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Correlation between thermodynamic functions of metal complex. formation and basicities of the iminodiacetate derivatives

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Abstract

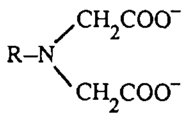
The heat developed by addition of a metal nitrate solution to that of a neutralized complexing agent has been determined at 25 °C and $I=0.1$ (KNO_3). By use of the known stability constants of the 1:1 complexes, it allows the calculation of the involved thermodynamic functions. The change of the free enthalpies of metal complex formation with substituted iminodiacetate derivatives of different basicities is correlated with that of the enthalpies of complex formation whereas the entropic term depends on the ligand size.

Introduction

It is well known that the stability constants of the 1:1 complexes $ML^{(\nu-z)-}$ formed by metal ions M^{z+} with a series of related ligands $L^{\nu-}$, having different basicities, depend strongly on their protonation constants K_{HL} of equilibrium (1)

$$H^+ + L^{\nu-} \rightleftharpoons HL^{(\nu-1)-} \tag{1}$$

which is given by $K_{HL}=[HL^{(\nu-1)-}]/(H^+][L^{\nu-}])$. One of the more convincing examples is provided by considering the substituted iminodiacetate ligands



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of type A because of their large range of values of K_{HL} (10^5 to 10^{10}). It has been found [1] that there is a linear relationship between K_{HL} and the stability constants of the 1:1 complexes $K_{ML}=[ML^{(\nu-z)-}]/(M^{z+}][L^{\nu-}])$ of the type shown in eqn. (2) (**a** and **b** are constants which depend on the metal ion M^{z+}).

$$\log K_{ML} = \mathbf{a} \log K_{HL} + \mathbf{b} \tag{2}$$

This equation, also known as linear free energy relationship, has found large interest [2].

This paper presents the thermodynamic data for the complex formation of aniline-*N*,*N*-diacetate ADA ($R=C_6H_5$), which together with those obtained for methyliminodiacetate MDA ($R=CH_3$) [3] and for iminodiacetate IDA ($R=H$) [4], allow a discussion of the enthalpy, ΔH_1, and the entropy, ΔS_1, changes by complex formation as a function of the basicity of the ligand, i.e. K_{HL}.

The formation of the 1:1 complexes takes place with equilibrium (3) by the substitution of some bonded H_2O molecules of M^{z+}(aq) and $L^{\nu-}$(aq) with three bonds between metal and ligand over one N and two O^- donors. As the number of H_2O molecules, bound to a charged species, diminishes by decrease of its charge [5], the complex $ML^{(\nu-z)-}$(aq) is formed by release of further solvent molecules, depending on the value of $(\nu-z)-$. The obtained values of ΔH_1 and ΔS_1 can then be considered as sum of two contributions: (i) release of H_2O molecules, (ii) metal ligand bonds formation. For the 1:1 complexes of one metal ion M^{z+} with the different iminodiacetate derivatives L^{2-} we can consider the contribution for ΔH_1 and ΔS_1 due to the H_2O release almost equal and thus the differences in the two quantities as due to differences in ligand basicity and ligand size.

$$M^{z+}(aq) + L^{\nu-}(aq) \rightleftharpoons ML^{(\nu-z)-}(aq) \tag{3}$$

For non-coordinating substituents R having similar molecular weights and number of atoms, it is expected that the change of the substituent causes changes of the values of the standard molar entropies [6] of the ligand $L^{\nu-}$ ($S°(L^{\nu-})$) and of the complex $ML^{(\nu-z)-}$ ($S°(ML^{(\nu-z)-})$) by a similar amount and thus, for each metal ion M^{z+}, the values of ΔS_1 are very near ($\Delta S_1 = S°(ML^{(\nu-z)}) - S°(M^{z+}) - S°(L^{\nu-})$) and independent of the basicity of the ligand. As ΔS_1 is almost constant, the variation of the basicity and of

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$\Delta G_1 = -RT \ln K_{ML}$ should be accompanied by a parallel variation of ΔH_1.

Experimental

Aniline-*N*,*N*-diacetic acid H_2L was prepared as already described [7]. After three recrystallizations its purity was controlled with alkalimetric titrations and elemental analysis. The calorimetric measurements (LKB 8700/2 reaction calorimeter) were done using freshly prepared solutions of the neutralized ligand, adding to it an exact volume of a solution of nitric acid or of a metal nitrate (Merck) and measuring the heat evolved. For low K_{ML} an excess of metal salt was added in order to reach a degree of complex formation ≥ 0.4. All measurements were controlled several times.

