Thermochimica Acta, 169 (1990) 121–132
Elsevier Science Publishers B.V., Amsterdam

RECENT ADVANCES IN LINEAR THERMODYNAMIC FUNCTION RELATIONSHIPS *

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(Received 11 October 1989)

ABSTRACT

Linear thermodynamic function relationships (LTFR) comprise the following three subjects: (1) linear free energy relationships (LFER), (2) linear enthalpy relationships (LER), and (3) linear entropy relationships (LSR). LFER have been extensively studied in the past few decades and cover a wide range of areas in chemistry. We have recently explored the subject of LER and LSR and found explicitly the existence of these linear energy relationships. The present article is devoted to a review of the most recent advances of these three linear relationships studied in our laboratory and finds that the compensation law in solution chemistry can be extended to this area.

INTRODUCTION

Linear free energy relationships (LFER) have been widely recognized in chemistry and several monographs on this subject have appeared during the last decade [1–3]. However, the author is particularly interested in coordination chemistry and had formulated equations to correlate quantitatively the stability of complex compounds with the acidity or basicity of ligands [4]. In the meantime, the existence of linear enthalpy relationships (LER) between heats of formation of complex compounds and heats of dissociation or protonation of ligands was also predicted and verified experimentally [4,5]. Furthermore, linear entropy relationships (LSR) were found to exist in binary and ternary systems [5,6]. It was therefore proposed to group together these three linear relationships, namely LFER, LER and LSR, and to name them linear thermodynamic function relationships (LTFR).

Three years have elapsed since the author reviewed LTFR in coordination chemistry [7] and more work along this line has been carried out in our laboratory. The purpose of the present article is to summarize our work in the interim period.

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* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P.R. China, 25–28 August 1989.

0040-6031/90/$03.50

I. LFER between stability constants of complex compounds and the acidity or basicity of ligands

This subject has been extensively studied in our laboratory. The metal ions studied are of the first transition series and the ligands include heteronuclear aromatic bases such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen), α-aminoacids (αAA) *N*-substituted phenyliminodiacetic acids (RPhIDA), *N*-substituted ethylenediamines (Ren), *para*-substituted tetraphenylporphyrins (RTPP), etc. We delineate herewith the results on the systems most recently investigated in our laboratory.

A. Binary systems

1. M(II)–N – (meta-substituted phenyl)iminodiacetic acid systems [M(II)–mRPhIDA] [8] (M(II) = Cu, Ni, Co, Zn; R = CH_3, H, CH_3O, Cl). Correlation equations for these systems are shown below where K_{ML} denotes the stability constant of the complex compound, K_2 represents the acid dissociation constant of the ligand on the imino group, and r is the correlation coefficient.

For the Cu(II)–mRPhIDA system

$\log K_{\mathrm{CuL}} = 2.74\mathrm{p}K_2 - 8.22 \qquad r = 0.999$

For the Ni(II)–mRPhIDA system

$\log K_{\mathrm{NiL}} = 0.77\mathrm{p}K_2 - 0.447 \qquad r = 0.994$

For the Co(II)–mRPhIDA system

$\log K_{\mathrm{CoL}} = 1.44\mathrm{p}K_2 - 4.30 \qquad r = 0.998$

For the Zn(II)–mRPhIDA system

$\log K_{\mathrm{ZnL}} = 1.90\mathrm{p}K_2 - 6.16 \qquad r = 0.999$

2. M(II)–N-(para-substituted phenyl)iminodiacetic acid system [M(II)–pRPhIDA].

For the Cu(II)–pRhIDA system

$\log K_{\mathrm{CuL}} = 2.28\mathrm{p}K_2 - 8.80 \qquad r = 1.000$

For the Ni(II)–pRPhIDA system

$\log K_{\mathrm{NiL2}} = 2.69\mathrm{p}K_2 - 7.63 \qquad r = 1.000$

For the Co(II)–pRPhIDA system

$\log K_{\mathrm{CoL2}} = 2.24\mathrm{p}K_2 - 6.52 \qquad r = 1.000$

For the Zn(II)–pRPhIDA system

$\log K_{\mathrm{ZnL2}} = 1.17\mathrm{p}K_2 - 0.79 \qquad r = 0.997$

3. Cu(II)–N-(ortho-substituted phenyl)iminodiacetic acid system [Cu(II)–oRPhIDA]. It is interesting to note that LFER were also found to exist in this system, which implies that steric effects are insignificant.

