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LINEAR THERMODYNAMIC FUNCTION RELATIONSHIPS IN COORDINATION CHEMISTRY

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CONTENTS

A. INTRODUCTION

In 1962, the author reported the formulation of the following equations to correlate quantitatively the stability constant of the complex compound with the acidity or basicity of the ligand [1]

$$K_{MA} = C_A K_A^{-\alpha} \quad (1)$$

$$K_{MB} = C_B K_B^{-\beta} \quad (2)$$

where K_{MA} and K_{MB} denote the stability constants of the complex compound with acid and base ligand, respectively, and K_A and K_B represent the dissociation constants of acid and base ligand, respectively, C_A and C_B are constants dependent upon temperature, pressure and the medium of the system, while α and β are also constants which account for the proper rate of change between the stability and dissociation constants. These equations

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manifest the principle of linear free energy relationships (LFER) in coordination chemistry.

There has been a large expansion in the literature regarding LFER in coordination chemistry since 1962, in the space available it would not be possible to cover all of these developments. However, some monographs have been published in the interim period [2,3]. Hence it is considered expedient to deal only with the works in which the author has been especially involved.

The author also predicted in 1962 [1], on theoretical grounds, the existence of linear enthalpy relationships between the heat of formation of the complex compound and the heat of dissociation (or protonation) of the ligand

$$\Delta H_M = Q - \beta \Delta H_B \tag{3}$$

where ΔH_M represents the heat of formation of the complex compound, ΔH_B the heat of dissociation or protonation of the ligand and Q is a constant with the dimension of heat. The validity of equation (3) was not verified experimentally until only recently when we tested it by both the temperature coefficient method and by a calorimetric method, these being in our laboratory. This work will be described later in the present article.

In the meantime we have discovered the existence of linear entropy relationships in some binary and ternary complex compound systems. Therefore, it is proposed to group together these three linear relationships, namely linear free energy, linear enthalpy and linear entropy relationships, and to call them the linear thermodynamic function relationships (LTFR) in coordination chemistry.

Since most of our work is published in Chinese (although with short English abstracts) which is not familiar to the majority of chemists in other countries, it is appropriate to herein delineate our work in some detail.

B. LINEAR FREE ENERGY RELATIONSHIPS (LFER)

(i) Historical background

The earliest and best known examples of linear free energy relationships in chemistry are the Brönsted Catalysis Law and the Hammett equation. The former deals with the reaction rates and ionization constants for general acid- or base-catalyzed reactions, while the latter correlates reaction rates and equilibrium constants for side-chain reactions of *meta*- and *para*-substituted benzene derivatives.

The existence of LFER in coordination chemistry was first pointed out by Calvin and Wilson in 1945 [4] in connection with the stabilities of cupric

chelates of a number of enolic substances, although they did not use the terminology LFER at that time. Bjerrum in 1950 [5] demonstrated that the hydrogen-ion dissociation constant (as pK_{H^+}) and the average complexity constant for some Ag(I) and Hg(II) complexes exhibited linear correlation, however, the name LFER was still not mentioned. Duncan [6], as well as Irving and Rossotti [7], expounded the thermodynamic aspects of this type of relationship and an empirical equation was subsequently used to correlate the stability constant of the complex compound and the basicity of the ligand as follows

$$\log K_{ML} = pKa(HL) + \frac{1}{2.303RT}\left(\bar{G}^0_{M^{z+}} - \bar{G}^0_{ML} - \bar{G}^0_{H^+} + \bar{G}^0_{HL}\right) \tag{4}$$

where $\bar{G}^0_{M^{z+}}$, $\bar{G}^0_{ML}$, $\bar{G}^0_{H^+}$, and $\bar{G}^0_{HL}$ are the partial molar free energies of the relevant species. $\bar{G}^0_{H^+}$ is zero by definition and $\bar{G}^0_{M^{z+}}$ will be constant for a given ion; the terms $\bar{G}^0_{HL}$ and $\bar{G}^0_{ML}$ may each depend on the nature of the ligand. If equation (4) is obeyed by a series of metal–ion complexes, both $\bar{G}^0_{HL}$ and $\bar{G}^0_{ML}$ are either small or both change with the nature of L in a similar way.

Most of the reactions studied by LFER were those that are nearest to being organic reactions i.e., those with an organic group attached to an inorganic reaction center. They included those of transition metal complexes (with organic substituents in the ligands), and the organic derivatives of the transition metals and main group elements.

Irving and Rossotti [7] also discussed the LFER which can be obtained by considering the stability constants, K_{ML} and $K_{M'L}$, of the complexes of metal ions M and M′ with the same series of ligands. They derived an equation of the form

$$\log K_{ML} = \log K_{M'L} + C + D \tag{5}$$

where C is a function of M, M′ and L, whereas D is a function only of M and M′. If C is a constant, or is small compared with $\log K_{M'L}$, a plot of $\log K_{ML}$ against $\log K_{M'L}$ will be a straight line of unit slope.

Another LFER discussed by Irving and Rossotti [7] is that obtained from the stabilities of complexes formed from a pair of ligands, L and L′, with a series of metal ions M. They derived the following expression,

$$\log K_{ML} = \log K_{ML'} + pKa(HL) - pKa(HL') + E \tag{6}$$

where E depends on ML, ML′, HL and HL′. Only if E is small will a plot of $\log K_{ML}$ against $\log K_{ML'}$ be a straight line of unit slope, with an intercept at $pKa(HL) - pKa(HL')$: such a plot was later illustrated by Tucci et al. [8]

(ii) LFER between the stability constants of complexes and the acidity and basicity of the ligands

We started work on this type of LFER in the early sixties soon after the equations (1) and (2) were derived [1] but, however, our work was interrupted during the so-called Cultural Revolution. The work was resumed after the Revolution and the results reported at the XX ICCC in Calcutta in 1979 and published in Acta Chimica Sinica [9]. The system we studied was M(II)–*p*RPhG complexes, where M(II) = Cu(II), Ni(II) and Zn(II), and *p*RPhG are *N*-(*para*-substituted phenyl)glycines with R = H, CH_3, CH_3O, Cl, NO_2. The results conform very nicely to equation (2) and the correlation expressions are shown below [9]

	correlation coefficient
For Cu(II)–*p*RPhG *:	
$\log K_{ML} = 1.585pK_2 - 2.544$	$r = 0.991$
$\log K_{ML_2} = 1.675pK_2 - 3.855$	$r = 0.980$
$\log \beta_2 = 3.031pK_2 - 5.278$	$r = 0.991$
For Ni(II)–*p*RPhG *:	
$\log K_{NiL} = 0.800pK_2 - 0.543$	$r = 0.990$
For Zn(II)–*p*RPhG *:	
$\log K_{ZnL} = 0.811pK_2 - 0.673$	$r = 0.977$

We also worked on M(II)–*m*RPhG [10] and M(II)–*o*RPhG [11] systems, where M(II) are Cu(II) and Ni(II); mRPhG and oRPhG are *N*-(*meta*-substituted phenyl) glycines and *N*-(*ortho*-substituted phenyl)glycines, respectively. It is surprising to find that the latter system also conforms nicely to equation (2), implying that no effect other than electronic is the dominating one in these cases. Their correlation equations are shown below.

