

ELECTROSTATIC AND NON-ELECTROSTATIC CONTRIBUTIONS TO ION ASSOCIATION IN SOLUTION

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ABSTRACT

The coordination behaviour of d^0 -cations on the one hand and that of d^{10} -cations of low charge on the other hand is designated as A- and B-character respectively. For A-character interactions the charges and radii and for B-character interactions the ionization potentials and electronegativities of the combining atoms are decisive (electrovalent and covalent behaviour). Generally A- and B-character may be developed to any extent and seem to be mixed in a complicated manner. The thermodynamic functions of the association processes are often a good criterion, the formation constant of the adduct being large because of a dominant positive $T \Delta S$ in the case of A-character interactions and because of a dominant negative ΔH in the case of B-character interactions.

The increase in entropy which is generally observed when the association process is due to electrostatic forces, is caused by the negative temperature coefficient of the dielectric constant (DK) of the solvent. However, the calculation leads to reasonable results only, if a smaller effective DK ϵ_e is used in place of the DK of the bulk of the solvent ϵ . Furthermore, $-\delta\epsilon_e/\delta T$ is considerably smaller than $-\delta\epsilon/\delta T$ and $\delta(\ln\epsilon_e)/\delta(\ln T)$ becomes less negative the more the electrostriction increases. This statement is substantiated experimentally with the aid of proton transfer reactions, which are controlled entirely by simple electrostatics. The greater the electrostriction around the species associating on account of purely electrostatic forces, the more exothermic the reaction will be. The structural changes exerted by a given metal cation on its solvation shell depend not only on its charge and radius, but also on its individuality.

1. COORDINATION SELECTIVITY

AN examination of the large body of facts on the solution stability of metal complexes which has accumulated during the past 30 years¹ reveals markedly different preferences of the various metal ions for the ligands offered to them in aqueous solution.

The d^0 -cations react only with fluoride and with oxygen donors to an appreciable extent. Insoluble fluorides are precipitated with alkali fluoride and often can be dissolved in an excess of the reagent. The hydroxides, carbonates and phosphates of almost all of the multivalent cations are

insoluble, and again mononuclear hydroxo- and carbonato-complexes are sometimes formed if the ligand is added in high enough concentration. Acetate is quite a general, although weak, complexing agent. The deprotonated carboxylic acid group reveals its potentialities more clearly as a ligand group of a multidentate agent such as oxalate, tartrate, citrate and the anions of aminopolycarboxylic acids such as EDTA, which are quite universal sequestering agents. All the d^0 -cations with a charge of more than one form of either insoluble oxalates or oxalato chelates and can be masked with tartrate, citrate and EDTA. However, d^0 -cations do not react with the heavy halide anions even when present in large excess. The basic ligands ammonia, cyanide and sulphide do not coordinate to d^0 -cations but act as deprotonating agents of the aquo complexes, so that again the metal hydroxides are precipitated.

The degree of condensation with fluoride and oxygen donors depends characteristically on the charges and radii of the interacting species, as is to be expected if the formation of the adduct is the result of simple electrostatic forces. The higher the charge of the cation, the more stable is usually the complex formed with a given ligand or the smaller is the solubility product of a precipitate. The stability of the complex increases also with decreasing radius in a series of metal ions of a given charge. Exceptions are encountered only with multidentate ligands when the smaller metal ion is unable to accommodate sterically the many ligand atoms offered by the chelating agent and is thereby at a disadvantage compared to the larger metal ion. It is in line with this electrovalent behaviour that the ammonia molecule with the smaller dipole moment cannot compete successfully with the larger dipole H_2O which is present in such an overwhelming excess. Furthermore it is understood readily that the smaller fluoride is preferred to the larger halide ions and that oxygen donors which bring up their charged ligand atom within a smaller distance to the metal cation are preferred to comparable sulphur donors. It is surprising, however, that even the anions of the heavy halides have difficulty in competing with the dipole molecules of the solvent. The d^0 -cations hardly form halogeno complexes even in concentrated solutions of HCl, HBr and HI (e.g. hexaquoaluminium chloride $[Al(H_2O)_6]Cl_3$ crystallizes from fuming hydrochloric acid which hardly contains any unprotonated H_2O but an overwhelming excess of Cl^-).

The complex formation of the low charged d^{10} -cations Cu(I), Ag(I), Au(I) reveals a totally different behaviour. The very soluble AgF (CuF and AuF are unstable to disproportionation) is highly dissociated in solution, but the heavy halides have small solubility products and dissolve when an excess of the corresponding alkali halide is added with the production of mononuclear chloro-, bromo- and iodo-complexes which are of an appreciable stability. The heavy halides therefore are strongly preferred as ligands to fluoride, and analogously sulphur donors to oxygen donors. The less polar molecule NH_3 is more strongly coordinated than the more polar H_2O and the phosphine adducts are even more stable than the ammine complexes. The cyano complexes of these noble metals have especially large stability constants.

