in the studied temperature range was found to be of the first order. And the two reactions were exothermic. The enthalpies were 22.9 and 188.0 kJ mol^{-1}, respectively.

2. The activation energies of the formation reactions of CDBS in the temperature range of 20–35°C and CSA in the temperature range of 44.6–62.8°C were very low; and the entropies of the formation reactions of CDBS and CSA in their studied temperature were high. The title reactions easily took place in the temperature range of 20–35 and 44.6–62.8°C.

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