For Cu(II)–*m*RPhG:	
$\log K_{CuL} = 1.757pK_2 - 3.242$	$r = 0.997$
$\log K_{CuL_2} = 3.006pK_2 - 9.643$	$r = 0.994$
$\log \beta_2 = 4.763pK_2 - 13.070$	$r = 0.999$

* L denotes *p*RPhG; pK_2 denotes the negative logarithm of the acid dissociation constant of an amino group (since the dissociation constants of the carboxyl groups did not change appreciably with different R's, pK_2 values were used to express the basicity of the aminoacids).

* Log K_{ML_2} values were not obtained by the pH method.

For Ni(II)–*m*RPhG:

$$\log K_{NiL} = 0.693pK_2 - 0.152 \qquad r = 0.994$$

For M(II)–*o*RPhG:

$$\log K_{CuL} = 2.06pK_2 - 4.92 \qquad r = 0.997$$

$$\log K_{NiL} = 0.519pK_2 + 0.673 \qquad r = 0.999$$

We have also worked on ternary mixed ligand systems with 2, 2′-bipyridyl or 1,10-phenanthroline as the first ligand and with mRPhG and pRPhG as the second ligand. The correlation expressions are as follows

For Cu(II)–phen–*p*RPhG [12]

$$\log K_{CuAL}^{CuA} * = 2.041pK_1 - 0.900 \qquad r_1 = 0.999$$

$$\log K_{CuAL}^{CuA} = 1.454pK_2 - 2.209 \qquad r_2 = 0.999$$

For Cu(II)–bipy–*p*RPhG [13]

$$\log K_{CuAL}^{CuA} = 1.590pK_2 = 2.728 \qquad r = 0.998$$

For M(II)–bipy–*m*RPhG [14]

$$\log K_{CuAL}^{CuA} = 1.195pK_2 - 1.249 \qquad r = 1.000$$

$$\log K_{NiAL}^{NiA} = 0.808pK_2 - 0.130 \qquad r = 0.997$$

$$\log K_{ZnAL}^{ZnA} = 0.805pK_2 - 0.435 \qquad r = 0.998$$

For Cu(II)–phen–*m*RPhG [13]

$$\log K_{CuAL}^{CuA} = 1.152pK_2 - 0.998 \qquad r = 0.997$$

It is interesting to note that these two ternary systems with a common second ligand but different first ligand also show linear relationships [13]

$$\log K_{Cu.bipy.pRPhG} = 1.076 \log K_{Cu.phen.pRPhG} - 0.399 \qquad r = 0.999$$

$$\log K_{Cu.bipy.mRPhG} = 1.032 \log K_{Cu.phen.mRPhG} - 0.191 \qquad r = 1.000$$

In addition to *N*-substituted phenylglycinates, we also studied both binary and ternary complexes formed by some transition metals with *N*,*N*′-bis(*para*-substituted phenyl)ethylenediamines (abbreviated to (*p*RPh)$_2$en with R = H, CH_3, CH_3O, Cl, NO_2). The experimental condi-

* A = phen or bipy; L = *p*RPhG or *m*RPhG.

tions were: 25 °C, $I = 0.10$ M $NaClO_4$, 50% (v/v) dioxane or 70% (v/v) ethanol. However, under these conditions no formation constants were obtained in the case of R = NO_2 due to limited solubility. The correlation expressions are shown as follows [15].

For binary systems M(II).(*p*RPh)$_2$en in 50% (v/v) dioxane

$$\log K_{CuL} = 0.322 \log K_{HL}\ ^* + 1.832 \qquad r = 0.999$$

$$\log K_{NiL} = 0.196 \log K_{HL} + 2.089 \qquad r = 1.000$$

while in 70% (v/v) ethanol

$$\log K_{CuL} = 0.360 \log K_{HL} + 1.699 \qquad r = 0.999$$

For ternary systems with bipy as the first ligand in 50% (v/v) dioxane, the correlation equations are

For Cu(II).bipy.(*p*RPh)$_2$en,

$$\log K^{CuA}_{CuAL} = 0.211 \log K_{HL} + 2.248 \qquad r = 1.000$$

For Ni(II).bipy.(*p*RPh)$_2$en,

$$\log K^{NiA}_{NiAL} = 0.250 \log K_{HL} + 1.973 \qquad r = 1.000$$

(iii) Correlation between the stability constants of complexes with the Hammett σ constant

Irving and Miles [16] have shown that the Hammett equation can correlate the stability constants of a series of complexes of a metal ion with ligands which are similar, except for the substituent on a benzene ring. They obtained equation (7)

$$\log(K_{ML'}/K_{ML_0}) = -a\rho\sigma \qquad (7)$$

where $K_{ML'}$ and M_{ML_0} are the stability constants of the substituted and unsubstituted ligand–metal complexes, respectively, a is a constant and ρ and σ are the Hammett constants. A plot of log $K_{ML'}$ against σ should give a straight line of slope $-a\rho$. There are, however, certain restrictions with regard to the application of equation (7): Tucci [8] has pointed out that plots of log K_{ML} against σ are not all straight lines.

In studying M(II)-substituted phenylglycine systems [9,10] we have found that the plots of log K_{ML} vs σ or pK_2 vs σ show linear relationships (Figs. 1

* K_{HL} is the first protonation equilibrium constant of the ligand:

$L + H^+ \overset{K_{HL}}{\rightleftharpoons} HL^+$.