It is obvious that this type of interaction is not governed by electrostatic forces. The larger Au(I) forms more stable associates than the smaller Cu(I), and of the halide ligands the one with the greatest radius is preferred to the

smaller anions. It is instructive to consider an isoelectronic series of d^{10} -cations, such as Ag(I), Cd(II), In(III), which demonstrates that the chloro-, bromo-, iodo-, ammine- and phosphine-complexes become less stable with increasing charge (Table 1), whereas the stability of the fluoro complexes as well as the stability of the adducts with oxygen donors increases in the series. The quantities which are decisive for the type of interaction of these low charged d^{10} -cations, seem to be the ionization potential of the metal (or the tendency of the metal cation to take up electrons) and the electronegativity of the element furnishing the ligand (or the tendency of the ligand atom to donate electrons). The production of these noble metal complexes must be due to the formation of new and more stable covalent bonds in the course of the reaction.

Instead of using expressions such as electrovalent and covalent behaviour, it commits one less to speak of *A-character* and *B-character* if one wishes to state that a given metal cation is behaving like a d^0 -cation or like a low charged d^{10} -cation. Anyhow, even the metal-oxygen and the metal-fluorine bonds may be covalent to a considerable extent, but nevertheless in aqueous solution the formation of the complex species involved is governed almost exclusively by electrostatic forces because of the replacement of one metal-oxygen bond ($M-OH_2$) by another metal-oxygen bond ($M-O-Donor$) or by the similar metal-fluorine bond. Furthermore, the formation of the adduct may benefit from ligand field stabilization effects which are non-electrostatic contributions to the stability although no covalency necessarily has to be involved.

The letters A and B used for characterizing the coordination selectivity have been borrowed from the assignments of the columns of the periodic table where the metals forming d^0 - and d^{10} -cations respectively have their places, just as the designation of the classes a and b by Ahrlund, Chatt and Davies². However, the more vague expressions A- and B-character which had already been suggested³ before the appearance of the paper of Ahrlund *et al.* seem more appropriate because it is impossible to classify the experimental facts into two categories only. There are many cases where a certain metal ion falls into class 'a' according to its behaviour with a first and into class 'b' with a second series of ligands. More recently the adjectives 'hard' and 'soft' have been suggested for A- and B-behaviour respectively⁴. It is certainly true that the A-character metal ions are generally less polarizable than the B-character metal ions and it is often also serviceable to be able to have a shorthand expression for gradations like hard, harder, hardest and soft, softer, softest. However, one should never forget that there is no simple correlation between coordination selectivity and polarizability⁵.

It goes without saying that the association energies due to simple electrostatic forces as well as those due to covalency both may be large or both may be small or that the one kind or the other may be dominant to any degree. It seems that in aqueous solution only F^- and oxygen donors are able to compete successfully with the solvent molecules on account of electrostatics. To an extent depending on the charge, these ligands coordinate to every metal cation. All the other ligands are selective and a certain degree of B-character is needed to obtain an adduct. B-character builds up in the series of transition metal cations nd^q with increasing q and increasing n and is the more pronounced the smaller the charge of the cation. The extreme B-charac-

ter of the univalent d^{10} -cations, on the other hand, is progressively replaced by A-character when the charge is increased (Table 1). However, there are many exceptions to these rules and somewhat different results may be obtained depending on the charge-type of the selective ligand used for the investigation of the degree of B-character⁹. For a more satisfactory description of coordination selectivity it would be highly desirable to find a method which would allow a separation of the electrostatic contribution to the free energy from the non-electrostatic part.

Table 1. Approximate stabilities of 1:1-complexes ($\log K_1$) of isoelectronic d^{10} -metal cations

Ligand	Ag ⁺	Cd ²⁺	In ³⁺	Ref.
Cl ⁻	3.4	1.9	~2	1
Br ⁻	4.2	2	1.8	1
I ⁻	7	2.3	1.7	1
HO-CH ₂ -CH ₂ -S ⁻	13.2	?	9.0	6.7
H ₃ N	3.2	2.5	ppt.	1
HO-CH ₂ -CH ₂ -P(Et) ₂	12	4	ppt.	8
F ⁻	-0.2	0.5	3.8	1
OH ⁻	2.9	4	10	1
EDTA-anion	7	16	25	1

ppt. : precipitation of metal hydroxide.

