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Thermodynamic relationships on complex formation. Part VII. ΔH–ΔS interplay in the equilibria for the formation of amine complexes in aqueous solution

Domenico De Marco[a,*], Antonino Giannetto[a], Wolfgang Linert[b]

[a] *Department of Inorganic, Analytical Chemistry and Molecular Structure, University of Messina, Salita Sperone 31, CP 30, 98166 S. Agata, Messina, Italy*

[b] *Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1050 Vienna, Austria*

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Abstract

ΔH–ΔS values for the protonation and complexing reaction series of amines in aqueous solution have been inspected for the occurrence of functional relationships or regular patterns. Both non-linear and anti-compensative relationships have been evidenced.

Keywords: Amine complexes; Enthalpy–entropy relationships; Isoequilibrium relationships

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1. Introduction

The occurrence of ΔH–ΔS relationships in chemical processes has been a debated topic during recent years and in the opinion of some scientists they are the consequence of statistical links between the two parameters associated with the experimental methods for their determination [1–4 and references cited therein].

Even acknowledging the possibility of the occurrence of statistical links, the parameters which describe the status of a system are mutually interconnected. With such a premise and on condition that the relationship within the describer parameters can be expressed by means of continuous functions, the changes in the system, expressed by changes in the values of the describers, follow precise functional behaviours.

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* Corresponding author.

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It has been widely demonstrated that in many cases the parameters of the Gibbs equation of a homologous series of reactions are pairwise linearly related [5–12]. In particular, linear ΔH–ΔS interplays have been found in the following complex formation equilibria:

(1) The complex formation reactions of Ag^+ with thiourea and N-substituted thioureas in aqueous solution in methanol and in ethanol [13–15];

(2) The complex formation reactions of Hg(II) with thiourea and N-substituted thioureas in aqueous solution [16];

(3) The complex formation reactions of Ag^+ complex substrata with different inorganic ligands in aqueous solution [8];

(4) The stepwise complex formation reactions of tervalent lanthanides with oxygen donor ligands in aqueous solution [7, 17].

Very tight linear compensative ΔH–ΔS interplay has also been observed in the stepwise self-protonation reaction series of the *N*-methyl-substituted derivatives of diethylenetriamine in aqueous solution [21] ($d(\Delta H)/d(\Delta S) = 0.321$; isoequilibrium temperature $t_{iso} = 48$°C) and in the series of gaseous reactions between trimethylboron and NH_3 or *N*-methylamines ($d(\Delta H)/d(\Delta S) = 0.542$; $t_{iso} = 259$°C. Fig. 1).

Knowledge of the factors responsible for actual behaviour is of paramount importance for a general theory on the isoequilibrium relationships. In the present article, the thermodynamic data for the series of protonation or complexation reactions of nitrogen bases (ammonia, amines, polyamines) in aqueous solution have been analysed for the occurrence of clear ΔH–ΔS interplay.

The investigated reactions have been organized according to the following series:

(1) The reactions of variable metal ions with ammonia;

(2) The reactions of variable monoamines with proton or Ag(I);

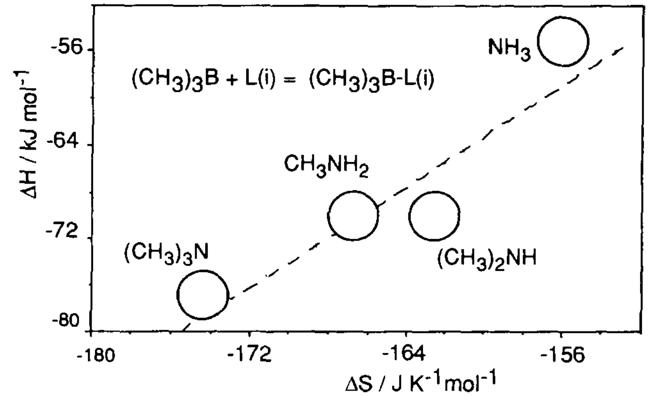


Fig. 1. ΔH–ΔS interplay in the gaseous reaction series for the formation of adducts between trimethylboron and ammonia or *N*-methylamines: $(CH_3)_3B + L_{(i)} = (CH_3)_3B–L_{(i)}$; $L_{(i)}$ is variable. Data from Ref. [22]; $t = 100$°C. Equation of the trends: $\Delta H = \Delta H_{res} + \tau\Delta S$; $\Delta H_{res} = -24.32 \pm 74$ kJ mol^{-1}; $\tau = 0.542 \pm 0.4$ K/1000; $R = 0.695$.