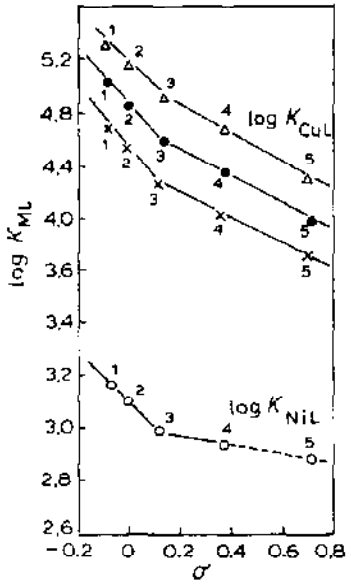

Fig. 1. Plot [10] of log K_{ML} of M(II)–mRPhG vs. σ; Δ, 15°C; ●, 25°C, ×, 35°C. R: 1, CH_3; 2, H; 3, CH_3O; 4, Cl; 5, NO_2.

and 2), but the lines break at R = H, with electron releasing substituent groups on one line and electron attracting substituent groups on another, the two having somewhat different slopes. Similar phenomena are also found in the case of M(II)–bipy–mRPhG [14] (Fig. 3) and M(II)–phen–pRPhG [12] ternary systems (Fig. 4). However, when σ′ values ($\sigma' = pK_2^0 - pK_2$, where pK_2^0 represents the pK_2 value with R = H) are used for the plot instead of σ, very good linear relationships are obtained [10,11,12,14] (Figs. 5–8). It is interesting to note that even a plot of σ vs σ′ gives a good straight line for the ligands [15] (Fig. 9).

Irving and Da Silva [17] suggested a new parameter, S_f, called the stabilization factor, defined by equation (8)

$$S_f = \log K_{ML'} - \log K_{ML_0} \tag{8}$$

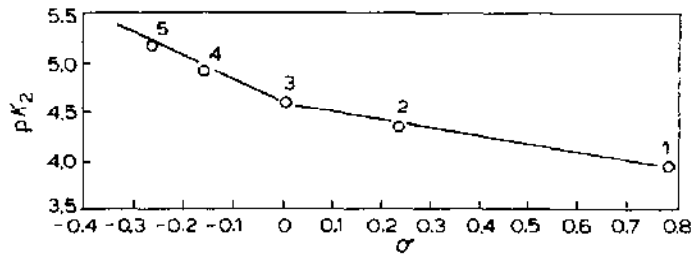

Fig. 2. Plot [9] of pK_2 for pRPhG vs. σ. R: 1, NO_2; 2, Cl; 3, H; 4, CH_3; 5, CH_3O.

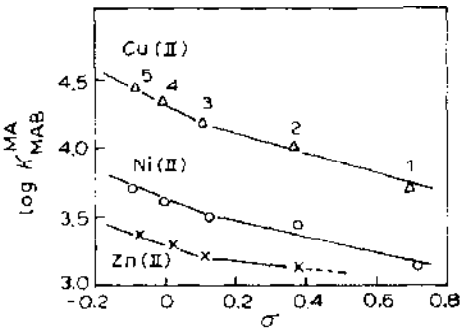

Fig. 3. Plot [14] of log K^{MA}_{MAB} vs. σ. A, bipy; B, *m*RPhG. R: 1, NO_2; 2, Cl; 3, H; 4, CH_3; 5, CH_3O.

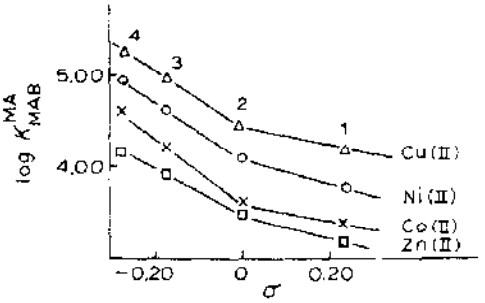

Fig. 4. Plot [12] of log K^{MA}_{MAB} vs. σ. A, phen; B, *p*RPhG. R: 1, Cl; 2, H; 3, CH_3; 4, CH_3O.

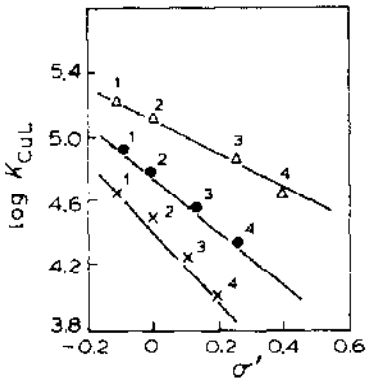

Fig. 5. Plot [10] of log K_{ML} for Cu(II)–*m*RPhG vs. σ'. Δ, 15 °C; ●, 25 °C, ×, 35 °C. R: 1, CH_3; 2, H; 3, CH_3O; 4, Cl.

where $K_{ML'}$ and K_{ML_0} are the stability constants for the formation of a complex of a metal with substituted ligands HL′ and the unsubstituted ligand HL, respectively. They proposed that this factor could be used as a measure of the π-stabilization additional to σ-bond formation, this being caused by back donation of *d*-electrons from the metal to suitable empty

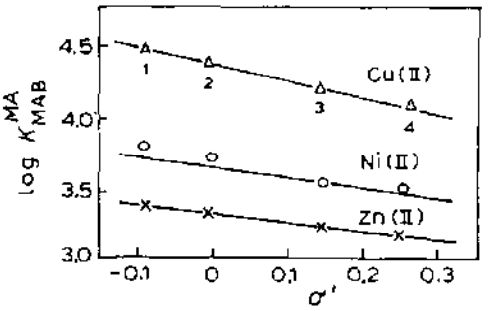

Fig. 6. Plot [14] of log K^{MA}_{MAB} for M(II)–*m*RPhG vs. σ. A, bipy; B, *m*RPhG. R: 1, CH_3; 2, H; 3, CH_3O; 4, Cl.

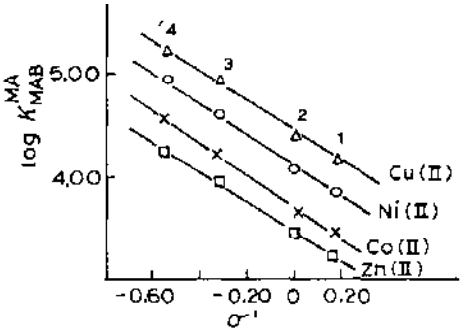

Fig. 7. Plot [12] of log K^{MA}_{MAB} vs. σ'. A, phen; B, pRPhG. R: 1, CH_3O; 2, CH_3; 3, H; 4, Cl.