$\log K_{\mathrm{CuL}} = 0.98\mathrm{p}K_2 + 0.90 \qquad r = 1.000$ (excluding $\mathrm{R} = \mathrm{CH_3}$)

B. Ternary systems

1. M(II)–bipyridyl / 1,10-phenanthroline-N-(meta-substituted phenyl)-iminodiacetic acid systems [M(II)-bipy/phen-mRPhIDA] [8]. In these systems, the metal ions and substituent groups are the same as those described in the Sect. (binary systems). For the sake of simplicity, first ligands (bipy or phen) and second ligands (mRPhIDA) are denoted by A and B, respectively. They are so expressed in all ternary systems throughout this article. The correlation equations obtained are listed as follows.

For the M(II)–phen–mRPhIDA systems

$\log K^{\mathrm{Cu\,A}}_{\mathrm{Cu\,A\,B}} = 1.769\mathrm{p}K_2 - 2.780 \qquad r = 0.999$ (excluding $\mathrm{R} = \mathrm{H}$)

$\log K^{\mathrm{Ni\,A}}_{\mathrm{Ni\,A\,B}} = 1.482\mathrm{p}K_2 - 3.786 \qquad r = 0.995$

$\log K^{\mathrm{Co\,A}}_{\mathrm{Co\,A\,B}} = 1.601\mathrm{p}K_2 - 4.106 \qquad r = 0.991$

$\log K^{\mathrm{Zn\,A}}_{\mathrm{Zn\,A\,B}} = 1.421\mathrm{p}K_2 - 2.895 \qquad r = 0.991$

For the M(II)–bipy–mRPhIDA systems

$\log K^{\mathrm{Cu\,A}}_{\mathrm{Cu\,A\,B}} = 0.936\mathrm{p}K_2 + 2.247 \qquad r = 1.000$ (excluding $\mathrm{R} = \mathrm{H}$)

$\log K^{\mathrm{Ni\,A}}_{\mathrm{Ni\,A\,B}} = 1.747\mathrm{p}K_2 - 5.205 \qquad r = 0.999$

$\log K^{\mathrm{Co\,A}}_{\mathrm{Co\,A\,B}} = 1.418\mathrm{p}K_2 - 3.384 \qquad r = 0.993$

$\log K^{\mathrm{Zn\,A}}_{\mathrm{Zn\,A\,B}} = 1.291\mathrm{p}K_2 - 2.548 \qquad r = 0.990$

According to Sigel [9] the stability of the ternary complex compounds may be related to $\Delta \log K_{\mathrm{M}}$ and $\log X$ parameters, where $\Delta \log K_{\mathrm{M}}$ is the difference in stability between ternary and the parent binary complexes and X is the equilibrium constant of the formation reaction of mixed ligand ternary complexes. These terms are also means to characterize tendencies towards formation of mixed ligand complexes. It is interesting to note that some linear relationships are found to exist between these parameters and $\mathrm{p}K_2$ values of the second ligand mRPhIDA, for example.

For the Ni(II)–phen–mRPhIDA system

$\Delta \log K_{\mathrm{M}} = 0.710\mathrm{p}K_2 - 3.339 \qquad r = 0.994$

$\log X = -1.280\mathrm{p}K_2 + 7.720 \qquad r = -0.988$

For the Ni(II)–bipy–mRPhIDA system

$\Delta \log K_{\mathrm{M}} = 0.975\mathrm{p}K_2 - 4.758 \qquad r = 0.991$

$\log X = -1.280\mathrm{p}K_2 - 7.400 \qquad r = -0.998$

2. Copper(II)–N-substituted phenyliminodiacetic acid–α-amino acid competitive ternary systems [Cu(II)–RPhIDA–αAA] [8]. This is the first time that we have discovered the existence of LFER in competitive ternary systems for all three *para-*, *meta-* and *ortho*-substituted phenyliminodiacetic acid as one ligand (first ligand) and a series of α-amino acids (glycine, isoleucine, α-aminoisobutyric acid, proline, serine, valine) as the other (second ligand). There are altogether 72 ternary complex compounds studied. We herewith list some typical examples.