(3) The reactions of variable metal ions with primary diamines;
(4) The reactions of variable *N*-methyl-substituted triamines with Ag(I).

2. ΔH–ΔS interplay in the series of reactions between proton or metal ions and nitrogen bases

2.1. Reaction series with NH_3 (*Fig. 2*)

The enthalpy changes for the stepwise coordination reactions of NH_3 to different metal ion – ammonia complexes ($M_{(i)}(NH_3)_{n-1} + NH_3 = M_{(i)}(NH_3)_n$, where $M_{(i)}$ is

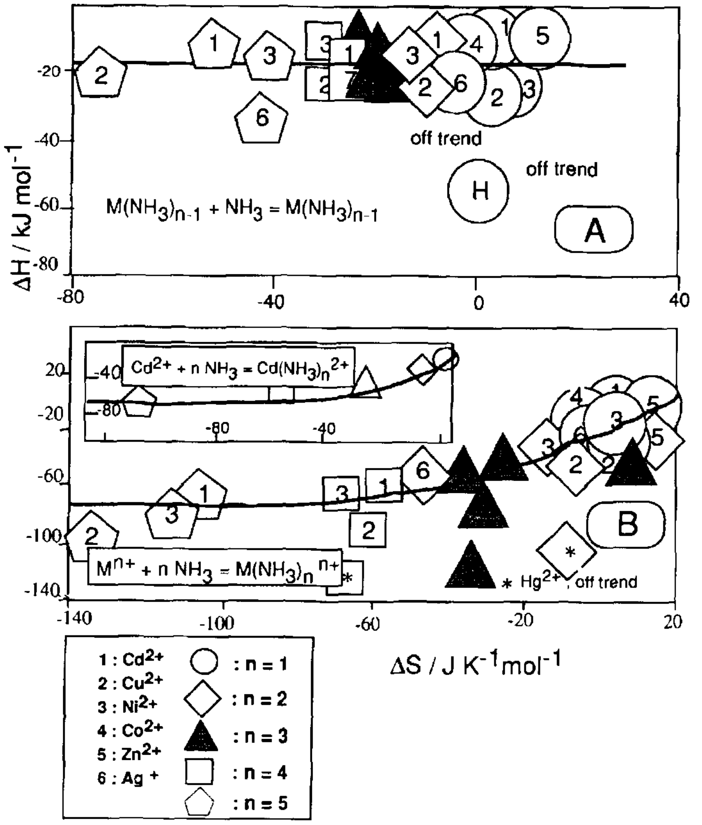
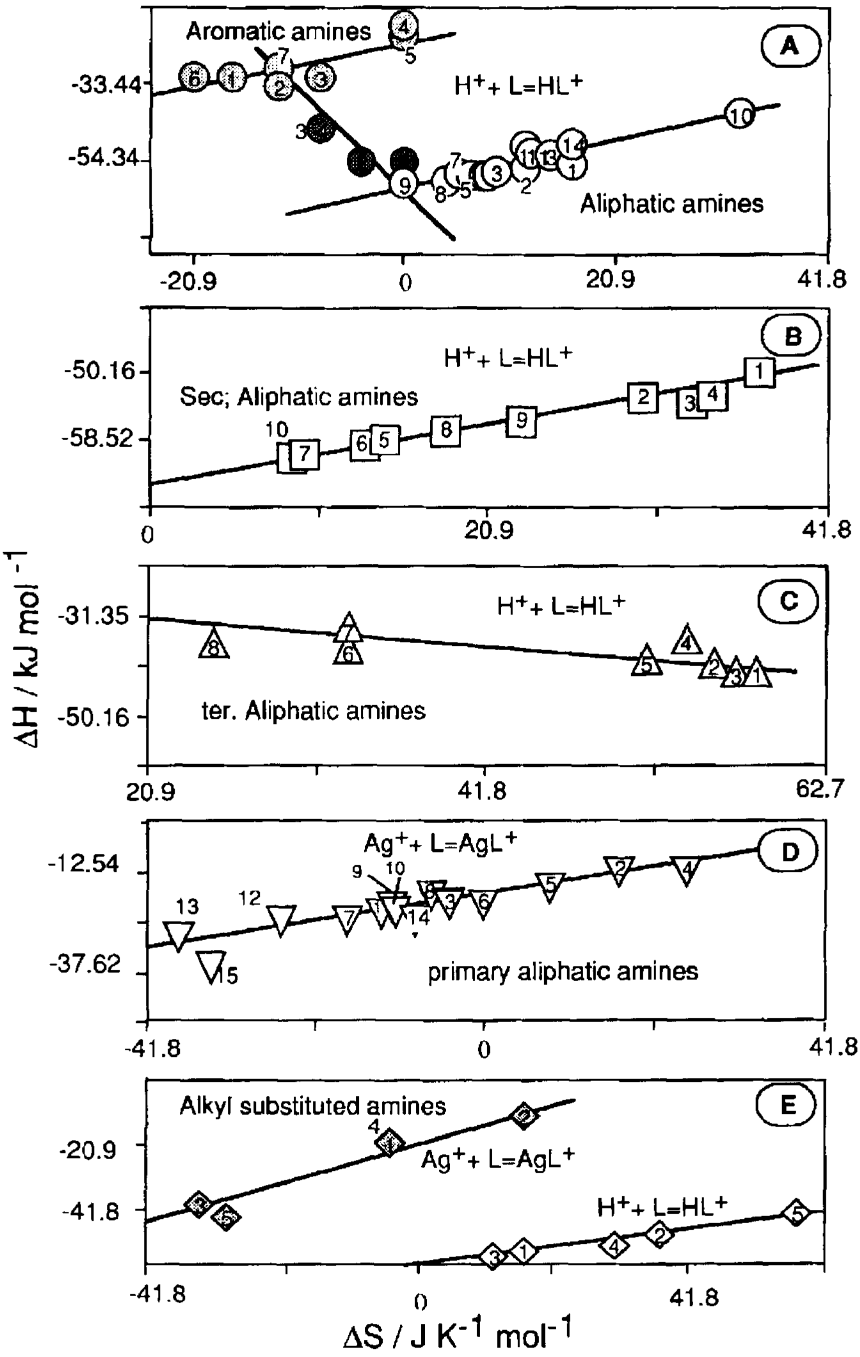