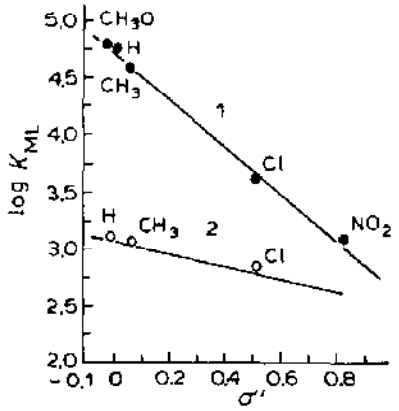

Fig. 8. Plot [11] of log K_{ML} for M(II)–*o*RPhG vs. σ'. 1, CuL; 2, NiL.

π-orbitals of the ligand. Da Silva and Calado [18] further showed that S_f could be correlated with the Hammett σ constants for a series of metal complexes with substituted ligands. They obtained equation (9)

$$S_f = J\rho\sigma \tag{9}$$

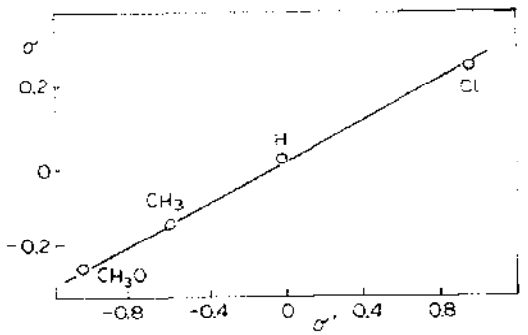

Fig. 9. Plot [15] of σ vs. σ' for $(p\text{RPh})_2$en in 50% (v/v) dioxane.

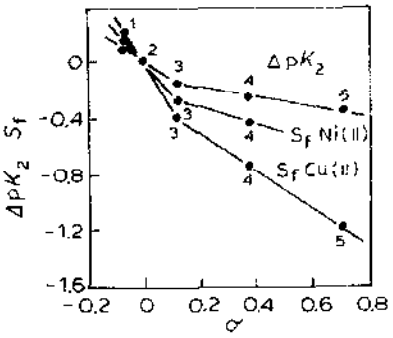

Fig. 10. Plot [10] of S_f and ΔpK_2 of M(II)–mRPhG vs. σ. R: 1, CH_3; 2, H; 3, CH_3O; 4, Cl; 5, NO_2.

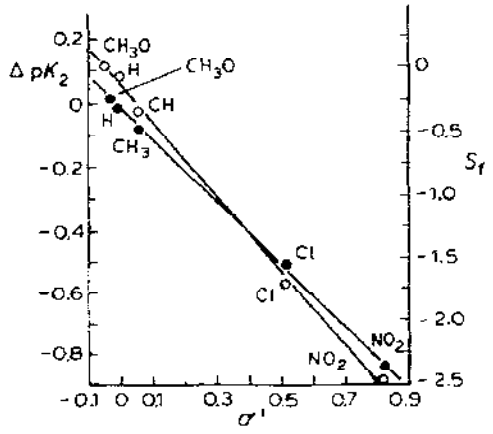

Fig. 11. Plot [11] of S_f vs. σ' and ΔpK_2 vs. σ' for Cu(II)–oRPhG. ○, ΔpK_2; ●, S_f(CuL).

where J is a constant for a given set of ligands. They applied this equation to both Cu(II)–benzoic acids series and Cu(II)–acetylacetonatepyridines series and obtained straight lines by plotting S_f against σ: the slopes of

these were positive. This means that the reaction studied was favored by electron withdrawal from the reaction center, and thus that the stabilization measured by the S_f parameter is due to back donation by *d*-electrons of the metal to antibonding orbitals in the ligand to form π-bonds.

There has been some criticism of this argument [19,20]. However, we found that in the M(II)–*N*-substituted phenyl glycinates [9–11], the plots of S_f against σ or σ' and ΔpK_2 against σ or σ' give negative slopes (Figs. 10, 11). This would imply no back π-bonding in these binary systems.

(iv) LFER between reaction rate constants and equilibrium constants

In 1952 Basolo and coworkers [21] measured the rate of hydrolysis of a series of *C*-substituted acetatopentammine cobalt(III) ions, $[(NH_3)_5Co \cdot OOCR]^{2+}$, and found a good correlation between the rate constant, log k, and log K_{eq}. The value of 0.8 for the slope of the line supported a dissociative reaction mechanism, with the departing group only weakly bonded in the transition state. Langford [22] showed that a plot of log k against log K_{eq} was a straight line of unit slope for the hydrolysis of a series of pentammine–cobalt(III) complexes, $[(NH_3)_5Co \cdot L]^{2+}$. This confirms that the leaving group, L, has an environment in the transition state similar to that in the product, i.e., that of a solvated anion.

Thorsteinson and Basolo [23] studied the kinetics of substitution of the reaction of $Co(NO)(CO)_3$ with phosphine and amine ligands; they found that there is a linear relationship between the rate constant log k and the basicity of the nucleophile, as measured by its half-neutralization potential ΔHNP, which is a linear function of pKa.

Recently [24,25] we have measured the rate constants of formation of the mixed-ligand complex-compounds Cu(II)–bipy–amino acids and Cu(II)–phen–amino acids by means of the temperature jump technique. The amino acids studied are proline, α-aminoisobutyric acid, valine and threonine. The rate constants of the complexation reaction represented by (10) and (11) can be evaluated by coupling them to the more rapid processes (12)–(14), where HIn is the acidic form of the indicator, methyl red, B denotes bipy or phen, L stands for amino acids

$$CuB + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuBL \tag{10}$$

$$CuB + HL \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CuBL + H^+ \tag{11}$$

$$H_2L \rightleftharpoons H + HL \tag{12}$$

$$HL \rightleftharpoons H + L \tag{13}$$

$$HIn \rightleftharpoons H + In \tag{14}$$

Charges have been omitted for the sake of simplicity.

The results showed that the plots of log k against log K_{eq} give straight lines, indicating the existence of a Brönsted-type of LFER. The log K_{eq} values were determined by the pH method (13) and the reverse reaction rate constants were calculated from the equilibrium constants and forward-reaction rate constants.

