Linear Thermodynamic Relationships for the Ternary System Copper(II)–5-substituted 1,10-phenanthroline-α-Amino Acid

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The heats of formation of the ternary complexes copper(II)–5-substituted 1,10-phenanthroline–α-amino acid and the heats of protonation of the ligands have been determined in aqueous solution at 25.0 ± 0.1 °C and ionic strength 0.1 mol dm^{-3} (KNO_3) by means of a calorimetric method. A number of linear thermodynamic relationships have been found to exist between the energy changes upon formation of the ternary complexes and thus upon protonation of the ligands.

When the senior author reported the formulation of equations to manifest the principle of linear free-energy relationships (l.f.e.r.s) in co-ordination chemistry[1] the existence of linear enthalpy relationships (l.e.r.s) was also predicted, on theoretical grounds, between the heat of formation of a complex compound and the heat of dissociation (or protonation) of a ligand. The validity of the latter linear relationships has been verified experimentally by a calorimetric method in our laboratory during the past decade.[2–5] In the meantime we have discovered the existence of linear entropy relationships. Therefore, it is proposed to group these three linear relationships together, namely linear free energy, linear enthalpy, and linear entropy, and to call them linear thermodynamic function relationships (l.t.f.r.s).[6]

In the study of some organic reactions, Leffler[7] and Brown[8] have discussed the linear enthalpy–entropy effect. This linearity is very common, both in relation to equilibria and to enthalpies and entropies of activation.[9] The general linear enthalpy–entropy effect has been called the compensation law and all of the l.f.e.r.s such as the Hammett equation and Brönsted catalysis equations are seen to arise as special cases within the compensation law.[8] However, Peterson[10] demonstrated that the related linear enthalpy–entropy plot can also be extremely deceptive and that it is not by itself a demonstration of any significant effect. It is therefore argued that the linear enthalpy–entropy effect is an empirical relation which does not really merit description as a law.[11]

The purpose of our work is to explore the generality of the enthalpy–entropy effect in solution chemistry, especially in the formation of complex compounds in co-ordination chemistry.

Experimental

Materials.—Copper(II) nitrate was an analytical reagent and recrystallized. 1,10-Phenanthroline(phen, A.R.) and 5-nitro-1,10-phenanthroline(nphen, A.R.) were obtained from Beijing chemical plant. 5-Chloro-1,10-phenanthroline(cphen) and 5-methyl-1,10-phenanthroline(mphen) were obtained from G. Frederick Smith Chemical Co. All the α-amino acids (2-methylalanine, isoleucine, valine, and serine; biochemical reagents) were obtained from Shanghai Chemical Reagent Station.

The concentration of copper(II) in the stock solution was analysed by a conventional method. All the copper(II) binary complexes with substituted phenanthrolines were prepared in warm redistilled water. The concentration of free acid in the copper(II) solution was determined with a standard base solution by pH measurement. The ionic strength was adjusted to 0.10 mol dm^{-3} with KNO_3.

Calorimetric Measurements.—A Calvet model MS 80 standard heat-conduction microcalorimeter was employed to measure the heat effects of reactions (1) and (2). Where A

$$MA + B \rightleftharpoons MA(B)\ \Delta H_{MA(B)},\quad K_{MA(B)} = [MA(B)]/[MA][B] \qquad (1)$$

$$H + A \rightleftharpoons HA\ \Delta H_{HA} \qquad (2)$$

denotes the first ligand 5R-phen, B denotes the second ligand α-amino acid and M denotes copper(II). The mixing device of the microcalorimeter was improved with an automatic mixing half-hollow inner tube. The instrumental constant K was determined to be $(6.70 \pm 0.06) \times 10^{-4}$ J unit^{-1} ($n = 19$) by electrical power calibration and was again checked by chemical calibration with a standard acid and base neutralization reaction [KOH(aq) + $HClO_4$(aq)]. The temperature of measurement was controlled to 24.9 ± 0.1 °C. The number of parallel experiments run (n) is indicated in Table 1. The data collected are average values.