Fig. 2. ΔH–ΔS interplay in the complexing reactions of ammonia with different cations in aqueous solution at $t = 26.8°$ or 25°C (see Ref.) and 2 M KNO_3. Data from Refs. [23,24]. A. Stepwise complexing reaction series $M_{(i)}(NH_3)_{n-1} + NH_3 = M_{(i)}(NH_3)_n$; $M_{(i)}$ is variable. $\Delta H = \text{Const.} = -17.58 \pm 3.7$ kJ mol^{-1}. B. Complexing reaction series: $M_{(i)} + nNH_3 = M_{(i)}(NH_3)_n$; $M_{(i)}$ is variable. Proposed equation for the trend: $\Delta H = \Delta H_x + D\exp(\alpha\Delta S)$: $\Delta H_x = -99.14 \pm 15$ kJ mol^{-1}; $D = 65.7 \pm 15$ kJ mol^{-1}; $\alpha = 0.26 \pm 0.12$ J^{-1} K mol.


A
Aromatic amines
H⁺+ L=HL⁺
Aliphatic amines
-33.44
-54.34
-20.9
0
20.9
41.8
B
H⁺+ L=HL⁺
Sec; Aliphatic amines
-50.16
-58.52
0
20.9
41.8
C
H⁺+ L=HL⁺
ter. Aliphatic amines
-31.35
-50.16
20.9
41.8
62.7
D
Ag⁺+ L=AgL⁺
primary aliphatic amines
-12.54
-37.62
-41.8
0
41.8
E
Alkyl substituted amines
Ag⁺+ L=AgL⁺
H⁺+ L=HL⁺
-20.9
-41.8
-41.8
0
41.8
ΔH / kJ mol -1
ΔS / J K-1 mol-1

variable. Fig. 2A: Charges are omitted for simplicity are exothermic in nature. The ΔH values ($\approx$ 4–6 kcl mol^{-1}) are independent of the coordination level n and the nature of the central ion for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Ag^{+}. Also the corresponding entropy changes do not depend on the nature of the central cations but are strictly related to the coordination level. On increasing the number of coordinated ligands, a systematic shift towards more unfavourable values is observed.

The protonation reaction of NH_3 is unusual, for more favourable enthalpy change being $\Delta S \approx 0$, inside the range of formation of 1:1 complexes.

The enthalpy–entropy interplay for the overall complexing reaction series $M_{(i)} + nNH_3 = M_{(i)}(NH_3)_n$, ($n$ is variable) (Fig. 2B), describes an upwards curvilinear trend. The trend is more evident if one refers to the complexing reactions of one cation.