The correlation equations are presented as follows

$$\log k_1 = 3.74 + 0.641 \log K^{Cu.bipy}_{Cu.bipy.L} \qquad r = 0.983$$

$$\log k_2 = 18.62 - 1.85 \log K^{Cu.bipy}_{Cu.bipy.L} \qquad r = -0.992$$

$$\log k_{-1} = 3.79 - 0.366 \log K^{Cu.bipy}_{Cu.bipy.L} \qquad r = -0.948$$

$$\log k_{-2} = 11.52 - 0.777 \log K^{Cu.bipy}_{Cu.bipy.L} \qquad r = -0.992$$

$$\log k_1 = 3.57 + 0.664 \log K^{Cu.phen}_{Cu.phen.L} \qquad r = 0.988$$

$$\log k_2 = 18.97 - 1.879 \log K^{Cu.phen}_{Cu.phen.L} \qquad r = -0.969$$

$$\log k_{-1} = 3.53 - 0.331 \log K^{Cu.phen}_{Cu.phen.L} \qquad r = -0.955$$

$$\log k_{-2} = 11.28 - 0.713 \log K^{Cu.phen}_{Cu.phen.L} \qquad r = -0.968$$

The correlation equations for the rate constants and dissociation constants of the amino acids are shown below

$$\log k_1^{bipy} = 6.06 - 0.296\ pK_2 \qquad r = 0.954$$

$$\log k_2^{bipy} = 12.24 - 0.886\ pK_2 \qquad r = -1.000$$

$$\log k_{-1}^{bipy} = 2.57 - 0.179\ pK_2 \qquad r = -0.979$$

$$\log k_{-2}^{bipy} = 8.82 - 0.369\ pK_2 \qquad r = -0.993$$

$$\log k_1^{phen} = 6.06 + 0.294\ pK_2 \qquad r = 0.956$$

$$\log k_2^{phen} = 12.43 - 0.881\ pK_2 \qquad r = -0.993$$

$$\log k_{-1}^{phen} = 2.39 - 0.156\ pK_2 \qquad r = -0.987$$

$$\log k_{-2}^{phen} = 8.79 - 0.334\ pK_2 \qquad r = -0.990$$

In addition, an LFER also exists between the rate constants of the mixed ligand complexes having common second ligands but different first ligands

$$\log k_1^{bipy} = -0.053 + 1.008 \log k_1^{phen} \qquad r = 1.000$$

$$\log k_2^{bipy} = -0.225 + 0.995 \log k_2^{phen} \qquad r = 0.995$$

$$\log k_{-1}^{bipy} = -0.177 + 1.156 \log k_{-1}^{phen} \qquad r = 0.999$$

$$\log k_{-2}^{bipy} = -0.832 + 1.093 \log k_{-2}^{phen} \qquad r = 0.989$$

The mechanisms of these complexation reactions have been discussed. It seems likely that with bipy and phen in the inner coordination sphere of the copper ion, the rate-determining step involves both bond-making and bond-breaking processes and the mechanism therefore falls into the Sn2 category.

We have also studied the kinetics and mechanisms of the formation reaction of Ni(II) with *N*-(*para*-substituted phenyl)glycines [26] by using the stopped-flow method. The reactions concerned are

$$Ni^{2+} + HL^{\pm} \xrightarrow{k_1} NiL^{+} + H^{+}$$

$$Ni^{2+} + L^{-} \xrightarrow{k_2} NiL^{+}$$

where L denotes *p*RPhG (R = CH_3O, CH_3, H, Cl) and $HL^{\pm}$ is the zwitter-ion of the substituted amino acid. It has been found that the rate constant and the equilibrium constants show an LFER as follows

$$\log k_1 = 5.36 - 0.432\ pK_2 \qquad r = 0.979$$

$$\log k_2 = 5.56 - 0.815\ pK_2 \qquad r = 0.974$$

$$\log k_2 = 4.84 - 0.973 \log K_{NiL}^{Ni} \qquad r = 1.000$$

The kinetics and mechanisms of formation of the mixed ligand complexes Cu(II)–5Rphen–threonine have also been studied by the stopped-flow method [27], where 5Rphen denotes 5-substituted-1,10-phenanthroline with R = H,, CH_3, Cl, NO_2, and L represents threonine.

The reactions proceed as follows

$$Cu(5Rphen) + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu(5Rphen)L$$

$$Cu(5Rphen)(H_2O)_2 + O\text{–}N\ ^{*} \overset{K_1}{\rightleftharpoons} \underset{\underset{N}{|}}{O}\text{–}Cu(5Rphen)(H_2O) + H_2O \qquad \text{fast}$$

$$\underset{\underset{N}{|}}{O}\text{–}Cu(5Rphen)(H_2O) \xrightarrow{k_2} \overset{O}{\underset{N}{|}}\!\!>Cu(5Rphen) + H_2O \qquad \text{slow}$$

It has been found that some LFER exist as follows

$$\log k_1 = 9.24 - 0.100\ pK_2\ ^{*} \qquad r = 0.959$$

$$\log k_{-1} = -0.167 + 0.274\ pK_2 \qquad r = 0.974$$

$$\log k_2 = 2.55 - 0.141\ pK_2 \qquad r = 0.942$$

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* O–N denotes the functional groups of threonine.

* $K_2 = [H][L]/[HL]$.

The kinetics and mechanisms of the following metal-ion exchange reaction has been studied spectrophotometrically [28]

$$Cu(5Rphen)^{2+} + Ni^{2+} \overset{K_{eq}}{\rightleftharpoons} Ni(5Rphen)^{2+} + Cu^{2+} \qquad (15)$$

with R = H, CH_3, Cl and NO_2. The mechanisms appear to follow three competitive reaction paths

1. Dissociation of CuL (where L = 5Rphen)

$$CuL^{2+} \xrightarrow{k_1} Cu^{2+} + L \qquad \text{slow}$$

$$L + Ni^{2+} \rightarrow NiL^{2+} \qquad \text{fast}$$

2. Acid catalyzed dissociation

$$CuL^{2+} + H^{+} \overset{K_H}{\rightleftharpoons} CuHL^{3+}$$

$$CuHL^{3+} \xrightarrow{k_H} Cu^{2+} + HL^{+}\,i \qquad \text{fast}$$

$$HL^{+} + Ni^{2+} \xrightarrow{k_2} NiL^{2+} + H^{+} \qquad \text{fast}$$

where $k_2 = k_H K_H$

3. Association–Substitution

$$CuL^{2+} + Ni^{2+} \xrightarrow{k_3} NiL^{2+} + Cu^{2+}$$

Again LFER have been found to exist between reaction rate constants and equilibrium constants as follows

$$\log k_1 = -0.288 - 0.349\ pK_2 \qquad r = 0.987$$

$$\log k_2 = 3.27 - 0.481\ pK_2 \qquad r = 0.995$$

$$\log k_3 = 2.47 - 0.502\ pK_2 \qquad r = 0.977$$

$$\log k_3 = -0.513 + 0.235 \log K_{eq} \qquad r = 1.000$$

where K_2 is the first acid dissociation constant of the ligand, and K_{eq} is the equilibrium constant of reaction (15).