Determination of Stability Constants.—A Beckman pH-meter model Φ 71 equipped with type 39501 combination electrodes was used to determine the dissociation constants of the ligands and the stability constants of the ternary complexes.[12] The results are expressed in terms of ΔG values and shown in Table 2.

Treatment of Data.—In the system investigated the first ligand Rphen forms very stable complexes with metal ions under the conditions studied and hence the ternary system may be considered essentially as a binary system with M^{II}(Rphen) as a hydrated metal ion. Equations (3)—(6) (a_H = activity of H^+)

$$H_2B \rightleftharpoons H + HB \qquad K_1 = a_H[B]/[H_2B] \qquad (3)$$

$$HB \rightleftharpoons H + B \qquad K_2 = a_H[B]/[HB] \qquad (4)$$

$$c_B = [B] + [HB] + [H_2B] + [MA(B)] \qquad (5)$$

$$c_M = c_A = [MA] + [MA(B)] \qquad (6)$$

may be established for the system investigated at constant temperature and fixed ionic strength. For the sake of simplicity, charges are omitted. Let $m = 1 + (a_H/K_2) + (a_H^2/K_1K_2)$. Equation (7) may be derived from (1) and (3)—(6).

Table 1. Formation enthalpies of the ternary complexes and protonation enthalpies of ligands A and B

			10^3c_M	10^3c_B				ΔH^A	$\Delta H_1^{B a}$	$\Delta H_2^{B a}$	$\Delta H_{MA(B)}$
MA	*n*	B	mol dm^{-3}		pH_1	pH_f	*Q*/*J*	kJ mol^{-1}			
Cu(nphen)	6	Mal	2.060	1.301	6.599	4.408	0.012 60 ± 0.000 87	−8.4 [b]	−51.9 ± 0.1	−1.5 ± 0.1	−31.5 ± 1.7
	6	Ile	2.060	1.300	6.559	4.247	0.012 26 ± 0.000 80	−8.4	−48.5 ± 0.1	−0.9 ± 0.1	−31.7 ± 1.3
	5	Val	2.060	1.299	6.497	4.242	0.010 85 ± 0.000 27	−8.4	−47.3 ± 0.1	0.35 ± 0.11	−32.0 ± 0.5
	6	Ser	2.060	1.300	6.476	4.114	0.011 39 ± 0.000 80	−8.4	−45.5 ± 0.1	−3.99 ± 0.06	−32.3 ± 1.0
Cu(cphen)	6	Mal	2.060	1.301	6.599	4.437	0.013 40 ± 0.000 47	−11.6	−51.9 ± 0.1	−1.5 ± 0.1	−30.2 ± 0.9
	5	Ile	2.060	1.300	6.559	4.247	0.012 40 ± 0.000 34	−11.6	−48.5 ± 0.1	−0.9 ± 0.1	−30.6 ± 0.6
	6	Val	2.060	1.299	6.497	4.254	0.011 32 ± 0.000 60	−11.6	−47.3 ± 0.1	0.35 ± 0.11	−30.8 ± 1.0
	8	Ser	2.060	1.300	6.476	4.127	0.012 06 ± 0.000 27	−11.6	−45.5 ± 0.1	−3.99 ± 0.06	−31.2 ± 0.4
Cu(phen)	6	Mal	2.060	1.301	6.599	4.459	0.013 40 ± 0.000 54	−15.1 [b]	−51.9 ± 0.1	−1.5 ± 0.1	−28.2 ± 1.2
	8	Ile	2.060	1.300	6.559	4.290	0.013 07 ± 0.000 34	−15.1	−48.5 ± 0.1	−0.9 ± 0.1	−28.7 ± 0.7
	6	Val	2.060	1.299	6.497	4.280	0.011 59 ± 0.000 34	−15.1	−47.3 ± 0.1	0.35 ± 0.11	−29.0 ± 0.7
	6	Ser	2.060	1.300	6.476	4.145	0.012 06 ± 0.000 94	−15.1	−45.5 ± 0.1	−3.99 ± 0.06	−29.6 ± 1.6
Cu(mphen)	6	Mal	2.060	1.301	6.599	4.471	0.013 40 ± 0.000 47	−16.7 [b]	−51.9 ± 0.1	−1.5 ± 0.1	−27.4 ± 1.2
	6	Ile	2.060	1.300	6.559	4.303	0.013 07 ± 0.000 54	−16.7	−48.5 ± 0.1	−0.9 ± 0.1	−28.1 ± 1.2
	8	Val	2.060	1.299	6.497	4.293	0.011 66 ± 0.000 34	−16.7	−47.3 ± 0.1	0.35 ± 0.11	−28.4 ± 0.8
	8	Ser	2.060	1.300	6.476	4.157	0.012 60 ± 0.000 87	−16.7	−45.5 ± 0.1	−3.99 ± 0.66	−28.9 ± 1.5