2. THE ENTHALPY-ENTROPY CRITERION

Our discussion so far has been based entirely on free energy data ($\Delta G = -RT \ln K$). The enthalpy changes for the associations were difficult to obtain before the development of thermistors, which allowed accurate direct calorimetric determinations of ΔH at low concentrations of the reactants in media of constant ionic strength. Reliable ΔH -values for metal complex formation reactions were still very scarce about ten years ago¹⁰, but the situation is much more favourable today. A survey of these data reveals that the enthalpy change taking place during the association is an excellent criterion to decide whether we are dealing with a mainly electrovalent or mainly non-electrovalent interaction^{11,12}. Associations with fluoride or oxygen donors are usually somewhat endothermic or only slightly exothermic and the stability of the adduct is almost entirely due to a large and positive entropy change. The addition of a selective ligand on the other hand is always of considerable exothermicity and ΔH is the dominant factor in the Gibbs-Helmholtz equation for making ΔG negative¹³.

$$\Delta G = \Delta H - T \Delta S \quad (1)$$

A-character associations: $T \Delta S$ dominant and positive

B-character associations: ΔH dominant and negative

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In *Table 2* the thermodynamic quantities for the formation of some halogeno complexes are listed. The monofluoroaquo cations have stability constants as high as 10^5 to 10^6 which originate entirely in the large entropy term. The enthalpy change is even unfavourable for the association in two of the three examples. The additions of heavy halide anions to extreme B-character cations, on the other hand, are all exothermic and ΔH is now the decisive factor for the stability of the complex, although $T \Delta S$ usually is again positive and makes a minor contribution to the negative ΔG .

Table 2. Formation of halide complexes, 25°C, kcal mole⁻¹

Reaction	μ	ΔG	ΔH	$T \Delta S$	Ref.
$\text{Be}^{2+} + \text{F}^- \rightarrow \text{BeF}^+$	1.0	- 6.7	- 0.4	+ 6.3	14
$\text{Al}^{3+} + \text{F}^- \rightarrow \text{AlF}^{2+}$	0.5	- 8.4	+ 1.1	+ 9.5	15
$\text{Fe}^{3+} + \text{F}^- \rightarrow \text{FeF}^{2+}$	0.5	- 7.1	+ 2.3	+ 9.4	16
$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$	0	- 4.5	- 2.7	+ 1.8	17
$\text{Hg}^{2+} + \text{Cl}^- \rightarrow \text{HgCl}^+$	0.5	- 9.2	- 5.5	+ 3.7	18
$\text{Hg}^{2+} + \text{Br}^- \rightarrow \text{HgBr}^+$	0.5	- 12.3	- 10.2	+ 2.1	18
$\text{Hg}^{2+} + \text{I}^- \rightarrow \text{HgI}^+$	0.5	- 17.5	- 18.0	- 0.5	18

Table 3. Complex formation with oxygen- and sulphur-donors, 25°C, kcal mole⁻¹

Reaction	μ	ΔG	ΔH	$T \Delta S$	Ref.
$\text{Fe}^{3+} + \text{OH}^- \rightarrow \text{FeOH}^{2+}$	1	- 16.1	- 3.0	+ 13.1	19
$\text{Cr}^{3+} + \text{OH}^- \rightarrow \text{CrOH}^{2+}$	0.1	- 10.6	- 3.0	+ 7.6	20
$\text{CH}_3\text{Hg}^+ + \text{SR}^- \rightarrow \text{CH}_3\text{HgSR}$	0.1	- 21.6	- 19.8	+ 1.8	21
$\text{Cd}^{2+} + \text{AcO}^- \rightarrow \text{CdOAc}^+$	2	- 1.7	+ 1.5	+ 3.2	22
$\text{Y}^{3+} + \text{AcO}^- \rightarrow \text{YOAc}^{2+}$	2	- 2.1	+ 3.3	+ 5.4	23
$\text{La}^{3+} + \text{AcO}^- \rightarrow \text{LaOAc}^{2+}$	2	- 2.1	+ 2.2	+ 4.3	23
$\text{UO}_2^{2+} + \text{SO}_4^{2-} \rightarrow \text{UO}_2\text{SO}_4$	1	- 2.4	+ 4.3	+ 6.7	24, 27
$\text{La}^{3+} + \text{SO}_4^{2-} \rightarrow \text{LaSO}_4^+$	1	- 1.9	+ 2.5	+ 4.4	25, 27
$\text{Ce}^{3+} + \text{SO}_4^{2-} \rightarrow \text{CeSO}_4^+$	1	- 1.7	+ 3.6	+ 5.3	25, 27
$\text{Th}^{4+} + \text{SO}_4^{2-} \rightarrow \text{ThSO}_4^{2+}$	2	- 4.5	+ 5.0	+ 9.5	26, 27