For the Cu(II)–mRPhIDA–valine system (R = CH_3, H, CH_3O, Cl)

$$\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} = 1.70\mathrm{p}K_2 + 3.29 \qquad r = 0.997$$

For the Cu(II)–mClPhIDA–αAA system

$$\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} = 0.69\mathrm{p}K_2 + 4.93 \qquad r = 0.998$$

For the Cu(II)–pClPhIDA–αAA system

$$\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} = 9.54\mathrm{p}K_2 + 6.61 \qquad r = 0.999$$

For the Cu(II)–oClPhIDA–αAA system

$$\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} = 0.49\mathrm{p}K_2 + 7.30 \qquad r = 0.998$$

3. Copper(II)–N-acetylglycine–α-amino acids competitive ternary system [10]. In this system, the α-amino acids studied were proline, α-aminoisobutyric acid, isoleucine, valine, glycine, serine, threonine. These amino acids are designated as B and *N*-acetylglycine is designated as A. The experimental results show that LFER not only exist between stability constants of the complex compounds with the pK_2 values of the amino acids, but also between the stability constants of ternary complexes and their parent binary complexes.

For $\log K^{\mathrm{Cu}}_{\mathrm{CuB}} = 5.07 + 0.323\mathrm{p}K_2 \qquad r = 0.973$
$\log \beta^{\mathrm{Cu}}_{\mathrm{CuB2}} = 8.36 + 0.693\mathrm{p}K_2 \qquad r = 0.973$
$\log K^{\mathrm{Cu}}_{\mathrm{CuAB}} = 6.79 + 0.391\mathrm{p}K_2 \qquad r = 0.980$
$\log K^{\mathrm{Cu}}_{\mathrm{CuAB}} = 0.931 + 1.176 \log K^{\mathrm{Cu}}_{\mathrm{CuB}} \qquad r = 0.999$
$\log K^{\mathrm{Cu}}_{\mathrm{CuAB}} = 2.06 + 0.565 \log \beta^{\mathrm{Cu}}_{\mathrm{CuB2}} \qquad r = 0.997$

The fact that the last two equations have better correlation coefficients than the other three might be ascribed to the mutual cancellation of possible steric effects due to the five-membered rings in the proline molecules.

4. Copper(II)–2,9-dimethyl-1,10-phenanthroline–α-amino acid ternary system [Cu(II)–2,9-Me₂phen–αAA] [11]. The amino acids involved were glycine, proline, isoleucine, 2-methylalanine, valine, serine (designated as B, while 2,9-Me_2phen is designated as A). The correlation equation obtained for the ternary complex compounds is

$$\log K^{\mathrm{CuA}}_{\mathrm{CuAB}} = 0.66 + 0.73\mathrm{p}K_2 \qquad r = 1.000$$

where K_2 is the basic dissociation constant of the amino acid.

5. Copper(II)–2,9-dimethyl-1,10-phenanthroline–N-substituted ethylenediamine ternary system [Cu(II)–2,9-Me$_2$phen–Ren] [11]. The *N*-substituted ethylenediamines studied were those with R = H, ethyl, *n*-propyl, *n*-butyl, isopropyl, cyclohexyl and phenyl. In these systems, certain steric effects due to the substituent R may be involved, and the stabilities of the complex compounds are related to both the Hammett constant σ and the steric constant E_s conforming to the Taft equation

$$\log K_{\mathrm{CuAB}}^{\mathrm{CuA}} = 8.81 + 0.06\sigma + 0.69E_s \qquad r = 0.97$$

From the above-mentioned examples, we can see that LFER seem to be phenomena commonly existing in solution chemistry.

