Phase Chemistry and Thermochemistry on Coordination Behavior of Zinc Chloride with Leucine

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The solubility property of the $ZnCl_2$-Leu-H_2O (Leu = *L*-α-leucine) system at 298.15 K in the whole concentration range was investigated by the semimicro-phase equilibrium method. The corresponding solubility diagram and refractive index diagram were constructed. The results indicated that there was one complex formed in this system, namely, Zn(Leu)Cl_2. The complex is congruently soluble in water. Based on phase equilibrium data, the complex was prepared. Its composition and properties were characterized by chemical analysis, elemental analysis, IR spectra, and TG-DTG. The thermochemical properties of coordination reaction of zinc chloride with *L*-α-leucine were investigated by a microcalorimeter. The enthalpies of solution of *L*-α-leucine in water and its zinc complex at infinite dilution and the enthalpy change of solid-liquid reaction were determined at 298.15 K. The enthalpy change of solid phase reaction and the standard enthalpy of formation of zinc complex were calculated. On the basis of experimental and calculated results, three thermodynamic parameters (the activation enthalpy, the activation entropy and the activation free energy), the rate constant and three kinetic parameters (the activation energy, the pre-exponential constant and the reaction order) of the reaction, and the standard enthalpy of formation of Zn(Leu)$^{2+}$ (aq) were obtained. The results showed that the title reaction took place easily at studied temperature.

Keywords zinc chloride, *L*-α-leucine, solid complex, phase chemistry, thermochemistry

Introduction

Zinc is a necessary trace element in human body. Many diseases arise from zinc element deficiency and have received considerable attention worldwide. *L*-α-amino acids are basic units of proteins. The complexes of zinc with α-amino acids as additives have wide application in medicine, food-stuff and cosmetics.[1-3] Preparative methods for zinc amino acids reported in literatures are as follows: adjusting pH of solution,[4] adding weak acid,[3,5] treating with organic solvent,[2,6,7] and electrolytic process.[8] It is noteworthy that the yield of the complexes prepared by the above-mentioned methods is low and the products are not soluble in water. At present, the solubility properties of zinc salt-amino acid-water systems have been investigated by the semimicro-phase equilibrium method at 298.14 K.[9] Under the direction of the phase equilibrium results, the soluble zinc amino acids which had not been reported previously, were prepared and their properties were investigated.[10-17]

L-α-Leucine (*L*-α-Leu) in the body is one of the essential amino acids that should be absorbed form food because human body can not synthesize them. The phase chemistry of $ZnSO_4$/$ZnOAc_2$-Leu-H_2O systems has been reported in literature.[18,19] However, phase chemistry and thermochemistry of coordination behavior of zinc chloride with Leu have not been reported in literature. In this paper, the solubility properties of the $ZnCl_2$-Leu-H_2O system at 298.15 K were investigated by the semimicro-phase equilibrium method. Based on phase equilibrium data, the congruently soluble complex of Zn(Leu)Cl_2, which has not been reported in the literature was synthesized and characterized. The thermochemical properties of coordination reaction and complex were investigated by a microcalorimeter. On the basis of experimental and calculated results, the thermodynamic parameters, the rate constant and kinetic parameters of the reaction were obtained. This work will provide a scientific basis for process of synthesis.

Experimental

Materials

The A.R. grade $ZnCl_2$ was dehydrated and conserved in desiccator. *L*-α-Leucine (B.R. grade) was recrystallized with the purity of greater than 99.9%. The concentration of solution of Leu was 0.005 mol/L. The other chemicals were of A.R. grade. The conductivity of the deionized water was 5.48×10^{-8} S/cm.