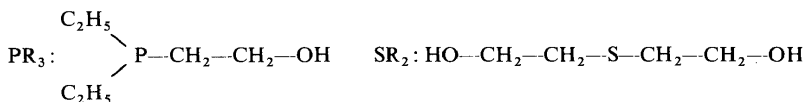
The formation of FeOH^{2+} and CrOH^{2+} (*Table 3*) is slightly exothermic, but $-\Delta H$ contributes only 20 to 30 per cent to $-\Delta G$. In the addition of a mercaptide anion to the B-character cation CH_3Hg^+ on the other hand, $-\Delta H$ contributes more than 90 per cent to the negative free energy change. The comparison of the trivalent Fe^{3+} and Cr^{3+} with the univalent CH_3Hg^+ certainly is not satisfactory, but there are no other data available which would be more suitable for the comparison of a sulphur analogue with OH^- . The study of the formation of simple hydroxy- and thio-complexes is made very difficult by the overwhelming tendency to form polynuclear species.

The central part of *Table 3* deals with 1:1-acetato and the lower part with 1:1-sulphato complexes. It is especially notable that the formation of these adducts, with only small stability constants, are reactions of considerable endothermicity. However, $+\Delta H$ is overcompensated by the still larger $-T \Delta S$, so that ΔG becomes negative.

The replacement of H₂O from the aquo shell of a metal cation by an uncharged ligand (*Table 4*) always seems to be an exothermic process. Because of the circumstance that ammonia, amines, phosphines and thioethers all have considerably smaller dipole moments than H₂O, it would be hard to imagine such a substitution to take place on the basis of Coulomb-forces. Obviously the bonds from the metal to N, P and S must be more covalent and more stable than the metal–oxygen bond which is reflected in the negative value of ΔH . The association becomes the more exothermic the more pronounced the B-character of the metal and the lower the electronegativity of the ligand atom. The large amount of heat produced in the addition of an aliphatic phosphine to Ag(I) and Hg(II) is remarkable⁸.

Table 4. Complexes of uncharged ligands, kcal mole⁻¹

Reaction	μ	ΔG	ΔH	$T \Delta S$	$t^\circ\text{C}$	Ref.
Ni ²⁺ + 2NH ₃ → Ni(NH ₃) ₂ ²⁺	2	-7.0	-7.6	-0.6	25°	1
Cu ²⁺ + 2NH ₃ → Cu(NH ₃) ₂ ²⁺	2	-10.6	-11.0	-0.4		1
Zn ²⁺ + 2NH ₃ → Zn(NH ₃) ₂ ²⁺	2	-6.7	-5.7	+1.0		1
Hg ²⁺ + 2NH ₃ → Hg(NH ₃) ₂ ²⁺	2	-23.6	-24.7	-1.1		1
Ag ⁺ + 2NH ₃ → Ag(NH ₃) ₂ ⁺	0	-9.9	-13.4	-3.5		28
Hg ²⁺ + 2PR ₃ → Hg(PR ₃) ₂ ²⁺	1	-50.4	-52.8	-2.4	20°	8
Ag ⁺ + 2PR ₃ → Ag(PR ₃) ₂ ⁺	1	-28.2	-35.8	-7.6		8
Ag ⁺ + 2SR ₂ → Ag(SR ₂) ₂ ⁺	1	-8.2	-14.8	-6.6		29



The entropy change in the reactions of *Table 4*, on the other hand, opposes the formation of the product. After all, it is normal that ΔS is negative in a condensation process and a comparison with the data of *Tables 2* and *3* reveals that a positive entropy change must be caused by a compensation of charges. Indeed, the lowering of the electrostatic fields around the solutes which takes place in the course of a charge compensation will increase the mobility of the molecules of the solvent exposed to these fields and must cause an entropy increase. Therefore it is to be expected that the entropy change in A-character associations, which are due to electrostatic forces mainly, is more positive than in B-character associations caused mainly by covalency or ligand field stabilization effects.