Results and discussion

The thermodynamic data thus obtained (see Table 1) were calculated using the stability constants already published [1]. Complementary stability constants of the 1:1 complexes with glutarate, GLU [8], as well as MDA and IDA are also given in Table 1. Glutarate has two carboxylate groups separated by the same number of atoms as in iminodiacetate. In the case of Mg^{2+} the value of log K_1 for ADA and GLU are similar and thus the coordination of the nitrogen atom seems questionable. On the other hand, for the 3d-divalent cations the difference in log K_1 is an indication for the coordination of N in the ADA complexes. As the coordination of the alkaline earth cations is doubtful, Mg^{2+} and Ca^{2+} will not be discussed further. The K_{ML} values of the complexes formed with the three iminodiacetate ligands show that the two more basic ligands have similar K_{HL} and K_{ML} values. Going to ADA a strong drop in K_{ML} is paralleled by the K_{HL} decrease. The change in K_{ML}, and thus in the free energy of complexation ΔG_1, can be due to changes in ΔH_1 or ΔS_1. As can be seen in Figs. 1 and 2 where plots of these last quantities for the complexes with ADA, IDA and MDA are shown, the changes in log K_1 (or ΔG_1) are mainly a ΔH_1 effect. The ΔH_1 values for the formation of the 1:1 complexes with ADA are approximately 7 kcal mol^{-1} more positive because of the decreased basicity of ADA, i.e. the lower ability to bind H^+ is reflected in the reduced ability to bind metal ions. The formation of M(ADA) takes place because of the large entropy change resulting in a negative ΔG_1 value; however, for ADA complex formation with all metal ions studied is entropy controlled. As already found with IDA and MDA, also ADA gives the largest $-\Delta H_1$ value with Ni^{2+} and only the largest ΔS_1 value for Cu^{2+} ensures that the more stable 1:1 complex is formed with Cu^{2+} followed by Ni^{2+}.

For ligands differing in the uncoordinated substituent R only, it is expected that the entropy ΔS_1 does not change as far as the substituent R is not coordinated. As shown in Fig. 2, the values of ΔS_1 increase going from IDA to MDA and to the ADA complexes and by almost comparable amounts for all cations considered. This can be explained by the substitution of one H atom in IDA with the more voluminous CH_3 in MDA and with C_6H_5 in ADA. Similar effects are already known for the introduction of CH_3 instead of H giving always a large increase of ΔS_1 because of the increase of the number of the released water molecules due to steric strain in

TABLE 1. Stability constants K_{ML} and thermodynamic data for the formation of M(ADA) for $I=0.1$ (KNO_3) and at 25 °C, and stability constants for the 1:1 complexes with GLU, IDA, and MDA for $I=0.1$ and at 25 or 20 °C (1 cal = 4.184 J)

	ADA				log K_{ML}		
	log K_{ML}	ΔG_1 (kcal mol^{-1})	ΔH_1 (kcal mol^{-1})	ΔS_1 (cal mol^{-1} K^{-1})	25 °C GLU	20 °C IDA	20 °C MDA
H^+	5.02[a](0.02)[b]	−6.85	1.38(0.1)	27.6(1.0)	5.01	9.45	9.65
Mg^{2+}	1.15(0.2)	−1.57	1.4(0.1)	10(1)	1.08	2.94	3.44
Ca^{2+}	1.5(0.2)	−2.05	1.6(0.2)	12(1)	1.06	2.59	3.75
Mn^{2+}	1.65(0.2)	−2.25	5.8(0.1)	27(1)	1.13	5.65	5.40
Co^{2+}	2.96(0.1)	−4.04	5.0(0.1)	30(1)	2.2	6.97	7.62
Ni^{2+}	3.58(0.1)	−4.88	3.6(0.1)	29(1)	1.6	8.19	8.73
Cu^{2+}	6.62(0.05)	−9.03	3.9(0.1)	43(1)	2.4	10.63	11.09
Zn^{2+}	3.27(0.1)	−4.46	4.3(0.1)	29(1)	1.6	7.27	7.66

[a] For $H^+ + HL^- \rightarrow H_2L$: log $K=2.42(0.05)$, $\Delta H=0.2(0.1)$ kcal mol^{-1}, $\Delta S=11.7$ cal mol^{-1} K^{-1}. [b] In parentheses three times the standard deviation for the experimental values of this work.

