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Linear enthalpy relationships between heats of formation of complex compounds and heats of protonation of ligands. Copper(II)–*N*-(*para*-substituted phenyl)iminodiacetic acid–α-amino acids ternary system and copper(II)–*N*-(*para*-substituted phenyl)iminoacetic acids binary system

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Abstract

The heats of protonation of *N*-(*para*-substituted phenyl)iminodiacetic acids (A, *p*-RPhIDA: R = CH_3O, CH_3, H, Cl) and the heats of formation of Cu(II)–*p*-RPhIDA binary complex compounds and of Cu(II)–*p*-RPhIDA–α-amino acids (B, AA: L-proline, L-isoleucine, L-valine, L-serine, glycine and α-aminoisobutyric acid) competitive ternary complex compounds have been determined at 25.0 ± 0.2 °C, and $I = 0.1$ mol dm^{-3} (KNO_3) by means of a model RD-1 automatic conduction calorimeter. In the meantime the entropy of protonation of the ligand A and the entropy of formation of the binary complex compounds Cu(II)–*p*-RPhIDA–AA have been calculated. The results showed the existence of linear enthalpy relationships between the heats of formation of these ternary complex compounds and the binary complex compounds and the heats of protonation of the ligands *p*-RPhIDA and the existence of linear entropy relationships between the entropy of formation of binary complex compounds, Cu(II)–*p*-RPhIDA and the entropy of protonation of ligands, *p*-RPhIDA.

Introduction

We have previously reported the linear enthalpy relationships of *N*-(*meta*-substituted phenyl)iminodiacetic acids ternary systems [1] and Cu(II), Ni(II), Zn(II)–α,α′-bipyridyl/phenanthroline-*N*-(*p*- or *m*-substituted phenyl)glycines ternary systems [2–7]. However, in these cases the first ligand (bipy/phen) forms very stable complexes with the metal ions under the conditions studied and hence the ternary system may be considered essentially as a binary system with M(II)–bipy (or phen) as an hydrated metal ion. But for a competitive ternary system it is something else. In order to explore this particular type of linear enthalpy relationship in competitive ternary systems, we have investigated the Cu(II)–*N*-(*para*-substituted phenyl)iminodiacetic acid (A, *p*-RPhIDA: R = CH_3O, CH_3, H, Cl)–α-amino acid (B, AA: L-proline, L-isoleucine, L-valine, L-serine, glycine, α-aminoisobutyric acid) ternary competitive systems. These studies would extend the investigation of linear enthalpy relationships to a wide variety of chemical systems and would provide some useful information about certain coordination-related heat effects in life processes.

Theoretical

We have previously reported the calculation method of calorimetric determination of the heats of formation of Cu(II)–*N*-acetylglycine–α-amino acids competitive ternary complex compounds [8]. A similar calculation method has been used in this paper but with some improvement in the treatment of the experimental data. The following eight independent equilibria have to be considered in the present system at constant temperature and ionic strength. In this treatment all charges are omitted for the sake of convenience.

$$H_2A \rightleftharpoons H + HA \qquad (1)$$
$$K_1^A = [H][HA]/[H_2A]$$

$$HA \rightleftharpoons H + A \qquad (2)$$
$$K_2^A = [H][A]/[HA]$$

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$$\begin{aligned}&H_2B \rightleftharpoons H + HB\\&K_1^B = [H][HB]/[H_2B]\end{aligned} \qquad (3)$$

$$\begin{aligned}&HB \rightleftharpoons H + B\\&K_2^B = [H][B]/[HB]\end{aligned} \qquad (4)$$

$$\begin{aligned}&M + A \rightleftharpoons MA\\&\beta_{10} = [MA]/[M][A]\end{aligned} \qquad (5)$$

$$\begin{aligned}&M + B \rightleftharpoons MB\\&\beta_{01} = [MB]/[M][B]\end{aligned} \qquad (6)$$

$$\begin{aligned}&M + 2B \rightleftharpoons MB_2\\&\beta_{02} = [MB_2]/[M][B]^2\end{aligned} \qquad (7)$$

$$\begin{aligned}&M + A + B \rightleftharpoons MAB\\&\beta_{11} = [MAB]/[M][A][B]\end{aligned} \qquad (8)$$

where, K_1^A, K_2^A, K_1^B, K_2^B denote the first and second dissociation constants of ligand A and B, respectively; β_{ij} denotes the consecutive formation constants of copper(II) with ligand A and B ($i = 0, 1$; $j = 0, 1, 2$). According to mass balance, we have