3. THE MOST SIMPLE HARD AND THE MOST SIMPLE SOFT ACID

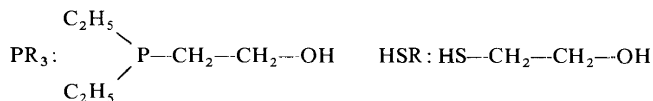
In the following sections the cations H⁺ and CH₃Hg⁺ play a prominent role because of the stoichiometric simplicity of their reactions. Both cations add practically only one single ligand. Coordination number two certainly has been observed, but the equilibria constants K_2 for the processes $\text{HL}^{(1-\lambda)} + \text{L}^{\lambda-} \rightarrow \text{HL}_2^{(1-2\lambda)}$ as well as $\text{CH}_3\text{HgL}^{(1-\lambda)} + \text{L}^{\lambda-} \rightarrow \text{CH}_3\text{HgL}_2^{(1-2\lambda)}$

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are exceedingly small. In the case of H^+ , the formation of hydrogen bridged HF_2^- takes place even in aqueous solution, but to a negligible extent only³⁰. Also the formation of $CH_3HgX_2^-$, where X is a heavy halogen or SCN, must be taken into account only at very high concentrations³¹ of X^- . While K_2 is very small, K_1 for the reactions $H^+ + L^{\lambda-} \rightarrow HL^{(1-\lambda)}$ and $CH_3Hg^+ + L^{\lambda-} \rightarrow CH_3HgL^{(1-\lambda)}$ is often extremely large²¹. The very exceptional position of the hydrogen ion in the history of chemistry as the real carrier of acidity is due to this peculiarity³² and the methylmercury cation is its counterpart.

Table 5. The most simple hard and the most simple soft acid, kcal mole⁻¹, 20°C

$B^{\lambda-} + H^+ \longrightarrow HB^{1-\lambda}$				$B^{\lambda-} + CH_3Hg^+ \longrightarrow CH_3HgB^{1-\lambda}$				
$HB^{1-\lambda}$	ΔG	ΔH	$T\Delta S$	$CH_3HgB^{1-\lambda}$	ΔG	ΔH	$T\Delta S$	Ref.
HF	- 4.0	+ 2.6	+ 6.6	CH_3HgF	- 2.0	?	?	21
HCl	(+9)	(+14)	(+5)	CH_3HgCl	- 7.0	- 6.0	+1.0	21
HOH	-21.3	-13.7	+7.6	CH_3HgOH	-12.6	- 8.5	+4.1	21
HSR	-12.8	- 6.5	+6.3	CH_3HgSR	-21.6	-19.8	-1.8	
HNH_3^+	-12.9	-12.8	+0.1	$CH_3HgNH_3^+$	-10.3	?	?	21
HPR_3^+	-11.0	- 8.3	+2.7	$CH_3HgPR_3^+$	-19.7	-22.6	-2.9	8
HCN	-12.3	-10.9	+1.4	CH_3HgCN	-18.8	-22.1	-3.3	21



From Table 5 it is apparent that the proton has dominant A-character whereas CH_3Hg^+ has pronounced B-character. This follows from the coordination selectivity, that is, from the fact that H^+ prefers F^- to Cl^- , OH^- to SH^- and an amine to a phosphine, whereas CH_3Hg^+ forms the more stable adduct with the ligand deriving from the second row element Cl, S or P. However, the A-character of H^+ is not pronounced. A cation of extreme A-character such as Al^{3+} does not coordinate at all to sulphur donors in aqueous solution and does not form any amine-, phosphine- or cyano-complexes.

The fact that H^+ has only a moderate although dominant A-character, whereas CH_3Hg^+ has extreme B-character, follows also from an inspection of the values ΔH and ΔS listed in Table 5. The formation of the proton complexes usually is a reaction of appreciable exothermicity, but $T\Delta S$ is also considerable if the ligand is an anion. For the formation of the methylmercury complexes, on the other hand, the term $T\Delta S$ makes a small contribution to ($-\Delta G$) only and sometimes is even opposed to the production of the adduct.

The position of H^+ as somewhere between the cations of extreme A- and extreme B-character fits in with the high charge density on the surface of the small proton (creating electrovalent behaviour) on the one hand and the appreciable covalency of even the most polar bonds between the ligand atom and H of the proton complexes (creating covalent behaviour) on the other hand.