II. Correlation between the stability constants of complexes and the Hammett constant [12]

We have reported a number of examples of this type of LFER [7]. We now wish to report some linear relationships existing between some thermodynamic parameters and the Hammett constant σ for the axial coordination reaction of *para*-substituted tetraphenylporphinatoiron(III) chloride [abbreviated as (p-X)TPPFeCl] with imidazole as shown in the equation

$$\text{(p-X)TPPFeCl} + n\ \text{L} \overset{\beta_n}{\rightleftharpoons} [\text{(p-X)TPPFeL}_n]^+\text{Cl}^- \qquad (1)$$

where X denotes the substituent groups Cl, H, CH_3, CH_3O, and L denotes imidazole(Im), 2-methylimidazole(MeIm) or 2-ethyl-4-methylimidazole(EMIm) and β_n is the equilibrium constant of reaction (1). Since there are four substituent groups in the porphin ring, it is logical to use 4σ rather than σ to represent the substituent parameter. At various temperatures the following correlation expressions were obtained for reaction (1) with Im as the ligand.

At 15 °C

$$\ln \beta_n = -0.080\ (4\sigma) + 14.53 \qquad r = 0.970$$

At 20 °C

$$\ln \beta_n = -0.130\ (4\sigma) + 13.91 \qquad r = 0.997$$

At 25 °C

$$\ln \beta_n = -0.240\ (4\sigma) + 13.32 \qquad r = 0.995$$

At 30 °C

$$\ln \beta_n = -0.277\ (4\sigma) + 12.73 \qquad r = 0.997$$

In the meantime, we have found that the standard molar enthalpies $\Delta H^\ominus$ (in kJ mol^{-1}) and standard molar entropies $\Delta S^\ominus$ (in J mol^{-1} K^{-1}) of the axial coordination reaction (1) are also linearly correlated to the Hammett σ values

$\Delta H^{\ominus} = -10.13\ \sigma - 86.58 \qquad r = 0.992$

$\Delta S^{\ominus} = -36.04\ \sigma - 179.6 \qquad r = 0.993$

III. LFER between reaction rate constants and equilibrium constants

We have recently studied several coordination reaction systems both kinetically and thermodynamically, and have found the existence of LFER between the reaction rate constants and the equilibrium constants of the systems. The following are some examples.

A. Axial coordination reaction of para-substituted tetraphenylporphinatoiron (III) chloride with imidazole [12]

The mechanism of this reaction involves pre-equilibria of ligand addition and is followed by rate-determining substitution reactions

$$\text{(p-X)TPPFeCl} + \text{Im} \overset{K}{\rightleftharpoons} \text{(p-X)TPPFeImCl} \tag{2}$$

$$\text{(p-X)TPPFeImCl} + \text{Im} \xrightarrow{k} [\text{(p-X)TPPFeIm}_2]^+\text{Cl}^- \tag{3}$$

where K is the equilibrium constant and k the reaction rate constant. X and β_n are substituent groups and equilibrium constants, respectively, as shown in eqn. (1). The correlation equations are

$\ln k = -4.575 \ln \beta_n + 59.54 \qquad r = 0.992$

$\ln k = -0.883 \ln K + 8.84 \qquad r = 0.991$

In addition, the rate constants are also linearly related to the Hammett constant σ as follows

at 15°C

$\ln k = -0.749\ (4\sigma) + 9.216 \qquad r = 0.95$

at 25°C

$\ln k = -0.962\ (4\sigma) + 10.08 \qquad r = 0.97$

at 35°C

$\ln k = -1.093\ (4\sigma) + 10.99 \qquad r = 0.97$

Since kinetic data are not as accurate as thermodynamic measurements, the correlation coefficients are not as good as those for equilibrium constants.

B. copper(II)–2,9-dimethyl-1,10-phenanthroline–α-amino acid ternary system [11]

The amino acids studied are those listed in Sect. II. The correlation expression is

$\log k_f = 2.97 - 0.52\text{p}K_2 \qquad r = 0.98$

where k_f is the rate constant of formation of the ternary complexes and pK_2 is the basic dissociation constant of the amino acid. This equation excludes proline which has a five-membered ring and thus introduces a steric factor into the system to deviate from linearity.