2.2. *Reaction series with monoamines* (*Fig. 3*)

In the series of protonation reactions of primary (aliphatic or aromatic), secondary or tertiary amines and in the complexing reactions of Ag^{+} with primary amines, linear ΔH–ΔS trends are found in all the analysed cases.

Fig. 3. ΔH–ΔS interplay in the reaction series of substituted monoamines with proton ($H^{+} + L = HL^{+}$) or Ag^{+} ($Ag^{+} + L = AgL^{+}$) at $t = 25°C$ and ionic strength = 0 (in Fig. 3D, symbols 8–11 refer to data at ionic strength 0.5). Data are from Ref. [23]. Equation of the trends: $\Delta H = \Delta H_{res} + \tau \Delta S$. A. Primary amines. Aliphatic amines: $\Delta H_{res} = -61.9 \pm 4.2$ kJ mol^{-1}; $\tau = 0.593 \pm 0.3$ K/1000; $R = 0.932$. Aromatic amines: $\Delta H_{res} = -21.4 \pm 4.2$ kJ mol^{-1}; $\tau = 0.677 \pm 0.2$ K/1000; $R = 0.836$. B. Secondary aliphatic amines. $\Delta H_{res} = -63.6 \pm 0.5$ kJ mol^{-1}; $\tau = 0.321 \pm 0.02$ K/1000; $R = 0.984$. C. Tertiary aliphatic amines ($H^{+} + L = HL^{+}$). $\Delta H_{res} = -29.5 \pm 3.3$ kJ mol^{-1}; $\tau = -0.171 \pm 0.07$ K/1000; $R = 0.668$. D. Primary aliphatic amines. $\Delta H_{res} = -19.5 \pm 3.3$ kJ mol^{-1}; $\tau = 0.339 \pm 0.04$ K/1000; $R = 0.915$. E. Amines. $H^{+} + L = HL^{+}$: $\Delta H_{res} = -60.8 \pm 0.8$ kJ mol^{-1}; $\tau = 0.285 \pm 0.03$ K/1000; $R = 0.988$. $Ag^{+} + L = AgL^{+}$: $\Delta H_{res} = -20.72 \pm 0.4$ kJ mol^{-1}; $\tau = 0.657 \pm 0.01$ K/1000; $R = 0.967$.

A: Primary amines.

Aliphatic amines: 1, methylamine; 2, ethylamine; 3, *n*-propylamine; 4, *n*-butylamine; 5, *n*-pentylamine; 6, *n*-hexylamine; 7, 2-methylpropylamine; 8, cyclopentylamine; 9, cyclohexylamine; 10, 2-aminoethanesulphonic acid; 11, 2-aminoethanol; 12, DL-1-amino-2-propanol; 13, 3-aminopropanol; 14, 2-methoxyethylamine. Shaded symbols: 1, prop-2-enylamine; 2, benzylamine; 3, glycine-methylester; 4, glycine-ethylester.

Aromatic amines: 1, aminobenzene; 2, 2-methylaniline; 3, 4-methylaniline; 4, 3-aminobenzensulphonic acid; 5, 4-aminobenzensulphonic acid; 6, 2-methoxyaniline; 7, 4-methoxyaniline.

B: Secondary amines.

1, Dimethylamine; 2, diethylamine; 3, tetramethylenimine; 4, pentamethylenimine; 5, DL-2-methylpiperidine; 6, DL-2-ethylpiperidine; 7, DL-2-propylpiperidine; 8, DL-3-methylpiperidine; 9, 4-methylpiperidine; 10, DL-2, 6-dimethylpiperidine.

C: Tertiary amines.

1, Triethylamine: 2, *N*-methylpiperidine; 3, *N*-ethylpiperidine; 4, 2-dimethylaminoethanol; 5, 2-diethylaminoethanol; 6, *N*-methylimino-di-2-ethanol; 7, triethanolamine; 8, tris(2-hydroxypropyl)amine.

D: Primary amines.

1, Ammonia; 2, methylamine; 3, ethylamine; 4, *n*-propylamine; 5, *n*-buthylamine; 6, *n*-penthylamine; 7, *n*-hexylamine; 8, 2-aminoethane-sulphonic acid; 9, 2-aminopropane-sulphonic acid; 10, 2-aminobutane-sulphonic acid; 11, 2- aminopentane-sulphonic acid; 12, 2-methoxyethylamine; 13, ethanolamine; 14, tris(hydroxymethyl)aminoethane; 15, 2-4-2-aminoethylthio ethanol.