C. LINEAR ENTHALPY RELATIONSHIPS

More than two decades ago the author [1] predicted, on theoretical grounds, that there should exist some linear enthalpy relationships between the heat of formation of complex compounds and the heat of dissociation of

the ligand as shown in equation (3). The validity of eqn. (3) was verified, very recently, experimentally, when we first worked on the Cu(II)–*m*RPhG binary system, by the temperature coefficient method [10] and then by a calorimetric method [29].

(i) Temperature coefficient investigations

It has been a common practice to evaluate the enthalpy change of a reaction by means of the temperature coefficient method whenever calorimetric facilities have not been feasible or available. We have evaluated the ΔH values of the Cu(II)–*m*RPhG binary systems [10] by the temperature coefficient method and obtained the following correlation expressions (ΔH_{ML} is the heat of protonation of the ligand. ΔH values are expressed in kJ mol^{-1}.)

at 15 °C: $\Delta H_{M1} = 13.06\ pK_2 - 118.4$ $r = 0.991$

$\Delta H_{M2} = -36.36\ pK_2 + 87.41$ $r = 0.994$

at 25 °C: $\Delta H_{M1} = 19.61\ pK_2 - 146.3$ $r = 0.998$

$\Delta H_{M2} = -54.51\ pK_2 + 164.7$ $r = 0.999$

$\Delta H_{M1} = -64.28 - 0.411\ \Delta H_{HL}$ $r = 0.993$

$\Delta H_{M2} = -63.15 + 1.145\ \Delta H_{HL}$ $r = 0.995$

at 35 °C: $\Delta H_{M1} = 22.76\ pK_2 - 158.9$ $r = 0.994$

$\Delta H_{M2} = -63.11\ pK_2 + 199.2$ $r = 0.993$

(ii) Calorimetric measurement of heats of protonation of ligand and heats of formation of metal complexes

Most recently we have measured the heat of formation of complex compounds and the heat of protonation of ligands of some binary and ternary systems by the calorimetric method. The binary systems studied are Cu(II)–*m*RphG [29], Cu(II)–*p*RphG [30], Ni(II)–*p*RPhG and Ni–*m*RPhG [31], where R = H, CH_3, CH_3O, Cl; the ternary system studied is Cu(II)–bipy–α-amino acids [32] where the amino acids are L-proline, L-valine, L-threonine and D,L-α-aminoisobutyric acid. The correlation expressions of these systems are shown below.

For M(II)–*m*RPhG binary system (ΔH expressed as kJ mol^{-1})

$\Delta H_{CuL} = -9.89 + 0.693\ \Delta H_{HL}$ $r = 0.999$

$\Delta H_{NiL} = -11.95 + 0.229\ \Delta H_{HL}$ $r = 0.995$

where ΔH_{ML} and ΔH_{HL} denote the first-step heat of formation of the complex compounds and the first-step protonation of the ligand, respectively. It is surprising to note that the results obtained from the temperature coefficient method and from the calorimetric method differ appreciably. Analogous phenomena have also been found by Izatt and coworkers [33] in the case of the Cu(II)–amino acids system.

For the M(II)–*p*RPhG binary system

$$\Delta H_{CuL} = -11.3 + 0.37\,\Delta H_{HL}\,(\text{kJ mol}^{-1}) \qquad r = 0.922$$

$$\Delta H_{NiL} = -8.55 + 0.425\,\Delta H_{HL} \qquad r = 0.999$$

For the Cu(II)–bipy–α-amino acids ternary system

$$\Delta H_{ML} = -64.2 - 0.646\,\Delta H_{HL} \qquad r = -0.995$$

The negative slope of the line plotted between ΔH_{ML} and ΔH_{HL} may be ascribed to the formation of a back π-bonding system between the metal ion and bipy [12,14].

D. LINEAR ENTROPY RELATIONSHIPS

As we have seen the existence of linear free energy relationships and linear enthalpy relationships in coordination chemistry, it is logical to anticipate the existence of linear entropy relationships. As a matter of fact, we have found such relationships in the study of M(II)–*N*-substituted phenyl glycinates binary systems. By means of the temperature coefficient method we have evaluated the ΔG and ΔH protonation values of *m*RPhG and also that of formation of their complex compounds with Cu(II); hence the corresponding ΔS values have been calculated [10]. The correlation expressions for the linear entropy relationships are as follows

at 25°C: $\Delta S_{M1} = -84.20 + 0.705\,\Delta S_{HL}\,(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.992$

$$\Delta S_{M2} = -133.5 + 0.658\,\Delta S_{HL}\,(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.993$$

where ΔS_{M1} and ΔS_{M2} are the entropy change for the first step and the second step of the formation reactions of the complex compounds, respectively; ΔS_{HL} is the entropy change for protonation of the ligand, *m*RPhG.

In addition, ΔS_{M1} and ΔS_{M2} show linear relationships with the pK_2 values of the ligand at different temperatures

at 15°C: $\Delta S_{M1} = 66.98\ pK_2 - 418.7(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.992$

$$\Delta S_{M2} = -61.04\ pK_2 + 171.5(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.987$$

at 25°C: $\Delta S_{M1} = 99.28\ pK_2 - 555.6(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.998$

$$\Delta S_{M2} = -91.83\ pK_2 + 302.7(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.993$$

at 35°C: $\Delta S_{M1} = 116.2\ pK_2 - 624.5(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.995$

$$\Delta S_{M2} = -105.3\ pK_2 + 356.2(\text{J mol}^{-1}\,\text{K}^{-1}) \qquad r = 0.981$$

However, from a calorimetric study of the same system we found the following correlation expression [25]

$$\Delta S_{ML} = 12.4 + 0.400\ \Delta S_{HL} \qquad r = 0.999$$

Here, the deviation is so large that further investigation should be made.