C. Nickel(II)–N-(para-substituted phenyl)glycine binary system [13]

The substituent groups are CH_3O, CH_3, H and Cl. A stopped-flow spectrophotometer was employed to study the reaction rate. It was found that not only the ligand anion, but also the zwitterion are attacking species in the complexation reaction. The following regression equations were obtained.

$$\log k_{-L^-} = 4.84 - 0.973 \log K^{Ni}_{NiL} \qquad r = 1.000$$

$$\log k_{-L^-} = 5.56 - 0.815 pK_2 \qquad r = 0.974$$

$$\log k_{HL^\pm} = 5.36 - 0.432 pK^2 \qquad r = 0.979$$

where k_{-L^-} denotes the rate constant of the reverse reaction and $k_{HL^\pm}$ denotes the rate constant of formation reaction of nickel ion with the zwitterion.

D. Copper(II)–5-substituted-1,10-phenanthroline–α-amino acid ternary system [Cu(II)–5-Xphen–αAA] [14]

In this system, the amino acids studied were glycine, alanine, threonine and isoleucine; the substituent groups on phen when $X = NO_2$, Cl, H and CH_3. The kinetic studies were carried out by means of temperature-jump and stopped-flow techniques. The following correlation equations were obtained.

For threonine

$$\log K^{CuA}_{CuAB} = 0.13 + 0.83 \log k_f \qquad r = 0.99$$

For valine

$$\log K^{CuA}_{CuAB} = -0.61 + 0.941 \log k_f \qquad r = 0.99$$

$$\log k_f = 9.1 - 0.082 pK_2 \qquad r = 0.97$$

E. LFER between the rate constants and basicities of N-substituted phenylglycines in orthopositronium–glycine complex formation [15]

The *N-para*-substituted phenylglycines (pRPhG) studied were those with $R = NO_2$, Cl, H, CH_3 and CH_3O. The complex reaction rate constants were obtained by means of a positron annihilation lifetime spectrometer with BaF_2 detectors. The experimental results showed that LFER exists between the rate constants and the basicities of the pRPhG in orthopositronium–glycine complex formation expressed as

$$\log k = -4.54 pK_2 + 22.85 \qquad r = 0.883$$

It is interesting to note that the relative rate constant is also linearly related to the corrected Hammett constant σ' as

$$\log(k_R/k_H) = 3.498\sigma' + 1.382 \qquad r = 0.883$$

IV. Linear correlations of substituent effects in ^1H NMR spectroscopy [16]

A. ^1H NMR study on the complexation of N(para-substituted phenyl) nitrogen-hetero-15-crown-5 (pRPhN15C5, R = CH_3O, CH_3, H, Cl) with the sodium ion

The stability constants of these sodium crown complexes have been determined by ^1H NMR spectroscopy in acetone. It was found that the stability constants and their limit chemical shifts (δ) are linearly correlated as

$$\log K = 3.95 + 0.409\delta_{NaL} \qquad r = 0.992$$

B. ^1H NMR study on para-substituted tetraphenylporphin [(p-x)TPP] and para-substituted tetraphenylporphinatoiron(III) chloride [(p-x)TPPFeCl] and their axially coordinated compounds

The following compounds have been studied in chloroform-*d* using an MSL-400 superconducting spectrometer at 400 MHz: (p-x)TPP, (p-x)-TPPFeCl, $[(p\text{-x})TPPFeIm_2]^+Cl^-$ (X = Cl, H, CH_3, CH_3O), axially coordinated complexes $[(p\text{-X})TPPFeY_n]^+Cl^-$ (Y = MeIm, EMIm, $n\text{-}C_3H_7NH_2$, $N(C_2H_5)_3$, $n = 1$ or 2). It was found that linear relationships exist between the chemical shifts (δ) and the Hammett constant σ as follows.