E: Amines

1, Ammonia; 2, methylamine; 3, dimethylamine; 4, ethylamine; 5, diethylamine; 6, triethylamine

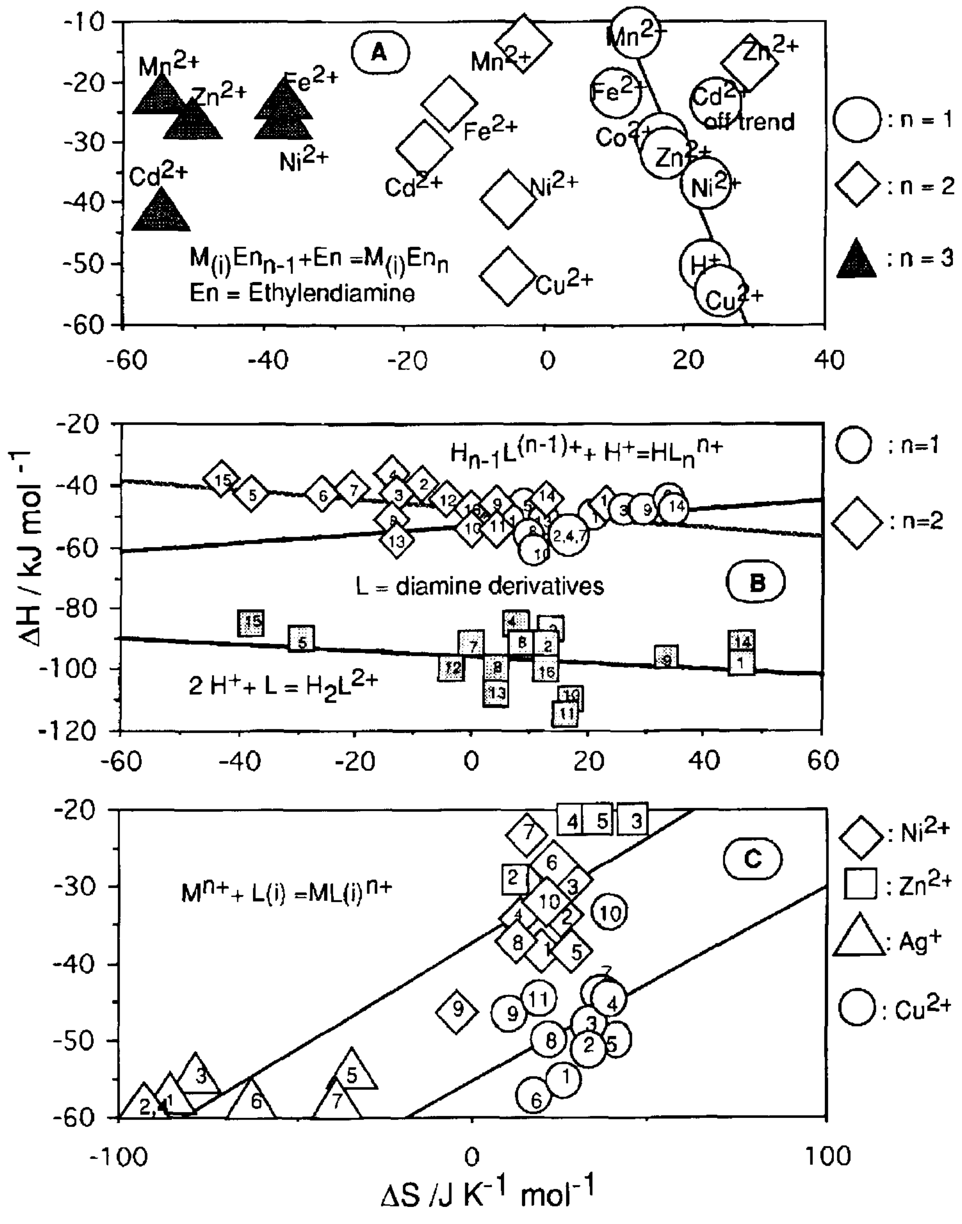


Fig. 4. ΔH–ΔS interplay in the series of reactions of primary diamines with proton or metal ions. Experimental conditions in the key. Data are from Ref. [23]. Equation of the trends: $\Delta H = \Delta H_{\mathrm{res}} + \tau \Delta S$. A. $\mathrm{L} + \mathrm{H}^+ = \mathrm{HL}^+$ or $\mathrm{L} + \mathrm{M}^{2+} = \mathrm{ML}^{2+}$; $\Delta H_{\mathrm{res}} = +18 \pm 7.1$ kJ mol^{-1}; $\tau = -2.76 \pm 0.4$ 4K/1000; $R = -0.95$. B. Stepwise protonations ($H_{n-1}\mathrm{L}^{(n-1)+} + \mathrm{H}^+ = \mathrm{H}_n\mathrm{L}^{n+}$; L is primary diamine): $n = 1$: $\Delta H_{\mathrm{res}} = -53 \pm 1.7$ kJ mol^{-1}; $\tau = 0.139 \pm 0.1$ K/1000; $R = 0.346$. $n = 2$: $\Delta H_{\mathrm{res}} = -47.6 \pm 0.8$ kJ mol^{-1}; $\tau = -0.153 \pm 0.1$ K/1000; $R = -0.456$. Overall protonation ($\mathrm{L} + n\mathrm{H}^+ = \mathrm{H}_n\mathrm{L}^{n+}$; L is primary diamine:

The protonation of primary amines describes two separated and almost parallel trends: the lower one for the aliphatic series, and the upper for the aromatic series. The trends are "linked" by means of a set of reactions whose ΔH–ΔS behaviour is anti-compensative (cooperative) in nature (Fig. 3A).

The ranges of the entropy changes move toward more favourable values according to the following sequences: primary aromatic (≈ -20–$0\,\mathrm{J\,K^{-1}\,mol^{-1}}$) < primary aliphatic ($\approx 0$–$+20\,\mathrm{J\,K^{-1}\,mol^{-1}}$) < secondary aliphatic ($\approx +10$–$+40\,\mathrm{J\,K^{-1}\,mol^{-1}}$) < tertiary aliphatic ($\approx +20$–$+60\,\mathrm{J\,K^{-1}\,mol^{-1}}$).

A different sequence is observed in the reactions series of *N*-substituted alkyl amines with Ag^+(Fig. 3E); therefore, the above tendency is not a general one but also depends on the acceptor.

The sensitivity of $d(\Delta H)/d(\Delta S) = \tau$ decrease sharply in the sequence: primary amines > secondary amines > tertiary amines. Unfortunately there are no data for deciding whether the observed tendency depends on the nature of the acceptor as well. The series of reactions of tertiary aliphatic amines shows anti-compensative behaviour ($\tau = -0.171$ K/1000).