$$T_A = [A] + [HA] + [H_2A] + [MA] + [MAB] \qquad (9)$$

$$\begin{aligned}T_B = {} & [B] + [HB] + [H_2B] + [MB]\\ & + 2[MB_2] + [MAB]\end{aligned} \qquad (10)$$

$$T_M = [M] + [MA] + [MB] + [MB_2] + [MAB] \qquad (11)$$

where, T_A, T_B and T_M are the total concentration of A, B and M, respectively. Let

$$n_A = 1 + [H]/K_2^A + [H]^2/K_1^A K_2^A \qquad (12)$$

$$\begin{aligned}&n_B = 1 + a_H/K_2^B + a_H{}^2/K_1^B K_2^B\\ &\qquad (a_H = \text{activity of } H^+)\end{aligned} \qquad (13)$$

Then the following three expressions for [M] can be obtained

$$[M] = (T_A - n_A[A])/(\beta_{10}[A] + \beta_{11}[A][B]) \qquad (14)$$

$$\begin{aligned}[M] = {} & (T_B - n_B[B])/(\beta_{01}[B] + 2\beta_{02}[B]^2\\ & + \beta_{11}[A][B])\end{aligned} \qquad (15)$$

$$\begin{aligned}[M] = {} & T_M/(1 + \beta_{10}[A] + \beta_{01}[B] + \beta_{02}[B]^2\\ & + \beta_{11}[A][B])\end{aligned} \qquad (16)$$

From eqns. (14) and (15), we obtain eqn. (17)

$$u[B]^2 + v[B] + w = 0 \qquad (17)$$

where

$$u = 2\beta_{02}(T_A - n_A[A]) + n_B\beta_{11}[A] \qquad (17a)$$

$$\begin{aligned}v = {} & -\beta_{11}n_A[A]^2 + [(T_A - T_B)\beta_{11}\\ & + n_B\beta_{10} - n_A\beta_{01}][A] + T_A\beta_{01}\end{aligned} \qquad (17b)$$

$$w = -T_B\beta_{10}[A] \qquad (17c)$$

Furthermore, if a and b denote the denominator of eqns. (14) and (16), respectively, then we obtain eqn. (18)

$$aT_M - b(T_A - n_A[A]) = 0 \qquad (18)$$

If an initial value of [A] is assumed, we can obtain a set of u, v and w values by using eqns. (17a)–(17c) and a reasonable value of [B] may be obtained by solving for eqn. (17). From the assumed [A] value and the calculated [B] value, a and b values can be calculated readily. If a and b values do not fit eqn. (18) well, a new [A] value may be assumed, the computation being repeated again and again until the absolute value of the left-hand side of eqn. (18) reaches a minimum (close to zero). In this way the concentration of the free ligands A, B and all other species in the equilibrium system can be evaluated. The concentration of the species existing in the initial solution may be obtained from the following equations

$$T_B = [B] + [HB] + [H_2B]$$

$$T_A = [A] + [HA] + [H_2A]$$

$$[B] = T_B/(1 + a_H/K_2^B + a_H{}^2/K_1^B K_2^B)$$

$$[A] = T_A/(1 + [H]/K_2^A + [H]^2/K_1^A K_2^A)$$

Then, for energy balance, the following thermochemical equation can be established

$$\begin{aligned}Q_c = Q_m - Q_b = R + {} & [([HA]_f + [H_2A]_f V_f\\ & - ([HA]_i + [H_2A]_i)V_i]\Delta H_1^A\\ & + ([H_2A]_f V_f - [H_2A]_i V_i)\Delta H_2^A\\ & + [([HB]_f + [H_2B]_f)V_f\\ & - ([HB]_i + [H_2B]_i)V_i]\Delta H_1^B\\ & + ([H_2B]_f V_f - [H_2B]_i V_i)\Delta H_2^B\\ & + [MA]_f V_f \Delta H_A^M\\ & + [MB]_f V_f \Delta H_{B1}^M [MB_2]_f V_f \Delta H_{B2}^M\\ & + [MAB]_f V_f \Delta H_{MAB}\end{aligned} \qquad (19)$$