[a] Ref. 12. [b] Ref. 13.

Table 2. Apparent standard formation free energies and apparent formation entropies of the ternary complexes and the protonated species of the first ligands [14]

		R			
		NO_2	Cl	H	CH_3
ΔG_{HA}*/kJ mol^{-1}		−18.4	−23.2	−28.1	−30.1
$\Delta G_{CuA(B)}$/ kJ mol^{-1}	2-Methylalanine	−45.5	−45.3	−44.9	−44.8
	Isoleucine	−44.2	−44.1	−43.7	−43.5
	Valine	−44.0	−43.8	−43.4	−43.2
	Serine	−42.6	−42.5	−42.1	−41.9
ΔS_{HA}/J K^{-1} mol^{-1}		33.5	39.0	43.7	44.9
$\Delta S_{CuA(B)}$/ J K^{-1} mol^{-1}	2-Methylalanine	47.0	50.7	56.1	58.2
	Isoleucine	42.1	45.2	50.2	51.7
	Valine	40.1	43.6	48.3	49.7
	Serine	34.7	37.8	41.9	43.6

* Values taken from ref. 13.

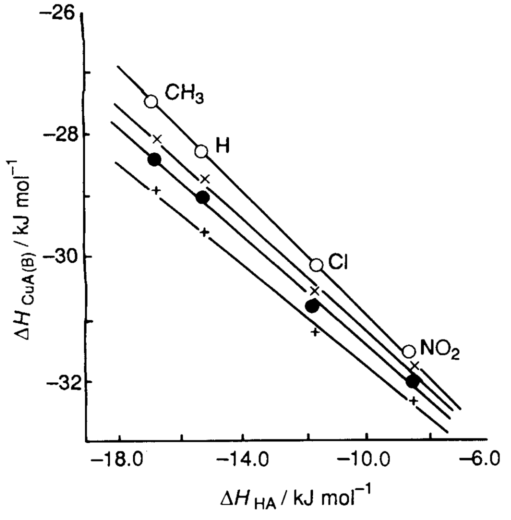

Figure 1. Linear enthalpy relationships for the system copper(II)–Rphen-α-amino acid. Amino acids: ○, 2-methylalanine; ×, isoleucine; ●, valine; and +, serine

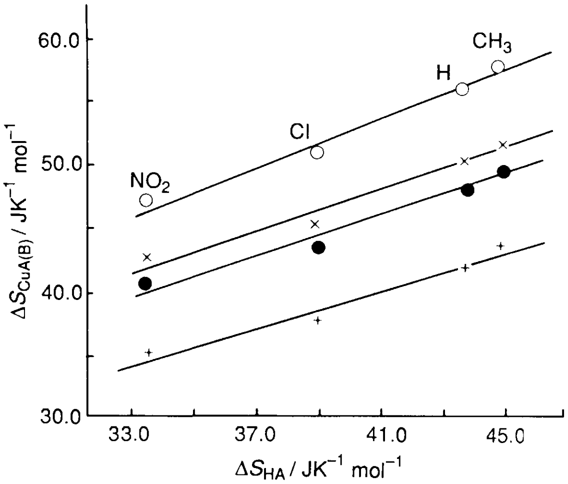

Figure 2. Linear entropy relationships for the system copper(II)-Rphen-α-amino acid. Symbols as in Figure 1