2.3. Reaction series with primary diamines (Fig. 4)

The 1 : 1 reactions of ethylenediamine with proton and with the divalent metal ions of the first transition row from Mn^{2+} to Zn^{2+} (Fig. 4A) show anti-compensative behav-

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(Fig. 4. Caption continued)

(30,1). C. For Zn^{2+} series: 1, ethylenediamine (25,1.4); 2, meso(*cis*)cyclohexane-1-2-diamine (25,0); 3, meso(*trans*)cyclohexane-1-2-diamine (25,0); 4, 2,2-dimethyltrimethylenediamine (30,1); 5, thiobis(2-ethylamine) (30,1).

$\Delta H_{\mathrm{res}} = -95.7 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$; $\tau = -0.1 \pm 0.1$ K/1000; $R = -0.246$. D: $L + M^{n+} = ML^{n+}$; L is primary diamine.

For Ni^{2+}, Zn^{2+} and Ag+ series: $\Delta H_{\mathrm{res}} = -33.4 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$; $\tau = 0.276 \pm 0.03$ K/1000; $R = 0.915$.

For Cu^{2+} series; $\Delta H_{\mathrm{res}} = -55.2 \pm 58\,\mathrm{kJ\,mol^{-1}}$; $\tau = 0.277 \pm 0.2$ K/1000; $R = 0.36$.

Key: °C and ionic strength in parentheses.

B. 1, Ethylenediamine (25, 1.4); 2, DL-1-methylethylenediamine (25,0); 3, DL-1-ethylethylenediamine (25,0); 4, 1,1-dimethylethylenediamine (25,0); 5, DL-1-phenylethylenediamine (25,0); 6, meso(*cis*)cyclohexane-1-2-diamine (25,0); 7, meso(*trans*)Cyclohexane-1-2-diamine (25.0); 8, trimethylenediamine (25,0.3): 9, 2.2-dimethyltrimethylenediamine (30,1): 10, tetramethylenediamine (25,0.5); 11, pentamethylenediamine (25,0.5): 12, 1.3-diamino-2-propanol (25,0); 13, oxybis(2-ethylamine) (25,0); 14, ethylenebis(oxy-2-ethylamine) (25,0); 15, D L-2,3-diaminopropanoic acid methylester (25,0.1); 16, thiobis(2-ethylamine)

For Ni^{2+} series: 1, ethylenediamine (25,1); 2, DL-1-methylethylendiamine (25,0); 3, 1,1-dimethylethylenediamine (25,0); 4, meso(*cis*)cyclohexane-1-2-diamine (25,0); 5, meso(*trans*)cyclohexane-1-2-diamine (25,0); 6, trimethylendiamine (25,0.3); 7, 2,2-dimethyltrimethylenediamine (25,0.3): 8, 1,3-diamino-2-propanol (25,0); 9, thiobis(2-ethylamine) (30,1); 10, ethylenbis(thio-2-ethylamine) (30,1).