where Q_c denotes the corrected heat quantity; Q_m denotes the average value of the measured heat effect of the reaction under investigation; Q_b denotes the average heat of the blank tests; R represents the heat produced by the association of H^+ and OH^- to form H_2O; $\Delta H_1^A(\Delta H_2^A)$ and $\Delta H_1^B(\Delta H_2^B)$ denote the heats of the first(second) step protonation of ligand A and B, respectively; ΔH_A^M denotes the heat of formation of ligand A with copper(II) ion; ΔH_{B1}^M and ΔH_{B2}^M denote the heats of formation of first and consecutive steps of ligand B with copper(II) ion, respectively; ΔH_{MAB} denotes the heat of formation of ternary complex compounds; the brackets $[\ \ ]_f$ and $[\ \ ]_i$ represent the molar concentration of the indicated species after and before the reaction taking place , respectively; V_f and V_i represent the total volume of final mixed solution and the volume of the initial solution, respectively. The heats of protonation of ligand B and the heats of formation of binary complex compounds of ligand B with copper(II) are known [8] and the heats of protonation of ligand A and the heats of formation of binary complex compounds of ligand A with copper(II) have been determined experimentally. The method of calculation is the same as that reported earlier [8]. Therefore, the heat of formation of the ternary mixed-ligand complex compounds can be calculated from a set of calorimetric measurements by means of eqn. (19).

Experimental

Copper nitrate (AR, from Tianjin Third Chemical Reagent Factory) was recrystallized from redistilled water. The concentration of Cu(II) in the stock solution was determined with standard EDTA titration. All the α-amino acids (biochemical reagents) were obtained from Beijing Chemical Reagent station. *N*-(*para*-substituted phenyl)iminodiacetic acids were synthesized by the method reported in the literature [10]. Potassium nitrate (AR, from Tianjin Third Chemical Reagent Factory) was recrystallized from redistilled water. The experimental procedure has been described previously [8]. A model RD-1 automatic conduction calorimeter (manufactured by Scientific Instrument Factory of Sichuan University) was used to measure the heat effects. The instrumental constant K was determined to be $(3.66 \pm 0.09) \times 10^{-3}$ J mm^{-2} ($n = 16$) by electrical power calibration and was again checked by the determination of the heat of neutralization at 25.0 ± 0.2 °C and $I = 0.01$ mol dm^{-3} for the reaction NaOH (aq.) + HCl (aq) giving a value -55.60 ± 0.25 kJ mol^{-1} (-13.29 ± 0.06 kcal mol^{-1}). After being corrected for the values given in the literature [11], a value of $\Delta H_N = -13.24$ kcal mol^{-1} was obtained which agrees very well with the literature value [12] within experimental error. The heat of neutralization was then determined for KOH (aq.) + HNO_3 (aq.) at 25.0 ± 0.2 °C and $I = 0.1$ mol dm^{-3} to be $\Delta H_N = -59.78 \pm 0.10$ kJ mol^{-3}. The pH values of the solutions were measured by a model pHS-2 pH meter (precision: 0.02 pH unit).

Two cm^3 of 0.05149 mol dm^{-1} $Cu(NO_3)_2$ solution (with 0.1 mol dm^{-3} KNO_3 in it) were put in the sample tube and 20.00 cm^3 of *p*-RPhIDA (0.01788 mol dm^{-3}) and AA (0.01038 mol dm^{-3}) solution (with 0.1 mol dm^{-3} KNO_3 in it and 95% of the H^+ neutralized with standard KOH solution) were put in the reaction chamber. Then heats of dilution for the solution in the sample tube were corrected by blank tests. The heats of dilution of the solution in the reaction chamber were neglected, since there were only slight changes in the concentration.

Results and discussion

The data in Table 1 are the determined heats of protonation of *N*-(*para*-substituted phenyl)iminodiacetic acids. The results in Table 2 are the heats of formation of binary complex compounds Cu(II)–*p*-RPhIDA. The apparent thermodynamic functions of ligand *p*-RPhIDA and of binary complex compounds Cu(II)–*p*-RPhIDA are listed in Table 3. The experimental data of the heats of formation of Cu(II)–*p*-RPhIDA–AA ternary complex compounds are shown in Tables 4–9. The formation constants of Cu(II)–*p*-RPhIDA–AA ternary complex compounds are shown in Table 10. The acid dissociation constants and the heats of protonation of the α-amino acid ligands are shown in Table 11. The data in Tables 10 and 11 are used for calculating the formation heats of Cu(II)–*p*-RPhIDA–AA ternary complex compounds. Plotting the heats of formation of Cu(II)–*p*-RPhIDA binary complex compounds against the heats of protonation of the ligands *p*-RPhIDA shows very good linear enthalpy relationships (see Fig. 1) with the correlation equation

$$\Delta H_A^M = -0.0347 + 0.833 \Delta H_1^A \qquad r = 0.997$$

When the entropy of formation of Cu(II)–*p*-RPhIDA binary complex compounds was plotted against the entropy of protonation of the ligands *p*-RPhIDA, linear entropy relationships are obtained (see Fig. 2) which may be expressed by the following regression equation:

$$\Delta S_A^M = 631.3 - 3.94 \Delta S_1^A \qquad r = -0.982$$

Plotting the heats of formation of Cu(II)–*p*-RPhIDA–AA ternary complex compounds against the heats of protonation of the ligands *p*-RPhIDA shows very good linear enthalpy relationships (see Fig. 3) with correlation coefficient, *r*, close to unity.