Analytical approach

Zn^{2+} was determined complexometrically with EDTA. Leu was analyzed by the formalin method. Before determining

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Leu, the Zn^{2+} was masked by $K_2C_2O_4$, and the blank titration was performed for comparison. Cl^- was determined by the Fajans method. Carbon, hydrogen and nitrogen analyses were carried out on a 2400 type elemental analyzer. The solubilities of Leu and $ZnCl_2$ were experimentally 1.87% and 81.00%, respectively, while the values in literature are 2.14%[20] and 81.20%,[21] respectively.

Equipment and conditions

The thermostat, with a temperature fluctuation of ±0.005 ℃, was made by ourselves. A WZS-1 type of Abbe refractometer, with a temperature fluctuation of ±0.02 ℃ and reading accuracy of ±0.0002 was used. The thermometer and all measuring vessels were calibrated. The RD496-III type microcalorimeter was made in Engineering Physical Institute of China,[22] which was equipped with two 15-mL vessels.[11] The microcalorimeter was calibrated by Joule effect and its sensitivity was (63.994±0.042), (64.308±0.027), (64.499±0.064), (64.638±0.078), (64.733±0.077) and (64.739±0.05) μV/mW at the experimental temperature of 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K, respectively. The experimental precision and accuracy were checked by measurement of the enthalpy of solution of crystalline KCl with special purity in deionized water at 298.15 K. The molar ratio of H_2O to KCl was 2000. The experimental value of $\Delta H^{\ominus}_{m,sol}$ [(17.238±0.048) kJ/mol] was in good agreement with that reported in the literature [(17.241±0.018) kJ/mol][23] indicating that the device used in this work was reliable. The precision of the measurements was in 0.5%.

A BRUKER EQ UNINOX-550-IR spectrophotometer with KBr pipette and a Perkin-Elmer TG-7 model thermogravimetric analyzer were used with sample of 1—2 mg, heating rate of 10 ℃/min and flow rate of 60 mL/min (O_2).

Experimental method

Phase chemistry was investigated by semimicro-phase equilibrium method. After 30 d, the system came to equilibrium. The composition of the sample including liquid phase and wet solid phase was analyzed by the methods referred above when the refractive index of each saturation liquid phase was determined. After the microcalorimeter was calibrated, calorimetric experiment began. When the microcalorimeter reached thermal equilibrium, the spacers of the sample and reference vessels were pushed down simultaneously by release button and the samples were mixed.

A thermochemical cycle was designed as follows:

$$ZnCl_2(s) + Leu(s) \xrightarrow[④]{\Delta H^{\ominus}_{r,(1)}} Zn(Leu)Cl_2(s)$$

$$① \downarrow \Delta H^{\ominus}_{s,(1)} \qquad\qquad ② \downarrow \Delta H^{\ominus}_{s,(2)}$$

$$ZnCl_2(s) + Leu(aq) \xrightarrow[③]{\Delta H^{\ominus}_{r,(2)}} Zn(Leu)^{2+}(aq) + 2Cl^-(aq)$$

Therefore, $\Delta H^{\ominus}_{r,(1)} = \Delta H^{\ominus}_{s,(1)} + \Delta H^{\ominus}_{r,(2)} - \Delta H^{\ominus}_{s,(2)}$

Results and discussion

Phase equilibrium results

The ternary system $ZnCl_2$-Leu-H_2O was investigated at 298.15 K. The solubility and index data of the system are presented in Table 1. The phase diagram of the system and the curve of refractive index-composition of dry salt are shown in Fig. 1. The eutectic point corresponds to break point of the refractive index-composition curve. As shown in Fig. 2, solubility curve consists of 3 branches, corresponding to solid phase of $ZnCl_2$, complex Zn(Leu)Cl_2 and Leu, respectively. The complex is a congruently soluble compound in water.