For Ag^+ series: 1, trimethylenediamine (25,0.3); 2, tetramethylenediamine (25,0.5); 3 1,3-diamino-2-propanol (25,0); 4, oxybis(2-ethylamine) (25,0); 5, ethylenbis(oxy-2-ethylamine) (25,0); 6, thiobis(2-ethylamine) (30,1); 7, 2[2-(2aminoethyloxy)ethylthio]ethylamine (25,0).

For Cu^{2+} series: 1, ethylenediamine (25,1); 2, DL-1-methylethylenediamine (25,0); 3, DL-1-ethylethylenediamine (25,0); 4, 1,1-dimethylethydiamine (25,0); 5, meso(*cis*)cyclohexane-1-2-diamine (25,0); 6, DL-(*trans*-)cyclohexane-1-2-diamine(25,0); 7, trimethylenediamine (25,0.3); 8, 2,2-dimethyltrimethylenediamine (30,1); 9, oxybis(2-ethylamine) (25,0); 10, ethylenbis(oxy-2-ethylamine) (25,0); 12, D,L-2,3-diaminopropanoic acid methylester (25,0.1).

iour ($d(\Delta H)/d(\Delta S) = -2.66 \pm 0.4$ K/1000; $R = -0.95$). By extending the series to ethylenediamine-related ligands (the data are not reproduced in Fig. 4A), the enthalpy–entropy correlation of the extended series becomes less obvious, but still maintains an anti-compensative aspect.

The reactions for the subsequent second and third stepwise ligand coordinations do not show well-defined functional interplay.

The stepwise protonation reactions of enthylenediamine and related ligands (Fig. 4B) show essentially constant stepwise protonation enthalpy changes, but the steps are discriminated for different entropy ranges: on increasing the protonation level, the entropy range moves towards more favourable values.

In the complexing reaction series with metal ions (actually with Ni^{2+}, Zn^{2+}, Cu^{2+} and Ag^{+}, Fig. 4C), the compensative ΔH–ΔS behaviour is fairly evident and different ions (Ag^{+}, Ni^{2+}, Zn^{2+}, but not Cu^{2+}) describe a single trend, as for the case of the series of reactions between metal ions and NH_3.

The series for Cu^{2+} is more favoured than the previous ones.

2.4. *Reaction series with N-methyl-substituted diethylenetriamines* (*Fig. 5*)

The stepwise protonations reaction series of *N*-methyl-substituted diethylenetriamines shows three trends related to the first, second and third stepwise protonation,