4. ION ASSOCIATION IN A STRUCTURELESS DIELECTRIC MEDIUM

The electrostatic energy to be gained by bringing two gaseous hard spherical ions of opposite charge ev^+ and $e\lambda^-$ from infinity up to a distance 'a' is per mole:

$$A_{ei} = Ne^2v\lambda/a \quad (2)$$

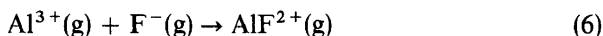
where N is Avogadro's number, and the thermodynamic functions of the process are given by:

$$\Delta G = -T\Delta S_t - A_{ei} \quad (3)$$

$$\Delta S = \Delta S_t \quad (4)$$

$$\Delta H = -A_{ei} \quad (5)$$

ΔS_t is the difference of the translational entropies of product and reactants of about -30 e.u. A_{ei} is a large quantity in comparison to the entropy term $T\Delta S$ (~ 10 kcal/mole at $T = 298^\circ\text{K}$) and amounts even in the case of singly charged ions ($v = \lambda = 1$) of usual size ($a \approx 2 \text{ \AA}$) to about 200 kcal/mole. In the electrostatic ion association in vacuum ΔG and ΔH therefore are both strongly negative and of the same order of magnitude. For the reaction 6,



taking for 'a' the sum of the atomic radii ($= 1.8 \text{ \AA}$), the result is:

$\Delta G = -550$ kcal/mole and $\Delta H = -560$ kcal/mole in comparison to an 'experimental' value of $\Delta H \approx -600$ kcal/mole.

Let us now approach the spherical ions in a medium of dielectric constant ϵ which we will consider to be structureless and homogeneous³³. The electric work is now much smaller and given by 7, and for the thermodynamic quantities we obtain equations 8 to 10:

$$A_{ei} = Ne^2v\lambda/a\epsilon \quad (7)$$

$$\Delta G = -T\Delta S_t - A_{ei} \quad (8)$$

$$\Delta S = \Delta S_t - A_{ei} \left\{ (1/\epsilon) (\delta\epsilon/\delta T) \right\} \quad (7)$$

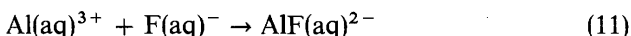
$$\Delta H = -A_{ei} \left\{ 1 + (T/\epsilon) (\delta\epsilon/\delta T) \right\} \quad (10)$$

It is important to recognize that for the solvent reaction, not only is ΔG very much less negative than in the corresponding vacuum process, but also ΔS is no longer given simply by the loss in translational entropy, but depends on the temperature coefficient of the dielectric constant. For water at 25°C ($\epsilon = 78.5$) the temperature coefficient is negative and numerically quite large ($\delta\epsilon/\delta T = -0.36$) so that the quantity within the brackets of 10 becomes negative ($= -0.36$) and ΔH positive. As a result of this simple consideration, therefore, we expect that the ion association in water indeed should be an endothermic process as is often found to be the case for A-character interactions (Tables 2 and 3).

With the equations 7 to 10, we have formulated what has been concluded already: through the neutralization of charges the solvent molecules surrounding the ions become more mobile causing an increase in ΔS . The large dielectric

constant ϵ of polar solvents (which are polarized in an electric field mainly by orientation of the molecules) as well as their temperature coefficients, are expressions of this mobility. The dielectric constant of water becomes smaller when the temperature is raised, with the consequence that the forces between the ions become larger, resulting in a displacement of the equilibrium towards the adduct, so that the association is expected to be an endothermic process.

However, the equations 7 to 10 fail to give quantitative results. Applied to process 6, now considered to take place in aqueous solution,



we find: $\Delta G \approx 0$ and $\Delta H = 2.6$ kcal/mole, which is to be compared with the experimental data of Table 2: $\Delta G = -8.4$ and $\Delta H = +1.1$ kcal/mole. Although we are somewhat in doubt about the value to be introduced in 8 for ΔS_i (reasonable values ranging from 8 to 40 e.u.), there is no doubt that 7 and 8 furnish a value for ΔG which is much too positive, corresponding to an association constant far too small. The electrostatic work A_{e1} therefore must be very much larger than that given by 7 and the discrepancies are so large that we cannot obtain a considerable improvement by changing the distance 'a' between the ions in the adduct. It is quite evident that the failure is due to the use of too large a value for the dielectric constant. Because of the electrostriction and dielectric saturation effects an effective constant ϵ_e should be used in equation 7 and must be considerably smaller than the dielectric constant of the bulk of the solvent ($\epsilon_e < \epsilon$).

Furthermore, this effective dielectric constant must be less dependent on temperature than the macro constant: $-(\delta\epsilon_e/\delta T) < -(\delta\epsilon/\delta T)$. It is not only reasonable to assume this to be so because of the expected reduced mobility of the electrostricted water molecules; it follows also from equation 10 which would furnish a much too positive ΔH if the replacement of ϵ by the smaller ϵ_e were not supplemented by substitution of $\delta\epsilon/\delta T$ by a less negative $\delta\epsilon_e/\delta T$. For reaction 11 for instance the experimental values for ΔG and ΔH are obtained from 7 to 10 with $\epsilon_e \approx 30$ and $\delta\epsilon_e/\delta T = -0.11$, using again 30 e.u. for ΔS_i .