For (p-X)TPP δ (pyrrole-H)

$$\delta = -0.039\sigma + 8.843 \qquad r = 0.89$$

For (p-X)TPP δ (N-H)

$$\delta = -0.233\sigma - 2.796 \qquad r = 0.99$$

For (p-X)TPPFeCl δ (pyrrole-H)

$$\delta = 1.310\sigma + 79.30 \qquad r = 0.97$$

For $[(p\text{-X})TPPFeIm_2]^+Cl^-$ δ (pyrrole-H)

$$\delta = -0.579\sigma - 16.47 \qquad r = 0.96$$

LINEAR ENTHALPY AND LINEAR ENTROPY RELATIONSHIPS

As we have stated in a previous paper [7], exploration of this field has only just begun and little information has appeared in the literature. In this paper we report work carried out in our laboratory during the past three years.

I. Copper(II)–5-substituted-1,10-phenanthroline–α-amino acid ternary system [Cu(II)–5-Xphen–αAA, where $X = NO_2$, Cl, H, CH_3; αAA = 2-methylalanine, isoleucine, valine, serine] [11]

Heats of protonation of the ligands and heats of formation of the ternary complex compounds were determined in water at 25 °C at an ionic strength 0.1 mol dm^{-3} (KNO_3) by means of an MS80 Calvet microcalorimeter.

The reactions involved are

$$H + A = HA \qquad \Delta H_{HA} \qquad (4)$$

$$CuA + B = CuAB \qquad \Delta H_{CuAB} \qquad (5)$$

where A denotes the first ligand, 5-Xphen, and B the second ligand, αAA. The ΔG values were calculated from equilibrium constants which were obtained from pH determinations. From the experimental data the following correlation equations are listed, taking valine as an example (ΔH in kJ mol^{-1}, ΔS in J mol^{-1} K^{-1})

$\Delta G_{CuAB} = -45.3 - 0.07\,\Delta G_{HA}$ $\quad r = -0.99$

$\Delta H_{CuAB} = -35.8 - 0.44\,\Delta H_{HA}$ $\quad r = -1.00$

$\Delta S_{CuAB} = 11.5 + 0.84\,\Delta S_{HA}$ $\quad r = 0.99$

$\Delta G_{CuAB} = -44.9 - 0.10\,\Delta H_{HA}$ $\quad r = -0.99$

$\Delta G_{CuAB} = -46.3 + 0.07\,\Delta S_{HA}$ $\quad r = 0.97$

$\Delta H_{CuAB} = -37.9 - 0.31\,\Delta G_{HA}$ $\quad r = -1.00$

$\Delta H_{CuAB} = -42.7 + 0.31\,\Delta S_{HA}$ $\quad r = 0.99$

$\Delta S_{CuAB} = 24.5 - 0.84\,\Delta G_{HA}$ $\quad r = -1.00$

$\Delta S_{CuAB} = 30.1 - 1.19\,\Delta H_{HA}$ $\quad r = -1.00$

$\Delta H_{CuAB} = -47.1 + 0.37\,\Delta S_{CuAB}$ $\quad r = 1.00$

$\Delta H_{HA} = 15.6 - 0.71\,\Delta S_{HA}$ $\quad r = -0.99$

It is well known that in a chemical reaction the change in enthalpy reflects the change in bonding energies of the reactants, and the change in entropy reflects the change in distribution or rearrangement of atoms in energy levels of molecules involved in the reaction. Hancock [17] pointed out that enthalpy data are more fundamental than free energies and should therefore be used in preference to free energies in correlating the properties of complexes in aqueous solution. We may henceforth arrive at the conclusion that for a chemical reaction the linear enthalpy relationships, the linear entropy relationships and the linear enthalpy–entropy relationships are the three fundamental linear thermodynamic function relationships, while the last of these is known as the compensation law [18] which can be applied to a wide range of areas in solution chemistry. LFER and other cross-linear thermodynamic function relationships listed above may be regarded as consequences of the mutual interactions of the three fundamental thermodynamic function relationships.

II. Nickel(II)–N,N′-bis(para-substituted phenyl)ethylenediamine binary system [Ni(II)–(pRPh)$_2$en, R = CH$_3$O, CH$_3$, H, Cl] [19]

Heats of protonation of the ligands and heats of formation of the complex compounds were determined by means of an MS80 Calvet microcalorimeter, with both LER and LSR found to exist between these two thermodynamic quantities.