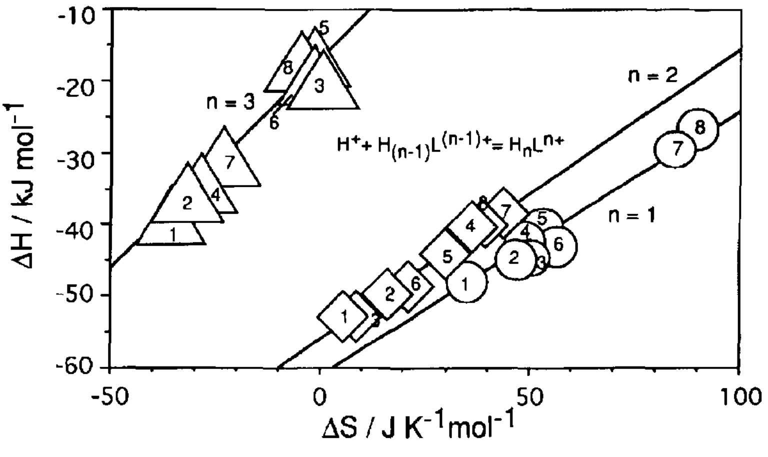

Fig. 5. ΔH–ΔS interplay in the reaction series for the stepwise protonation of *N*-methyl-substituted ethylenetriamines $H_{n-1}L^{(n-1)+} + H^+ = H_nL^{n+}$ at $t = 25°C$ and 1.3 M for KNO_3. Data are from Ref. [21]. General equation of the trends: $\Delta H = \Delta H_{res} + \tau\, \Delta S$. Reaction series: $H_{n-1}L^{+} + H^{+} = H_nL^{n+}$.
For $n = 1$: $\Delta H_{res} = -61.1 \pm 1.3$ kJ mol^{-1}; $\tau = 0.368 \pm 0.02$ K/1000; $R = 0.989$.
For $n = 2$: $\Delta H_{res} = -55.9 \pm 0.8$ kJ mol^{-1}; $\tau = 0.401 \pm 0.03$ K/1000; $R = 0.979$.
For $n = 3$: $\Delta H_{res} = -16.7 \pm 0.8$ kJ mol^{-1}; $\tau = 0.587 \pm 0.04$K/1000; $R = 0.980$.
Key: 1, diethylenetriamine, 2, 1-methyldiethylenetriamine; 3, 1,1-dimethyldiethylenetriamine; 4, 1,1,4-trimethyldiethylenetriamine; 5, 1,4-dimethyldiethylenetriamine; 6, 1,47-trimethyldiethylenetriamine; 7, 1,1,7,7-tetramethyldiethylenetriamine; 8, 1,1,4,7,7-pentamethyldiethylenetriamine.

respectively. The trends related to the first and second protonations are parallel and very similar, but clearly distinct from that related to the third stepwise protonation.

3. General remarks

The functional relationship between ΔH and ΔS in a series of homologous reactions series is not necessarily a linear one. When such relationship does occur, it is very important, yet also very difficult, to decide on the actual relationship between the two variables, which depends on the particular coupling of the enthalpy levels with the corresponding entropy levels for the specific series of reactions.

The proposed exponential dependence of the ΔH values on the respective ΔS values in Fig. 2B is founded on an empirical basis, namely (a) the asymptotic shape of the ΔH–ΔS trend and (b) the value of the sensitivities which follow approximately linearly the ΔS values.

The homologous series of reactions represented in Fig. 2B is obtained by changing (i) the number of NH_3 groups bound to the central ion and (ii) the central ion itself. The complexing reactions of the whole set of cations, except Hg^{2+}, describe one trend even though the cations are different in nature.

From the uniqueness of the behaviour, an appreciable "Shielding Effect" exerted by the solvent on the properties of a single (gaseous) ion can be proposed, which results in a smoothing of the differences in the specific properties of the different ions.

In a homologous series of reactions with precise ΔH–ΔS interplay, the mutual influence between the changes in the values of the parameters is not necessarily compensative in nature.

4. Specific remarks

In the protonation reactions of primary monoamines, the sensitivities, $d(\Delta H)/d(\Delta S) = \tau$, are related to the number of alkyl substituents to the nitrogen atom. The protonation reactions of primary aliphatic and aromatic monoamines describe two linear and parallel trends distinguished by their intercepts. For the series of primary, secondary and tertiary monoamines, the slope τ decreases according to the sequence $\tau_{\text{primary}} > \tau_{\text{secondary}} > \tau_{\text{tertiary}}$. The lack of data for the complexing reactions of metal ions with secondary and tertiary monoamines prevents any decision about the general effectiveness of this sequence.

The actual value of τ in a series of related reactions depends both on the nature of the central ion and the ligand.

The ΔH values for the series of protonation reactions of diamines show lower sensitivity to the ΔS changes than the corresponding series of monoprotonation reactions of primary monoamines. The same tendency is found for the 1:1

complex formation with Ag^+ (Fig. 3D and Fig. 4C). Moreover, in the case of diamines, the ΔH for the isoentropy reaction belonging to the trend is about twice as favourable.

In the case of primary diamines, the first proton probably interacts with both the amine groups. Such a hypothesis is suggested by the different behaviour of the series of monoamines compared with diamines in the protonation reactions.

For the *N*-methyl-substituted derivatives of diethylenetriamine, the reaction for the first and second protonation reactions describes two parallel closely linear ΔH–ΔS trends and reveals the occurrence of the single mechanism responsible for the energetics of the two series of reactions. Moreover, it can be observed that the parameters of the trends are very similar to the values for the series related to the protonation of monoamines and generated by means of successive different substitutions to the nitrogen atom (Fig. 3E, $\Delta H_{res} = -14.52 \pm 0.2$ and $\tau = 0.285 \pm 0.03$). As a consequence, it is very probable that the first and second protonations occur at the terminal nitrogen atom, which exerts the least reciprocal influence.

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