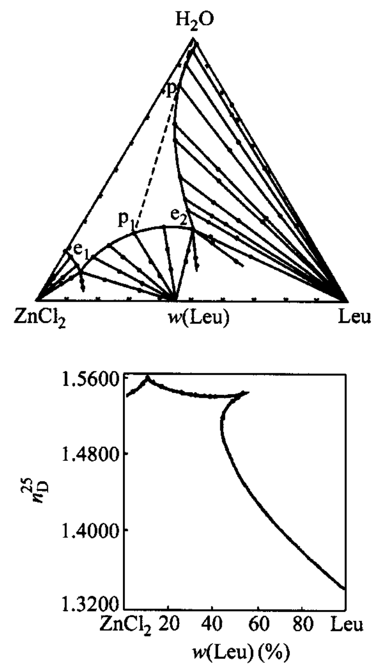

Fig. 1 Solubility diagram and refractive index-composition curve of the ternary system $ZnCl_2$-Leu-H_2O at 298.15 K.

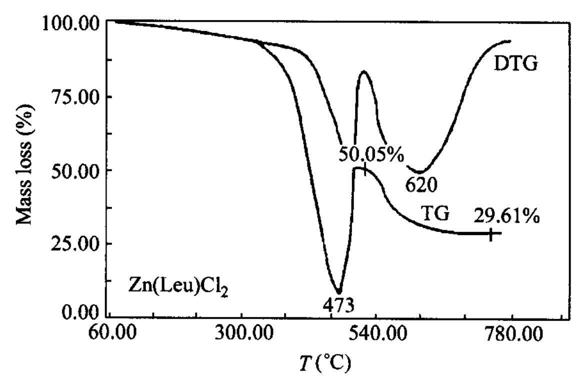

Fig. 2 TG-DTG curve for the solid complex of Zn(Leu)Cl_2.

Preparation and characterization of the complex

The complex was prepared as follows: $ZnCl_2$ and Leu with the molar ratio of 1:1 were dissolved in deionized water,

Table 1 Solubility data and refractive index of ternary system $ZnCl_2$-Leu-H_2O at 298.15 K

Composition of synthetic phase (%)		Composition of liquid phase (%)		Composition of wet solid phase (%)		$\frac{m_{Leu}}{m_{ZnCl_2}+m_{Leu}} \times 100\%$	Refractive index	Equilibrium[a] solid phase
$ZnCl_2$	Leu	$ZnCl_2$	Leu	$ZnCl_2$	Leu			
90.00	—	80.00	—	—	—	100.00	1.5412	$ZnCl_2$
87.00	4.00	79.91	6.25	95.02	1.5	90.25	1.5529	$ZnCl_2$
84.00	7.00	80.00	8.64	88.01	5.0	90.25	1.5590	$ZnCl_2$
81.00	11.00	79.92	8.70	82.13	12.45	90.18	1.5592	$ZnCl_2$ + Comp.
74.01	17.38	80.03	8.80	64.82	31.43	90.09	1.5594	Comp.
67.30	21.24	73.12	9.93	62.17	30.73	38.04	1.5558	Comp.
63.92	19.00	65.91	12.05	61.00	26.10	84.54	1.5513	Comp.
50.37	29.26	55.89	18.14	55.03	34.36	75.50	1.5453	Comp.
48.00	32.07	45.21	27.07	50.54	37.16	62.55	1.5421	Comp.
41.38	38.84	35.73	36.06	44.34	40.18	49.77	1.5452	Comp.
40.86	41.00	35.82	36.47	42.13	44.24	49.55	1.5450	Comp. + Leu
32.38	45.00	35.67	36.38	28.00	56.11	49.51	1.5458	Leu
32.07	43.06	36.03	36.00	22.87	60.00	50.02	1.5440	Leu
29.84	30.87	33.88	31.63	23.76	51.74	51.72	1.5210	Leu
27.06	39.88	32.43	28.01	24.83	45.67	53.66	1.5364	Leu
24.13	37.45	30.00	22.42	19.84	48.96	57.23	1.5213	Leu
18.37	35.00	24.28	14.03	12.00	57.18	63.18	1.5411	Leu
16.08	32.87	21.65	10.93	10.14	57.66	66.45	1.5425	Leu
9.26	33.00	17.03	4.99	5.34	61.54	72.29	1.5440	Leu
5.06	34.00	7.12	2.94	2.14	68.38	70.78	1.5437	Leu
—	27.13	—	1.87	—	—	0.00	1.3647	Leu