TABLE 1. Determination of the heats of protonation of *p*-RPhIDA at 25.0±0.2 °C, $I=0.1$ mol dm^{-3} (KNO$_3$)

R	*n*	$T_A \times 10^2$ (mol dm^{-3})	$T_H \times 10^2$ (mol dm^{-3})	pH$_i$	pH$_f$	Q_c (J)	pK_1^A	pK_2^A [9]	ΔH_1^A (kJ mol^{-1})	ΔH_2^A (kJ mol^{-1})
CH$_3$O	4	1.824	1.916	6.78	3.94	0.337±0.04	3.25	5.62	1.49±0.12	−2.46±0.23
	4	0.9118	1.916	6.97	2.42	−0.161±0.02				
CH$_3$	7	1.368	1.916	10.45	2.98	0.520±0.02	2.64	5.28	4.09±0.10	−2.40±0.10
	6	1.824	1.916	10.50	3.95	1.04±0.02				
H	6	1.824	1.916	7.37	3.65	2.24±0.02	2.535	5.10	5.79±0.05	−0.34±0.10
	4	0.9118	1.916	7.29	2.43	1.11±0.03				
Cl	6	1.824	1.916	8.24	3.60	2.64±0.02	2.584	4.92	7.10±0.04	−2.63±0.09
	7	0.9118	1.916	7.62	2.44	1.08±0.02				

TABLE 2. Determination of the heats of formation of the binary complex compounds Cu(II)–*p*-RPhIDA at 25.0±0.2 °C, $I=0.1$ mol dm^{-3}) (KNO$_3$)

R	*n*	$T_A \times 10^2$	$T_M \times 10^{3}$[a]	pH$_i$	pH$_f$	*Q* (J)	log K_A^M [9]	ΔH_A^M (kJ mol^{-1})
CH$_3$O	6	4.559	4.680	9.35	6.63	1.36±0.02	7.41	13.91±0.20
CH$_3$	8	9.118	4.680	10.25	8.17	1.39±0.02	6.43	16.15±0.19
H	5	9.118	4.680	7.35	6.91	1.83±0.02	5.89	17.75±0.19
Cl	7	9.118	4.680	9.00	7.25	1.89±0.02	5.40	18.48±0.20

[a]The units are the same as in Table 1, also for the remaining Tables.

TABLE 3. The apparent thermodynamic functions of the ligand *p*-RPhIDA and of the binary complex compounds Cu(II)–*p*-RPhIDA at 25.0±0.2 °C, $I=0.1$ mol dm^{-3} (KNO$_3$)[a]

R	ΔG_1^A	ΔG_2^A	ΔH_1^A	ΔH_2^A	ΔS_1^A	ΔS_2^A	ΔG_A^M	ΔH_A^M	ΔS_A^M
CH$_3$O	−32.09	−18.56	1.49	−2.46	112.6	54.0	−42.31	13.91	188.5
CH$_3$	−30.15	−15.13	4.09	−2.40	114.8	42.7	−36.71	16.15	177.3
H	−29.12	−14.44	5.79	−0.34	117.1	47.3	−33.63	17.75	172.3
Cl	−28.09	−14.73	7.10	−2.63	118.0	40.6	−30.83	18.48	165.4

[a]The unit of $\Delta G(\Delta H)$ is kJ mol^{-1} and of ΔS is J mol^{-1} K^{-1}.

TABLE 4. Determination of the heats of formation of the Cu(II)–*p*-RPhIDA–proline ternary system at 25.0±0.2 °C, $I=0.1$ mol dm^{-3} (KNO$_3$)

R	*n*	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH$_i$	pH$_f$	*Q* (J)	ΔH_{MAB} (kJ mol^{-1})
CH$_3$O	7	1.419	9.453	4.680	11.03	9.41	−5.80±0.02	−15.51±1.29
CH$_3$	7	1.429	9.465	4.680	10.80	8.37	−4.37±0.02	−13.71±0.59
H	5	1.118	7.110	4.680	10.50	6.69	−1.35±0.02	−12.12±0.38
Cl	5	1.419	9.466	4.680	10.68	7.18	−3.50±0.02	−11.34±0.33