The model suggested therefore is to treat the solvent as a *structureless*, but *non-homogeneous* medium in which the dielectric constant to be used and its temperature coefficient vary with the distance of the interacting ions. In the following sections we shall see whether we can obtain some information on this local dielectric constant.

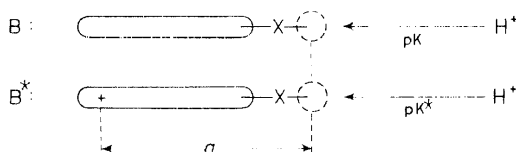
5. THE INFLUENCE OF CHARGE ON BASICITY

The role of solvent electrostriction and the dielectric saturation effects in the enormous electric fields occurring in the vicinity of ions are difficult to assess. According to calculations on models^{34, 35, 36}, the local dielectric constant ϵ'_e is believed to rise abruptly from low values in the immediate neighbourhood of the ion and to reach the usual macroscopic constant within a distance of a few Ångström units. The quantity ϵ_e to be introduced in

equation 7 is a sort of mean value of the local constant ϵ'_e , as becomes evident from 12

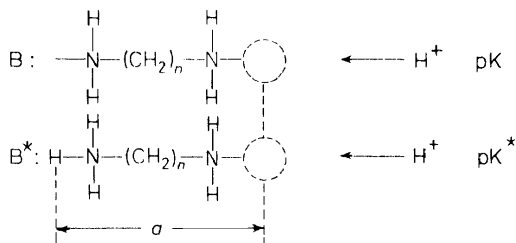
$$\int_0^a (e^2 \nu \lambda / a^2 \epsilon'_e) da = e^2 \nu \lambda / a \epsilon_e \quad (12)$$

Because it is impossible to obtain any reliable values for ϵ_e from theory, it is interesting to calculate the effective dielectric constant and its temperature coefficient from the thermodynamic quantities of reactions, which are controlled entirely by Coulomb forces. Imagine two basic molecules B and B[★], with identical basic groups X, which differ from one another solely by a charge situated somewhere on the molecule of B[★] at a distance 'a' from X³⁷:



On protonation of X, the free energy changes of the reactions with B and B[★] differ from each other only because of the energy needed to bring up the hydrogen ion in the additional field of the charge situated on B[★]. This electrostatic energy therefore can be obtained from $\Delta pK = (pK - pK^*)$ and we can calculate an experimental value of ϵ_e when the distance 'a' is known. Correspondingly the temperature coefficient of ϵ_e is accessible from the enthalpy change of the proton transfer from the base B and B[★]. Three different types of such pairs have been investigated.

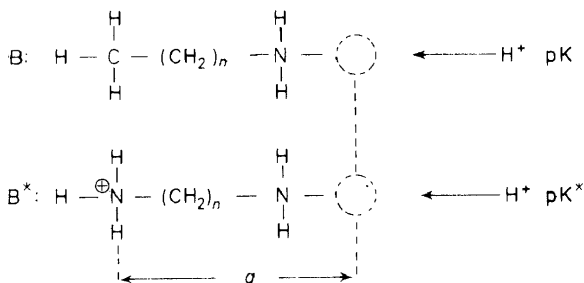
Type I: The uncharged B is a symmetrically built diamine molecule and B[★] its first protonation product. In the case of an unbranched, primary polymethylenediamine, the formulae are:



It will be readily recognized that the second hydrogen ion during the protonation of B[★] has to be brought up in the field of the charge of the first proton attached during the protonation of B and the length 'a' therefore is the intramolecular distance between the two acidic protons in the diammonium ion H₂B²⁺ (or HB^{★2+}), which almost certainly will be a fully stretched zigzag chain because of the repulsion of the two charges, so that 'a' is easily obtained from models.

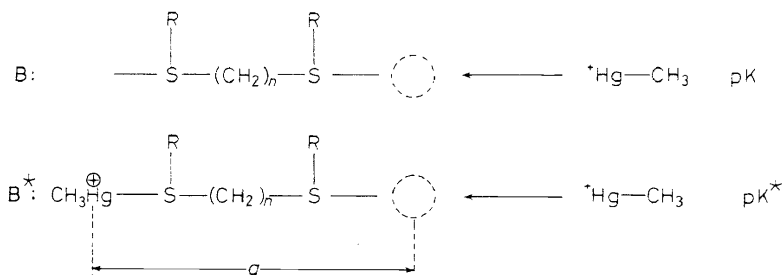
Type II: The uncharged B here is a monoamine and the formula of B[★] is

obtained by replacing a carbon atom of B by nitrogen with its higher nuclear charge. The base B for instance may be a primary non-branched aliphatic amine and B[★] the monoprotonated form of the polymethylenediamine with one carbon atom less than the molecule of B:



Obviously, the length 'a' is now somewhat smaller than the intramolecular distance of the two acidic protons in the diammonium ion [HB[★]]²⁺, namely the distance between one of the acidic protons of the first ammonium group and the nitrogen nucleus of the second ammonium group.