[a] Comp. = $Zn(Leu)Cl_2$.

and the mixture was stirred in a 60—70 ℃ water bath for 4 h. The pH of the mixture solution was controlled to 6. After being cooled to room temperature, the crystal was precipitated from the solution, then filtered by suction, washed with a small amount of acetone, and kept in a desiccator containing P_4O_{10} until the weight of the complex became constant. The analytical results of composition are given in Table 2, indicating that the complex fitted into the composition of Zn(Leu)Cl_2.

Table 2 Analytical results of composition of the complex (%)

	Zn	Leu	Cl^-	C	H	N
Calculated values	23.66	51.80	25.81	26.94	4.86	5.24
Experimental values	23.12	51.69	25.66	26.83	4.89	5.27

The IR absorptions of main groups of the complex and ligand are given in Table 3. The IR spectrum for the complex showed that characteristic absorption peaks of amino acid carboxyl groups had a great shift as compared to those in the ligand, indicating that nitrogen and oxygen atoms in the complex coordinated to Zn^{2+} in a bidentate fashion.

Table 3 IR absorptions of main groups of the complex and ligand (cm^{-1})

Compound	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$
L-α-Leu	3453.8	2958.3	1613.4	1514.2	1583.3	1407.3
Zn(Leu)Cl_2	3484.1	2962.2	1630.9	1481.8	1630.9	1412.9

The TG-DTG curve of the solid complex of Zn(Leu)Cl_2 is presented in Fig. 2. Based on the experimental and calculated results of the complex decomposition (the values in parentheses are the calculated ones of remaining compounds), the thermal decomposition mechanism of the complex is postulated to be as follows:

$$Zn(Leu)Cl_2 \xrightarrow[50.05\%\ (50.96\%)]{50—473—520\ ℃} ZnCl_2 \xrightarrow[29.61\%\ (30.43\%)]{520—620—748\ ℃} ZnO$$

Thermochemical measurement results

The solution reactions of *L*-α-leucine, and of zinc complex in water as well as solid-liquid reaction of zinc chloride with solution of *L*-α-leucine could be expressed as follows:

$$L\text{-}\alpha\text{-Leu (s)} \xrightarrow{\Delta H^{\ominus}_{s,(1)}} L\text{-}\alpha\text{-Leu (aq)} \quad (1)$$

$$Zn(Leu)Cl_2(s) \xrightarrow{\Delta H^{\ominus}_{s,(2)}} Zn(Leu)^{2+}(aq) + 2Cl^-(aq) \quad (2)$$

$$ZnCl_2(s) + Leu\ (aq) \xrightarrow{\Delta H^{\ominus}_{r,(2)}} Zn(Leu)^{2+}(aq) + 2Cl^-(aq) \quad (3)$$

The experimental results of $\Delta H^{\ominus}_{s,(1)}$, $\Delta H^{\ominus}_{s,(2)}$ and $\Delta H^{\ominus}_{r,(2)}$ are listed in Table 4, where r is the molar ratio $n(H_2O)/n$(*L*-α-Leu or zinc complex). Under the experimental conditions, the values of $\Delta H^{\ominus}_{s}$ remained constant with changing the values of r. Therefore, the mean value of $\Delta H^{\ominus}_{s}$ in Table 4 could be considered at infinite dilution. The Zn^{2+} coordinated to leucine in water in a molar ratio of 1:1.[24]

The enthalpy change of solid-liquid reaction of zinc chloride with *L*-α-leucine was calculated by the above thermochemical cycle:

$$\Delta H^{\ominus}_{r,(1)} = \Delta H^{\ominus}_{s,(1)} + \Delta H^{\ominus}_{r,(2)} - \Delta H^{\ominus}_{s,(2)} = (-22.286 \pm 0.210)\ \text{kJ/mol}$$