TABLE 5. Determination of the heats of formation of the Cu(II)–*p*-RPhIDA–α-aminoisobutyric acid ternary system at 25.0±0.2 °C, $I=0.1$ (KNO$_3$)

R	*n*	$T_A \times 10^2$	$T_B \times 10^3$	$T_M \times 10^3$	pH$_i$	pH$_f$	*Q* (J)	ΔH_{MAB} (kJ mol^{-1})
CH$_3$O	6	1.419	9.475	4.680	10.46	8.57	−3.37±0.02	−14.09±0.55
CH$_3$	6	1.493	9.463	4.680	10.50	8.54	−3.43±0.02	−11.47±0.58
H	6	1.491	9.500	4.680	10.36	7.67	−2.80±0.02	−10.37±0.38
Cl	4	1.483	9.452	4.680	10.40	7.48	−2.97±0.02	−9.14±0.35

TABLE 6. Determination of the heats of formation of the Cu(II)-*p*-RPhIDA–isoleucine ternary system at 25.0±0.2 °C, $I=0.1$ (KNO_3)

R	*n*	$T_A\times10^2$	$T_B\times10^3$	$T_M\times10^3$	pH_i	pH_f	*Q* (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3O	5	0.6938	9.603	4.680	9.90	7.40	−3.48±0.02	−15.95±0.51
CH_3	7	1.494	9.451	4.680	10.12	8.40	−3.95±0.02	−14.08±0.69
H	6	1.491	9.524	4.680	9.97	7.40	−3.40±0.02	−12.57±0.41
Cl	6	1.487	9.451	4.680	9.98	7.14	−3.36±0.02	−11.52±0.37

TABLE 7. Determination of the heats of formation of the Cu(II)-*p*-RPhIDA–valine ternary system at 25.0±0.2 °C, $I=0.1$ (KNO_3)

R	*n*	$T_A\times10^2$	$T_B\times10^3$	$T_M\times10^3$	pH_i	pH_f	*Q* (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3O	7	1.492	9.457	4.680	10.44	8.40	−5.04±0.02	−14.10±0.63
CH_3	6	1.494	9.463	4.680	10.05	8.12	−3.49±0.02	−12.22±0.57
H	6	1.490	9.452	4.680	9.92	7.35	−2.93±0.02	−10.51±0.40
Cl	6	1.493	9.491	4.680	9.89	7.00	−2.79±0.02	−9.60±0.35

TABLE 8. Determination of the heats of formation of the Cu(II)-*p*-RPhIDA–glycine ternary system at 25.0±0.2 °C, $I=0.1$ (KNO_3)

R	*n*	$T_A\times10^2$	$T_B\times10^3$	$T_M\times10^3$	pH_i	pH_f	*Q* (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3O	7	1.491	9.458	4.680	10.04	8.04	−3.91±0.02	−15.51±0.51
CH_3	7	1.493	9.469	4.680	10.13	7.99	−4.16±0.02	−13.49±0.52
H	7	1.491	9.482	4.680	9.93	7.31	−3.28±0.02	−11.98±0.40
Cl	6	1.493	9.465	4.680	9.95	6.94	−3.35±0.02	−11.09±0.34

TABLE 9. Determination of the heats of formation of the Cu(II)-*p*-RPhIDA–serine ternary system at 25.0±0.2 °C, $I=0.1$ (KNO_3)

R	*n*	$T_A\times10^2$	$T_B\times10^3$	$T_M\times10^3$	pH_i	pH_f	*Q* (J)	ΔH_{MAB} (kJ mol^{-1})
CH_3O	6	1.493	9.480	4.680	9.58	7.79	−3.73±0.02	−14.08±0.51
CH_3	4	1.492	9.445	4.680	9.66	7.76	−3.87±0.02	−12.23±0.54
H	6	1.491	9.468	4.680	9.45	7.06	−3.09±0.02	−10.77±0.41
Cl	5	1.494	9.438	4.680	9.51	6.81	−3.29±0.02	−9.69±0.38

Cu(II)-*p*-RPhIDA–isoleucine ternary system
$\Delta H_{MAB} = -17.2 + 0.794\Delta H_1^A$ $\quad r = 0.999$

Cu(II)-*p*-PRPhIDA–serine ternary system
$\Delta H_{MAB} = -15.3 + 0.785\Delta H_1^A$ $\quad r = 0.999$

Cu(II)-*p*-RPhIDA–proline ternary system
$\Delta H_{MAB} = -16.7 + 0.760\Delta H_1^A$ $\quad r = 0.998$