$\Delta H_{\mathrm{M}} = -99.5 - 1.98\ \Delta H_1^{\mathrm{H}}$ $\quad r = -0.99$

$\Delta S_{\mathrm{M}} = -148 - 11.2\ \Delta S_1^{\mathrm{H}}$ $\quad r = -1.00$

III. Nickel–2,2′-bipyridyl–N,N′-bis(para-substituted phenyl)ethylenediamine ternary system [Ni(II)–bipy–(pRPh)$_2$en, R = CH$_3$O, CH$_3$, H, Cl] [19]

The experimental conditions are the same as the parent binary systems, with both LER and LSR obtained as follows

$\Delta H_{\mathrm{MAB}}^{\mathrm{MB}} = -109 - 2.71\ \Delta H_1^{\mathrm{H}}$ $\quad r = -0.99$

$\Delta S_{\mathrm{MAB}}^{\mathrm{MB}} = -131 - 15.1\ \Delta S_1^{\mathrm{H}}$ $\quad r = -1.00$

IV. Copper(II)–N-(para-substituted phenyl)iminodiacetic acid binary system [Cu(II)–pRPhIDA, R = CH$_3$O, CH$_3$, H, Cl] [20]

In Sect. I.A.2, we have reported the LFER in this system. In the meantime, we have also determined at 25 °C and at an ionic strength of 0.10 mol dm^{-3} (KNO$_3$) heats of protonation of the ligand (L) and heats of formation of the complex compounds. The following linear enthalpy relationships and the corresponding linear entropy relationships were obtained (ΔH in kJ mol^{-1}; ΔS in J mol^{-1} K^{-1})

$\Delta H_{\mathrm{CuL}} = -0.035 + 0.833\ \Delta H_{\mathrm{HL}}$ $\quad r = 0.997$

$\Delta S_{\mathrm{CuL}} = 631 - 3.94\ \Delta S_{\mathrm{HL}}$ $\quad r = -0.982$

V. Copper(II)–N-substituted phenyl iminodiacetic acid–α-amino acid competitive ternary systems [Cu(II)–RPhIDA–αAA, R = CH$_3$O, CH$_3$, H, Cl] [20]

The systems with mRPhIDA as first ligands, A, and αAA as second ligands, B, to form ternary complexes with Cu(II) were investigated calorimetrically. The αAA used were proline, α-aminoisobutyric acid, isoleucine, valine, glycine and serine. Altogether 48 correlation equations of LER have been obtained. We list here only CH_3PhIDA as first ligands, A, and valine as second ligand, B, as examples.

For the Cu(II)–pRPhIDA–valine system

$$\Delta H_{\mathrm{CuAB}} = -15.4 + 0.82\ \Delta H_{\mathrm{HA}} \qquad r = 0.998$$

$$H_{\mathrm{CuAB}} = -27.8 + 0.98\ \Delta H_{\mathrm{CuA}} \qquad r = 0.997$$

For the Cu(II)–pCH_3PhIDA–αAA system

$$\Delta H_{\mathrm{CuAB}} = 7.92 + 0.77\ \Delta H_{\mathrm{CuB}} \qquad r = 0.972$$

For the Cu(II)–mRPhIDA–valine system

$$\Delta H_{\mathrm{CuAB}} = -19.2 + 1.30\ \Delta H_{\mathrm{HA}} \qquad r = 0.998$$

$$\Delta H_{\mathrm{CuAB}} = -50.6 + 2.30\ \Delta H_{\mathrm{CuA}} \qquad r = 0.997$$

For the Cu(II)–mCH_3PhIDA–αAA system

$$\Delta H_{\mathrm{CuAB}} = 2.35 + 0.56\ \Delta H_{\mathrm{CuB}} \qquad r = 0.997$$

In the systems investigated so far, no good LSR have been observed.

As pointed out earlier [7], even though some good LFER and LER exist in certain systems, it does not always follow that good linear entropy relationships will be found in the same system. Since ΔS values are invariably calculated from the equation $\Delta H = \Delta G + T\Delta S$, experimental errors in measuring both ΔH and ΔG values will enter the calculation and thus contribute more seriously in the evaluation of ΔS. This might be an explanation for the deviation of entropy terms from linearity in these systems.

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