In comparison with leucine, the UV characteristic absorption peak of the complex had a red shift of 2 nm, indicating that the coordination of the Zn^{2+} to leucine forms $Zn(Leu)Cl_2$. The UV spectra of the two solutions after reactions (2) and (3) overlap each other and the two solutions had the same value of n^{25} ($n^{25} = 1.3371$), indicating that their thermodynamic states were the same and the thermochemical cycle designed by us was correct.

The standard enthalpies of formation of *L*-α-Leu (aq), $Zn(Leu)Cl_2$ and $Zn(Leu)^{2+}$(aq) were calculated by Hess's law according to the following thermochemical equations:

$$\Delta H^{\ominus}_{m,f}[L\text{-}\alpha\text{-Leu (aq)}] = \Delta H^{\ominus}_{s,(1)} + \Delta H^{\ominus}_{m,f}[L\text{-}\alpha\text{-Leu (s)}] \quad (4)$$

$$\Delta H^{\ominus}_{m,f}[\text{Zn (Leu)Cl}_2(s)] = \Delta H^{\ominus}_{r,(1)} + \Delta H^{\ominus}_{m,f}[L\text{-}\alpha\text{-Leu (s)}] + \Delta H^{\ominus}_{m,f}[\text{ZnCl}_2(s)] \quad (5)$$

$$\Delta H^{\ominus}_{m,f}[\text{Zn (Leu)}^{2+}(aq)] = \Delta H^{\ominus}_{r,(2)} - 2\Delta H^{\ominus}_{m,f}[\text{Cl}^-(aq)] + \Delta H^{\ominus}_{m,f}[\text{Zn (Leu)Cl}_2(s)] \quad (6)$$

where $\Delta H^{\ominus}_{m,f}$[*L*-α-Leu (s)] = (−649.93 ± 1.95) kJ/mol,[25] $\Delta H^{\ominus}_{m,f}[ZnCl_2(s)]$ = −415.05 kJ/mol,[26] $\Delta H^{\ominus}_{m,f}[Cl^-(aq)]$ = (−167.080 ± 0.088) kJ/mol.[27] Therefore, the calculated results are $\Delta H^{\ominus}_{m,f}$[*L*-α-Leu (aq)] = (−644.81 ± 1.95) kJ/mol, $\Delta H^{\ominus}_{m,f}[Zn(Leu)Cl_2(s)]$ = (−1087.266 ± 1.960) kJ/mol. $\Delta H^{\ominus}_{m,f}[Zn(Leu)^{2+}(aq)]$ = (−1447.944 ± 1.977) kJ/mol.

The typical thermokinetic (TK) curve of the solid-liquid formation reaction of $ZnCl_2$ with *L*-α-Leu is shown in Fig. 3. The original data obtained from the TK curve are shown in

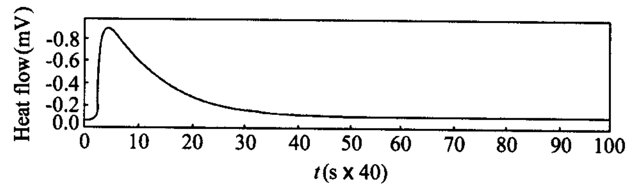

Fig. 3 Thermokinetic curve of the reaction (298.15 K).