Cu(II)-*p*-RPhIDA–valine ternary system
$\Delta H_{MAB} = -15.4 + 0.817\Delta H_1^A$ $\quad r = 0.998$

Cu(II)-*p*-RPhIDA–α-aminoisobutyric acid ternary system
$\Delta H_{MAB} = -15.3 + 0.868\Delta H_1^A$ $\quad r = 0.997$

Cu(II)-*p*-RPhIDA–glycine ternary system
$\Delta H_{MAB} = -16.7 + 0.798\Delta H_1^A$ $\quad r = 0.999$

On plotting the heats of formation of Cu(II)-*p*-RPhIDA–AA ternary complex compounds against the heats of formation of Cu(II)-*p*-RPhIDA and Cu(II)–AA binary complex compounds, respectively (see Figs. 4 and 5), some good linear enthalpy relationships are also found to exist and the following regression equations with correlation coefficient, *r*, are obtained

TABLE 10. The formation constants log β_{11} [13] of Cu(II)-*p*-RPhIDA–AA ternary complex compounds at 25.0±0.2 °C, $I=0.1$ mol dm^{-3}

R	AA					
	Proline	α-Aminoiso-butyric acid	Isoleucine	Valine	Glycine	Serine
CH_3O	13.28	12.77	12.57	12.54	12.50	12.30
CH_3	13.07	12.62	12.41	12.34	12.33	12.11
H	12.79	12.34	12.10	12.07	12.03	11.82
Cl	12.65	12.22	11.95	11.92	11.89	11.67

TABLE 11. The dissociation constants [14] and the protonation heats [8] of some α-amino acids and the formation constants [14] and heats of formation of Cu(II)–AA binary complex compounds at 25.0±0.2 °C, $I=0.1$ mol dm^{-1}

AA	pK_1^B	pK_2^B	log β_{01}	log β_{02}	ΔH_1^B	ΔH_2^B	ΔH_{B1}^M (kJ mol^{-1})	ΔH_{B2}^M
Proline	1.77	10.39	8.80	16.30	−43.3±0.1	0.1±0.2	−27.9±0.3	−56.4±0.4
Aminoiso-butyric A	2.44	10.08	8.34	15.35	−51.9±0.1	−1.5±0.1	−25.8±0.3	−53.4±0.6
Isoleucine	2.30	9.60	8.16	15.02	−48.5±0.1	−0.9±0.1	−28.9±0.4	−57.6±0.6
Valine	2.34	9.57	8.15	14.97	−47.3±0.1	−0.35±0.1	−26.0±0.3	−53.3±0.6
Glycine	2.36	9.56	8.16	14.97	−47.7±0.2	−0.38±0.1	−28.0±0.4	−56.3±1.0
Serine	2.29	9.05	7.95	14.52	−45.5±0.1	−3.99±0.06	−26.1±0.2	−53.4±0.4

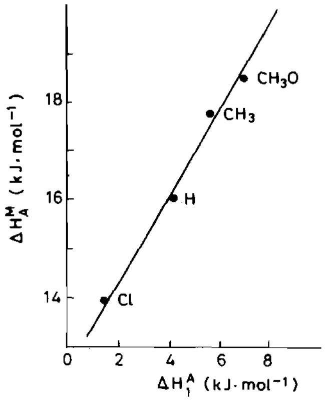

Fig. 1. Plot of the heats of formation of Cu(II)-*p*-RPhIDA binary systems, ΔH_A^M vs. the heats of protonation of the ligands, *p*-RPhIDA, ΔH_1^A.

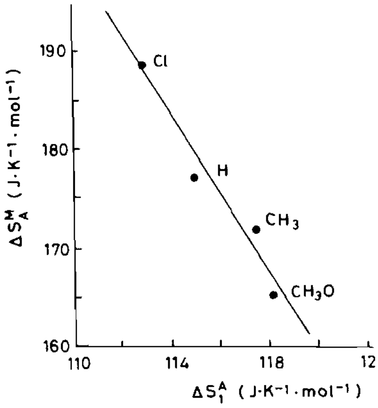

Fig. 2. Plot of the entropies of formation of Cu(II)-*p*-RPhIDA binary systems, ΔS_A^M vs. the entropies of protonation of the ligands, *p*-RPhIDA, ΔS_1^A.