Calorimetric measurement for the Ni(II)–*p*RPhG binary system generates:

$$\Delta S_{NiL} = -1.72 + 0.335\ \Delta S_{HL} \qquad r = 0.990$$

and for the Ni(II)–*m*RPhG binary system

$$\Delta S_{NiL} = 5.46 + 1.01\ \Delta S_{HL} \qquad r = 0.983$$

E. CORRELATION ANALYSIS ON VARIOUS ENERGY PROPERTIES

LFER and its application in fields other than coordination chemistry have been reviewed in some monographs [2,3]. In this article we present only some of our work on various energy properties.

When we studied the dipole moment of nine *N*-substituted phenyl glycine ethyl esters ($RC_6H_4NHCH_2COOC_2H_5$, R = *p*-CH_3O, *p*-CH_3, *p*-Cl, *p*-NO_2, H, *m*-CH_3O, *m*-CH_3, *m*-Cl, *m*-NO_2) [34], LFER were found to exist between the dipole moment of these ethylglycinates and their base strengths (log K values; Fig. 12) and some other related parameters such as pK_2 values of the corresponding amino acids (Fig. 13), Hammett σ values (Fig. 14), stability constants of the corresponding amino acids with Cu(II) (log K_{ML}) (Fig. 15), etc. These curves show breaks with electron attracting substituent groups on one line and electron releasing substituent groups on another.

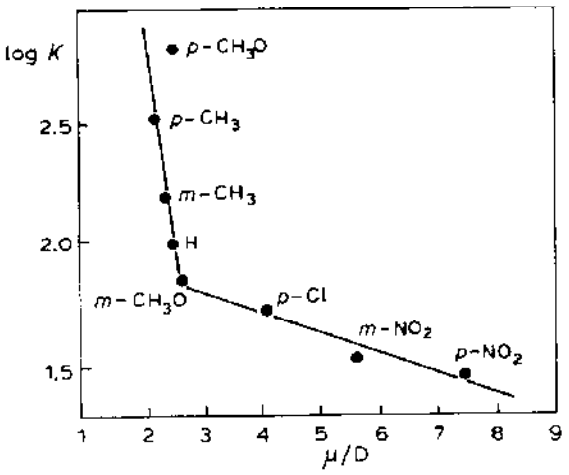

Fig. 12. Plot [34] of log K for RPhGEt vs. dipole moment μ in 30% (v/v) dioxane.

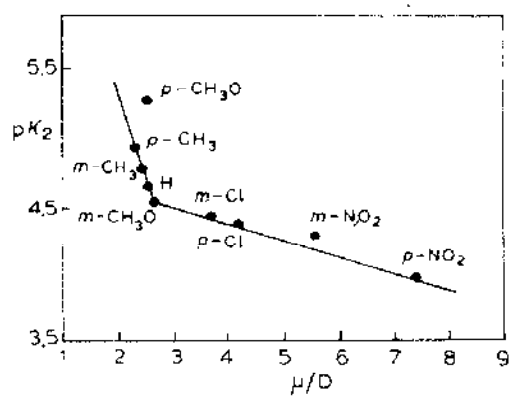

Fig. 13. Plot [34] of pK_2 for RPhG vs. dipole moment μ for RPhGEt.

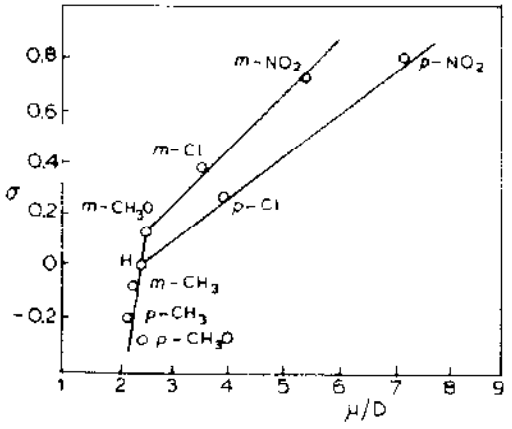

Fig. 14. Plot [34] of σ for RPhG vs. dipole moment μ for RPhGEt.

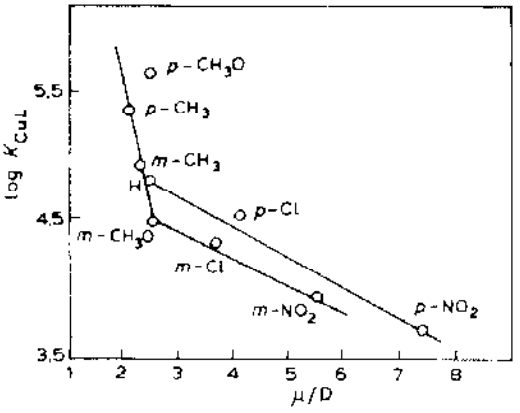

Fig. 15. Plot [34] of log K_{ML} for Cu(II)–RPhG vs. dipole moment μ for RPhGEt.

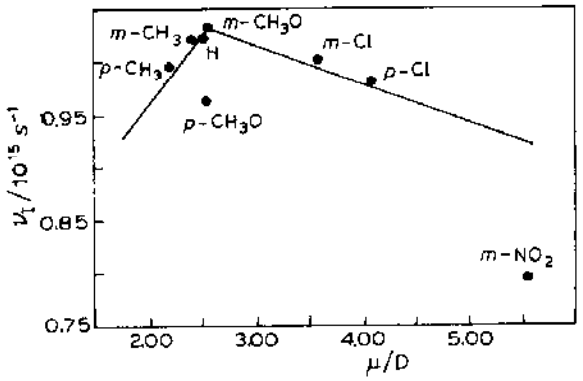

Fig. 16. Plot [35] of ν_1 vs. dipole moment μ for RPhGEt.