Table 4 Experimental data of the $\Delta H^{\ominus}_{s,(1)}$, $\Delta H^{\ominus}_{s,(2)}$ and $\Delta H^{\ominus}_{r,(2)}$ at 298.15 K

No.	Solute (mg)	Solvent (mL)	r [n(solvent)/n(solute)]	Q (mJ)	$\Delta H^{\ominus}$ (kJ/mol)
1	Leu, 5.250	H_2O, 8.00	11096	205.587	5.137
2	Leu, 5.250	H_2O, 8.00	11096	205.685	5.139
3	Leu, 5.190	H_2O, 8.00	11233	202.553	5.119
4	Leu, 5.300	H_2O, 8.00	10991	206.496	5.110
5	Leu, 5.310	H_2O, 8.00	10979	208.404	5.148
6	Leu, 5.290	H_2O, 8.00	11021	204.831	5.079
mean					$\Delta H^{\ominus}_{s,(1)}$ = 5.122 ± 0.010
1	$Zn(Leu)Cl_2$, 10.650	H_2O, 8.00	11152	−1067.280	−26.804
2	$Zn(Leu)Cl_2$, 10.650	H_2O, 8.00	11080	−1054.662	−26.315
3	$Zn(Leu)Cl_2$, 10.650	H_2O, 8.00	10998	−1100.878	−27.264
4	$Zn(Leu)Cl_2$, 10.650	H_2O, 8.00	11049	−1060.554	−26.388
5	$Zn(Leu)Cl_2$, 10.650	H_2O, 8.00	11121	−1036.832	−25.967
6	$Zn(Leu)Cl_2$, 10.650	H_2O, 8.00	11398	−1027.354	−26.371
mean					$\Delta H^{\ominus}_{s,(2)}$ = −26.518 ± 0.185
1	$ZnCl_2$, 5.290	Liquor of Leu, 8.00	11438	−2103.490	−54.197
2	$ZnCl_2$, 5.320	Liquor of Leu, 8.00	11373	−2099.190	−53.781
3	$ZnCl_2$, 5.400	Liquor of Leu, 8.00	11204	−2144.255	−54.122
4	$ZnCl_2$, 5.350	Liquor of Leu, 8.00	11329	−2123.451	−54.097
5	$ZnCl_2$, 5.340	Liquor of Leu, 8.00	11329	−2100.324	−53.608
6	$ZnCl_2$, 5.320	Liquor of Leu, 8.00	11373	−2097.89	−53.748
mean					$\Delta H^{\ominus}_{r,(2)}$ = −53.926 ± 0.099

Table 5. On the basis of these experimental data and calculated results, the thermodynamic parameters, the rate constant and the kinetic parameters of the reaction were obtained (Table 6) through Eq. (7)—Eq. (10):[28]

$$\ln\left[\frac{1}{H_0}\frac{dH_t}{d_t}\right] = \ln k + n\ln\left[1-\frac{H_t}{H_0}\right] \quad (7)$$

$$\ln k = \ln A - \left[\frac{E}{RT}\right] \quad (8)$$

$$\Delta G_{\neq}^{\ominus} = RT\ln\left[\frac{RT}{Nhk}\right] \quad (9)$$

$$\ln\left[\frac{k}{T}\right] = \frac{\Delta H_{\neq}^{\ominus}}{RT} + \frac{\Delta S_{\neq}^{\ominus}}{R} + \ln\left[\frac{k_B}{h}\right] \quad (10)$$

where H_0 is the total reaction enthalpy (corresponding to the global area under the TK curve), H_t the reaction heat in a certain time (corresponding to the partial area under the curve), dH_t/dt the exothermic rate at time t, k the rate constant of reaction, n the reaction order, A the per-exponential constant, E the apparent activation energy, R the gas constant, T the absolute temperature, $\Delta G_{\neq}^{\ominus}$ the activation free-energy, N Avogadro number, h Plank's constant, $\Delta H_{\neq}^{\ominus}$ the activation enthalpy, $\Delta S_{\neq}^{\ominus}$ the activation entropy, and k_B Boltzamann's constant.