Cu(II)-*p*-RPhIDA–isoleucine ternary system
$\Delta H_{MAB} = -29.2 + 0.947\Delta H_A^M$ $\quad r = 0.996$

Cu(II)-*p*-RPhIDA–serine ternary system
$\Delta H_{MAB} = -27.2 + 0.935\Delta H_A^M$ $\quad r = 0.995$

Cu(II)-*p*-RPhIDA–proline ternary system
$\Delta H_{MAB} = -28.3 + 0.910\Delta H_A^M$ $\quad r = 0.998$

Cu(II)-*p*-RPhIDA–valine ternary system
$\Delta H_{MAB} = -27.8 + 0.978\Delta H_A^M$ $\quad r = 0.997$

Cu(II)-*p*-RPhIDA–α-aminoisobutyric acid ternary system
$\Delta H_{MAB} = -28.4 + 1.03\Delta H_A^M$ $\quad r = 0.993$

Cu(II)-*p*-RPhIDA–glycine ternary system
$\Delta H_{MAB} = -28.8 + 0.955\Delta H_A^M$ $\quad r = 0.999$

Cu(II)-*p*-CH_3OPhIDA–AA ternary system
$\Delta H_{MAB} = 3.07 + 0.662\Delta H_{B1}^M$ $\quad r = 0.993$

Cu(II)-*p*-CH_3PhIDA–AA ternary system
$\Delta H_{MAB} = 7.92 + 0.767\Delta H_{B1}^M$ $\quad r = 0.972$

Cu(II)–RPhIDA–AA ternary system
$\Delta H_{MAB} = 8.04 + 0.716\Delta H_{B1}^M$ $\quad r = 0.993$

Cu(II)-*p*-ClPhIDA–AA ternary system
$\Delta H_{MAB} = 10.5 + 0.771\Delta H_{B1}^M$ $\quad r = 0.977$

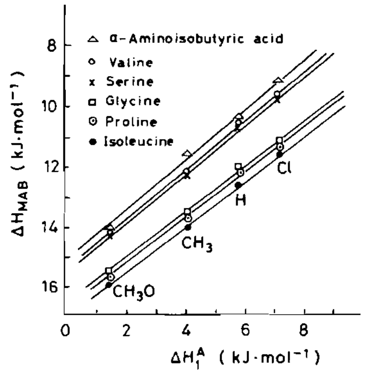

Fig. 3. Plot of the heats of formation of Cu(II)-*p*-RPhIDA-AA ternary systems, ΔH_{MAB} vs. the heats of protonation of the ligands, *p*-RPhIDA, ΔH_1^A.

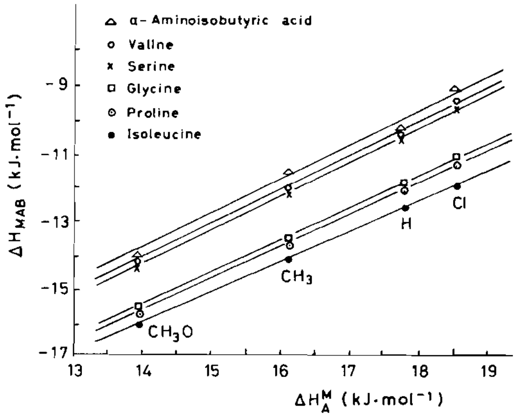

Fig. 4. Plot of the heats of formation of Cu(II)-*p*-RPhIDA-AA ternary systems, ΔH_{MAB} vs. the heats of formation of Cu(II)-*p*-RPhIDA binary systems, ΔH_A^M.

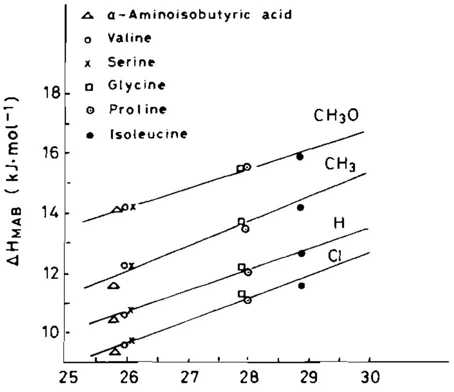

Fig. 5. Plot of the heats of formation of Cu(II)-*p*-RPhIDA-AA ternary systems, ΔH_{MAB} vs. the heats of formation of Cu(II)-AA binary systems, ΔH_{B1}^M.