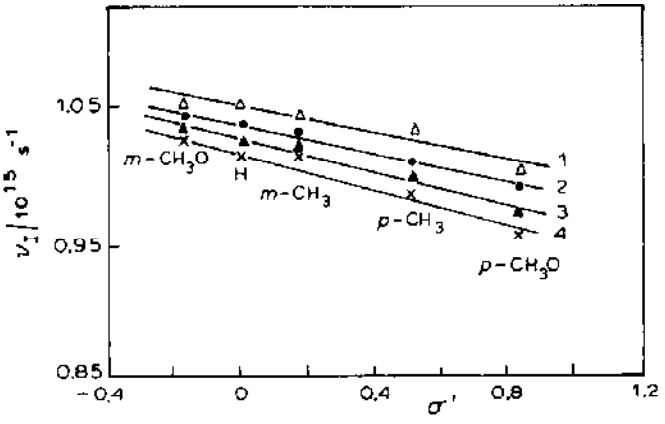

Fig. 17. Plot [35] of ν_1 vs. σ' for RPhGEt. 1, in water; 2, in 30% dioxane; 3, in ethanol; 4, in benzene.

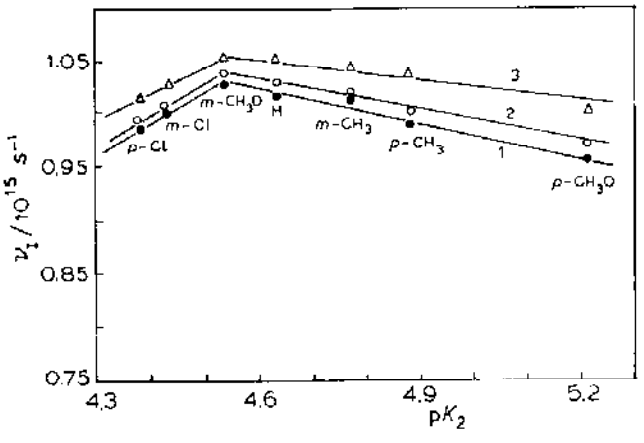

Fig. 18. Plot [35] of ν_1 for RPhGEt vs. pK_2 for RPhG. 1, in benzene; 2, in ethanol; 3, in water.

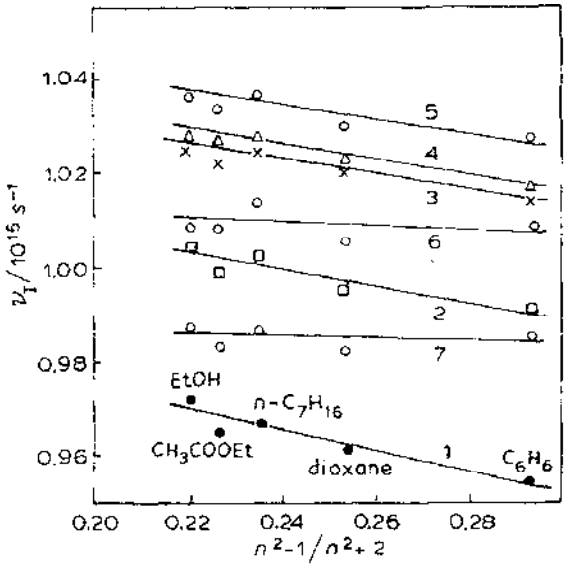

Fig. 19. Plot [35] of ν_i for RPhGEt vs. $(n^2-1)/(n^2+2)$ of solvents: 1, p-CH_3O; 2, p-CH_3; 3, m-CH_3; 4, H; 5, m-CH_3O; 6, m-Cl; 7, p-Cl.

We have also investigated the UV spectra of the *N*-substituted phenyl ethylglycinates mentioned above in various solvents such as water, dioxane, ethanol, ethyl ester, heptane, benzene, etc. [35]. The results show that linear relationships exist between the following pairs of parameters: (1) dipole

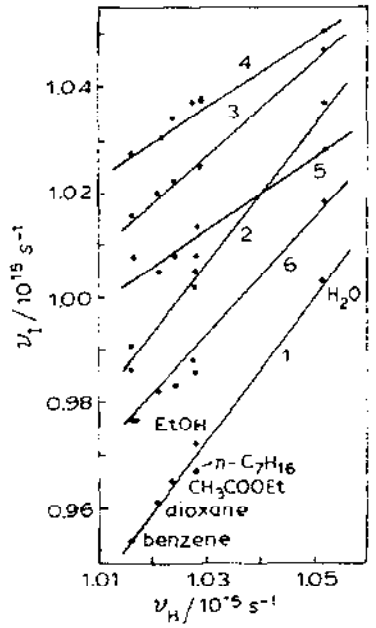

Fig. 20. Plot [35] for RPhGEt vs. ν_i for PhGEt in different solvents: 1, p-CH_3O; 2, p-CH_3; 3, m-CH_3; 4, m-CH_3O; 5, m-Cl; 6, p-Cl.

moment of these esters and the frequency ν_I of UV absorptions in various solvents (Fig. 16); (2) ν_I of these esters and their σ' values (Fig. 17); (3) ν_I of the esters and pK_2 values of their corresponding amino acids (Fig. 18); (4) ν_I of the esters and the $(n^2-1)/(n^2+2)$ values of solvents, where n is the refraction index of the solvent (Fig. 19); (5) the ν_I values of the same substituted RPhGEt and the ν_H values of the unsubstituted PhGEt (Fig. 20). Again it was found that some of the curves show breaks with electron attracting substituent groups on one line and electron releasing substituent groups on another, similar to those which were found in the case of the Hammett σ parameter and dipole moment relationships.

F. CONCLUDING REMARKS

Of the three linear thermodynamic function relationships discussed in coordination chemistry, only LFER has been extensively studied in the past few decades and abundant data have been accumulated in the literature to verify its validity. There is no doubt that the method of LFER is still the most practical method for predicting substituent effects on reactions in liquid solution, not only in coordination chemistry but also in many other branches of chemistry and related subjects. It has a sound theoretical basis [36] and should not be disparaged as being an empirical method.

We have recently explored the subject of linear enthalpy and linear entropy relationships and our preliminary investigations show explicitly their validity as expressed in the form of equation (3). However, this virgin land is only beginning to be explored and undoubtedly there will be new adventures as more precise calorimeters are commercially available. We can foresee that there will be an upsurge in solution calorimetric studies and the trend will be from binary to ternary and even higher systems. This new field will see its horizon lying ahead.

The subject of linear entropy relationships has not been as extensively expounded as LFER and linear enthalpy relationships. Even though some good LFER and linear enthalpy relationships exist in a certain system, it does not always follow that a good linear entropy relationship 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 of measuring both ΔH and ΔG values will enter the calculation and thus contribute to more serious errors in the evaluation of ΔS. This might be an explanation for the deviation of entropy terms from linearity.

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