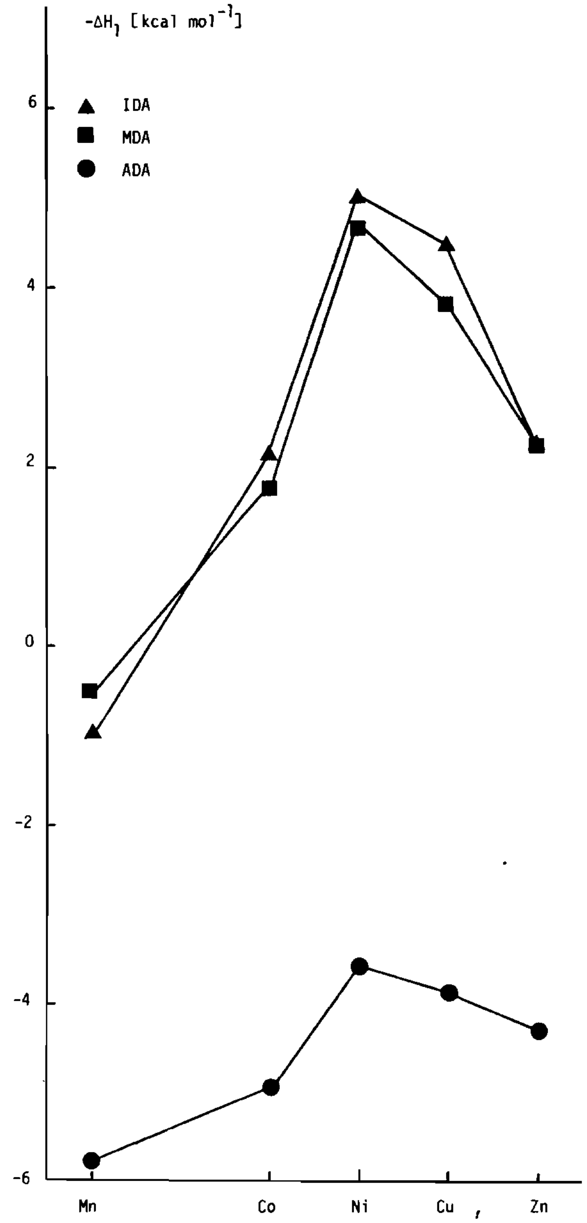

Fig. 1. The enthalpies of complex formation of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with some iminodiacetate derivatives.

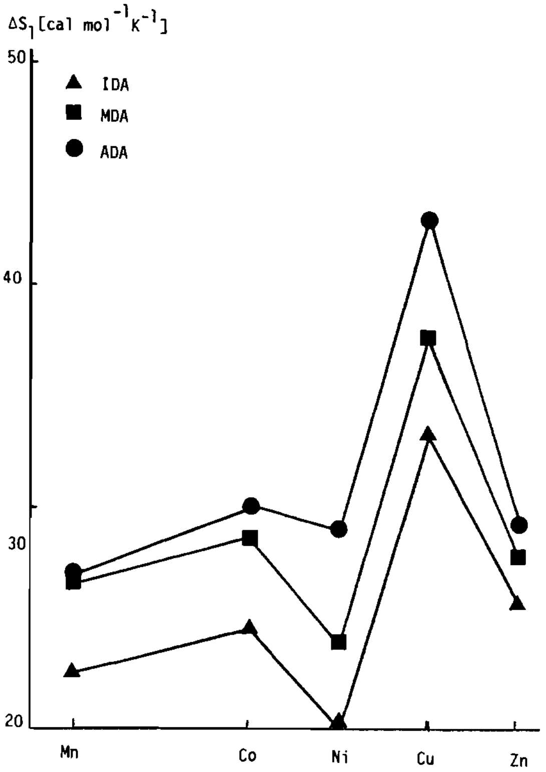

Fig. 2. The entropies of complex formation of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with some iminodiacetate derivatives.

the 1:1 complex [9, 10]. This effect should increase remarkably by inserting the larger C_6H_5 group, in agreement with our results. This ΔS_1 increase is accompanied by that of ΔH_1 for the break of the involved M–H_2O bondings. If we consider the Gibbs–Helmholtz relation $\Delta G_1 = \Delta H_1 - T\Delta S_1$, one realizes that this last change, due to the ligand size, leads to terms in ΔH_1 and ΔS_1 which mainly compensate each other so that the corresponding ΔG_1 is low and can be negligible. In this way the existence of a linear free energy relationship for the formation of 1:1 iminodiacetate complexes can be explained by the fact that eventual changes in ΔS_1 are compensated by those in ΔH_1 thus ΔG_1 remains practically unaltered and only K_{HL} dependent, i.e. the basicity of the ligand HL. Compensation effects between the above quantities in the case of protonation [11] and complex formation [12] processes are documented in the literature.

From the trends of the different data in Fig. 1 and 2 it appears that only in the case of ADA do the ΔH_1 values diverge and differ from each other much less with respect to those for the other two ligands. Further the mean value for ΔH_1 is positive (*c.* 4 kcal mol^{-1}) and not negative as that for the other two ligands. Thus the metal ligand interaction is in the first case much weaker and not strongly dependent on the involved divalent metal ion. A similar trend is for instance found in the case of the 1:1 NTA complexes [13] in which because of the large ligand charge the entropy ($\Delta S_1 = 52$ (Cu^{2+}), 45.5 (Zn^{2+}) cal mol^{-1} K^{-1}) in comparison with the enthalpic term ($\Delta H_1 = -1.87$ (Cu^{2+}), -0.87 (Zn^{2+}) kcal mol^{-1}) prevails. The basicity of the N atom in ADA is so strongly decreased that the interaction with a metal ion is mainly a consequence of its negative charge giving rise to a release of H_2O

molecules and the contribution of the N atom is almost screened from the above effect.

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