From the data in Tables 4 to 9, it is interesting to note that, first of all, the heats of formation of Cu(II)-*p*-RPhIDA-AA ternary complex compounds, ΔH_{MAB}, like the heats of formation of Cu(II)-*N*-acetylglycine-AA ternary complex compounds [8], were nearly equal to the sum $(\Delta H_A^M + \Delta H_{B1}^M)$. This would mean that no π-backbonding formation and no interaction exist between ligands A and B in these ternary systems. Secondly, the magnitude of the heat of formation of Cu(II)-*p*-RPhIDA-AA ternary complex compounds is largely dependent upon the magnitude of the heats of formation of Cu(II)-AA and Cu(II)-*p*-RPhIDA binary complex compounds. However, from the data in Tables 1 to 6, it is also seen that no linear enthalpy relationships exist between the heats of formation of Cu(II)-*p*-RPhIDA-AA ternary complex compounds and the heats of protonation of the ligand B(AA). Since the heat of protonation of the ligand depends mainly upon its strength of basicity and the extent of solvation on solution, while the heat of formation of the complex compound depends not only upon the basicity of ligand and its degree of solvation but also depends upon the steric effect due to the ligands which might play a role in these systems and fail

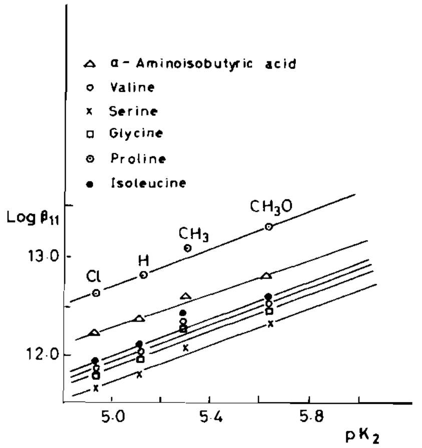

Fig. 6. Plot of the formation constants of Cu(II)-*p*-RPhIDA-AA ternary systems, log β_{11} vs. the dissociation constants of the ligands, *p*-RPhIDA, pK_2.

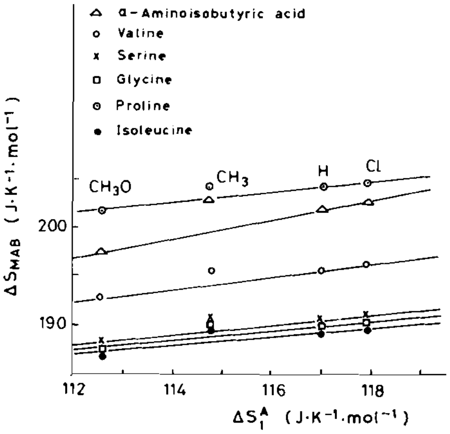

Fig. 7. Plot of the entropies of the formation of Cu(II)-*p*-RPhIDA-AA ternary systems, ΔS_{MAB} vs. the entropies of protonation of ligands, *p*-RPhIDA, ΔS_1^A.

TABLE 12. The entropy of the formation of Cu(II)-p-RPhIDA–AA ternary complex compounds, ΔS_{MAB}; 25.0±0.2 °C, $I=0.1$ mol dm^{-3} (KNO$_3$)

R	AA					
	Proline	α-Aminoiso-butyric acid	Isoleucine	Valine	Glycine	Serine
CH_3O	202.2	197.2	187.2	192.8	187.3	188.3
CH_3	204.3	203.2	190.4	195.3	190.8	190.8
H	204.2	201.5	189.5	195.8	190.2	190.2
Cl	204.2	203.3	190.2	196.0	190.5	190.9

to manifest linear enthalpy relationships, but manifest linear enthalpy relationships existing between the heats of formation of Cu(II)-p-RPhIDA–AA ternary complex compounds and the heats of protonation of ligand A(p-RPhIDA). Because ligands A have similar structures, their steric effect which might play a role in these systems is almost identical. When ligand B(AA) is unchanged, the variance of the heats of formation of Cu(II)-p-RPhIDA–AA ternary complex compounds depends mainly upon its strength of basicity of ligand A and the extent of solvation in solution. The entropies of formation of Cu(II)-p-RPhIDA–AA ternary complex compounds are calculated from the data in Tables 4 to 10. The results obtained are shown in Table 12. The plotting of the formation constants of Cu(II)-p-RPhIDA–AA ternary complex compounds, log β_{11} versus the dissociation constants of the ligands p-RPhIDA shows that the point of methyl substitution deviates from linearity [13] (see Fig. 6). The plotting of the entropies of formation of Cu(II)-p-RPhIDA–AA ternary complex compounds, ΔS_{MAB}, versus the entropies of protonation of ligands p-RPhIDA indicates that the point of methyl substitution also deviates from linearity (see Fig. 7); a similar phenomenon had been observed in LFER [15]. These results indicate that linear enthalpy relationships and linear entropy relationships seem to be more fundamental than LFER in coordination chemistry.

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