The results in Table 6 clearly indicate that the higher the temperature of the reaction, the faster the reaction and the reaction is of the first order. The values of E and $\Delta H_{\neq}^{\ominus}$ were very low, but $\Delta S_{\neq}^{\ominus}$ was high. These facts show that the reaction took place easily in the temperature range of 298.15—323.15 K. This result corresponds with greater value of $\Delta H_{m,f}^{\ominus}[Zn(Leu)^{2+}(aq)]$.

The final solution collected after each experiment was concentrated in a 343.15—353.15 K water bath till crystal membrane was formed, and was put into desiccator with

Table 5 Thermokinetic data of the reaction[a]

t (s)	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	H_t/H_0	$(dH/dt)\times 10^4$ (J·s^{-1})	H_t/H_0	$(dH/dt)\times 10^4$ (J·s^{-1})	H_t/H_0	$dH/dt\times 10^4$ (J·s^{-1})	H_t/H_0	$(dH/dt)\times 10^4$ (J·s^{-1})	H_t/H_0	$(dH/dt)\times 10^4$ (J·s^{-1})	H_t/H_0	$(dH/dt)\times 10^4$ (J·s^{-1})
50		38.63	0.0881	45.11	0.0601	49.64	0.1255	53.19	0.1121	56.73	0.1179	62.19
100	0.1079	34.92	0.2111	40.41	0.1554	46.76	0.2811	46.95	0.2473	49.64	0.2537	52.08
150	0.2452	28.26	0.3195	36.13	0.2421	43.46	0.4106	38.78	0.3630	42.20	0.3678	42.37
200	0.3622	24.09	0.4146	31.22	0.3186	36.19	0.5189	32.07	0.4615	32.82	0.4629	35.56
250	0.4619	20.62	0.4982	26.92	0.3864	31.78	0.6097	26.39	0.5461	28.84	0.5429	31.73
300	0.5473	17.65	0.5717	23.14	0.4468	29.37	0.6856	21.49	0.6189	23.95	0.6116	26.91
350	0.6207	15.07	0.6361	19.73	0.5011	25.75	0.7488	17.29	0.6819	17.97	0.6710	22.63
400	0.6836	12.76	0.6925	16.75	0.5501	23.92	0.8013	13.73	0.7361	15.30	0.7226	19.88
450	0.7375	8.99	0.7417	14.08	0.5942	20.78	0.8446	10.62	0.7837	11.43	0.7672	17.03
500	0.8219	7.51	0.7844	12.41	0.6342	17.82	0.8801	7.92	0.8218	9.35		
600	0.8824	5.09	0.8530	8.31	0.7073	14.80			0.8828	5.94		
650	0.9055	4.12	0.8804	7.05					0.9062	4.85		
700	0.9249	3.31										
750	0.9410								0.9416	2.81		

[a] H_0 = 3.211, 3.520, 3.590, 3.619, 3.836 and 4.066 J.

Table 6 Values of n, k, A, E, $\Delta G_{\neq}^{\ominus}$, $\Delta H_{\neq}^{\ominus}$ and $\Delta S_{\neq}^{\ominus}$ of the reaction

T (K)	Eq. (7)			Eq. (8)			Eq. (9)	Eq. (10)		
	$k\times 10^3$ (s^{-1})	n	r[a]	E (kJ/mol)	ln A	r[a]	$\Delta G_{\neq}^{\ominus}$ (kJ/mol)	$\Delta H_{\neq}^{\ominus}$ (kJ/mol)	$\Delta S_{\neq}^{\ominus}$ [kJ/(mol·K)]	r[a]
298.15	2.005	0.921	0.999	31.18	6.37	0.999	88.42	28.60	−200.6	0.999
303.15	2.490	0.931	0.999				89.40			
308.15	3.036	1.091	0.995				90.41			
313.15	3.734	0.943	0.997				91.38			
318.15	4.448	1.027	0.999				92.42			
323.15	5.297	0.967	0.996				93.44			

[a] The correlation coefficient.

P_4O_{10} to remove trace water. The analytical results show that they have the same composition of $Zn(Leu)Cl_2$.

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