$$K_{MA(B)}[MA]^2 + (m + K_{MA(B)}c_B - K_{MA(B)}c_M)[MA] - mc_M = 0 \quad (7)$$

The value of [MA] can be obtained by solving equation (7), since the equilibrium constants expressed by equation (1)—(4) are determined experimentally, while c_M and c_B are known from experimental data. Therefore, the molar concentrations of all species in equilibria before and after the determination can be calculated.

For energy balance, the thermochemical equation (8) can be established: where Q_c denotes the corrected heat quantity, Q_m

$$Q_c = Q_m - Q_b = R + \{([HB]_f + [H_2B]_f)V_f - ([HB]_i + [H_2B]_i)V_i\}\Delta H_1^B + ([H_2B]_fV_f - [H_2B]_iV_i)\Delta H_2^B + [MA(B)]_fV_f\Delta H_{MA(B)} \quad (8)$$

the average value of the measured heat effects of the reaction under investigation, Q_b the average heat of the blank tests, *R* the heat produced by the association of H^+ and OH^- to form H_2O, $\Delta H_1^B(\Delta H_2^B)$ the heats of the first(second) protonation of ligand B, $\Delta H_{MA(B)}$ the heat of formation of the ternary complex; $[\ ]_f$

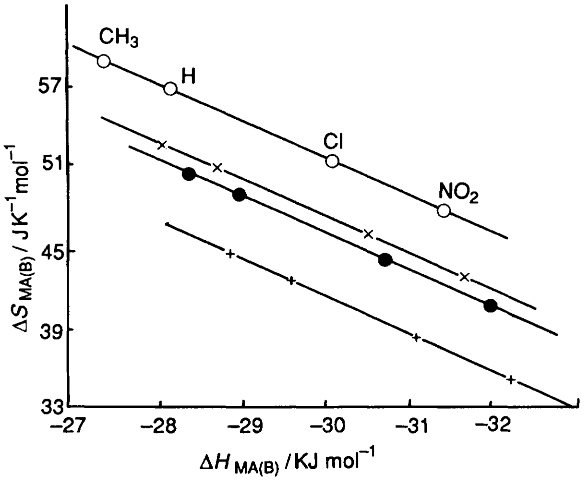

Figure 3. Plot of $\Delta S_{MA(B)}$ *vs.* $\Delta H_{MA(B)}$ for the system copper(II)–Rphen-α-amino acid. Symbols as in Figure 1

and [ ]$_i$ the molar concentrations (mol dm^{-3}) of the indicated species after and before the reaction, respectively, V_f and V_i represent the total volume of the final mixed solution and the volume of the initial solution, respectively. Since the heats of protonation of ligand B are known,[12] the heat of formation of the ternary mixed-ligand complex can be calculated readily from a set of calorimetric measurements by means of equation (8).

Results and Discussion

All the results of the calorimetric experiments are listed in Table 1. The apparent Gibbs energy of formation was obtained from the equilibrium constant of reaction (1)[13,14] and corresponding apparent formation entropy was calculated from enthalpy and Gibbs energy terms. These values are shown in Table 2. Plotting the data in Tables 1 and 2, both linear enthalpy relationships and linear entropy relationships are found to exist between the apparent standard formation thermodynamic functions of the ternary complex compounds and the apparent standard protonation thermodynamic functions of the first ligands (see Figures 1 and 2). In the systems investigated the electronic effect due to substituent groups at the 5 position on the phen molecule is not pronounced enough to separate the thermodynamic parameters appreciably. Taking into consideration the experimental standard deviation of $\Delta H_{MA(B)}$, the linearity in Figure 1 would be demurred to some extent. Nevertheless, the data point to interesting linear relationships between enthalpy and entropy parameters (Figure 3).

Acknowledgements

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