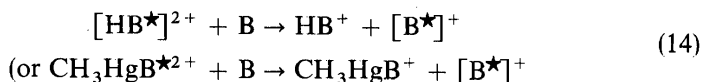
Type III: The pair is analogous to the type I pair, but the basic atoms are sulphur of thioether groups, which are very selective ligands, coordinating only to metal cations of extreme B-character. Instead of a proton, the equally singly charged CH₃Hg⁺ is used as the electrophilic cation³⁸.



Corresponding to type I, the length 'a' is the intramolecular distance between the two metal atoms in the cation of dimercurated dithioether. As substituent R, the hydroxyethyl group HO—CH₂—CH₂— has been chosen which makes the dithioethers water soluble. The pKs are analogously defined as with the proton acceptors type I and II and are the logarithms of the stability constants of the methylmercury complexes according to 13:

$$\text{pK} = \log \frac{[\text{CH}_3\text{HgB}]}{[\text{CH}_3\text{Hg}][\text{B}]} \quad \text{pK}^\star = \log \frac{[(\text{CH}_3\text{Hg})_2\text{B}]}{[\text{CH}_3\text{Hg}][\text{CH}_3\text{HgB}]} \quad (13)$$

The free energy of the transfer of H⁺ (or CH₃Hg⁺) from the base B[★] to the base B:



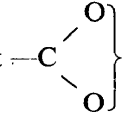
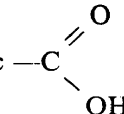
is calculated from $\Delta pK = (pK - pK^*)$ and is given by 15:

$$\Delta G = -2.305RT \Delta pK = -A_{el} - TS_{st} \quad (15)$$

A_{el} now is the electrostatic energy gained by removing to infinity the charge of the proton (or the methylmercury cation) from the equally positive charge 'e' situated at the distance 'a' on the molecule of base B^*

$$A_{el} = Ne^2/a\epsilon_e \quad (16)$$

Equation 15 is valid if the basic groups X on B and B^* are exactly alike. The additional charge on B^* should not change the group X electronically (it should not change its internal basicity). Furthermore, in the case of the pairs types I and III, the electron densities around N and S should not change appreciably on protonation or mercuration respectively. The latter condition would be poorly fulfilled if carboxylate groups³⁹ were used as basic groups

X because of the transition from the symmetrically built  to the asymmetric  on protonation. We therefore did not calculate the

electrostatic energy A_{el} from the pK-difference of dicarboxylic acids.

There is no change in the number of solute particles during process 14 and no 'cratic' or translational entropy terms have to be taken into consideration. The last term in equation 15 merely takes care of the circumstance that H^+ or CH_3Hg^+ can add to either of the two basic sites of B (pairs I and III) and that either of the two acidic protons of HB^* (pairs I and II) or either of the two methylmercury cations of CH_3HgB^* (pair III) may be given off. Therefore: $S_{st} = R \ln 4$ in the case of pairs types I and III and $S_{st} = R \ln 2$ in the case of pair type II. For the entropy and enthalpy change of process 14 we obtain:

$$\Delta S = -A_{el}[(1/\epsilon_e)(\delta\epsilon_e/\delta T)] + S_{st} \quad (17)$$

$$\Delta H = -A_{el}[1 + (T/\epsilon_e)(\delta\epsilon_e/\delta T)] \quad (18)$$

Table 6 contains the results of equilibrium and calorimetric measurements which were all carried out in the same solvent of ionic strength 1.0. The pKs of the unbranched primary mono- and di-amines have been obtained with good precision. The stability constants of the methylmercury complexes of the three *S,S'*-bis (hydroxyethyl)-dithioethers which were investigated, however, could not be obtained so accurately³⁸. An indirect pH-method was applied²¹ by studying the displacement of OH^- from CH_3HgOH by thioethers, the methylmercuryhydroxide being in equilibrium with CH_3Hg^+ and $(CH_2Hg)_2OH^+$. Also the results of the calorimetric measurements are not as accurate as desirable, especially the ΔH -values of the CH_3Hg^+ -additions.

A combination of the data of Table 6 furnishes ΔG and ΔH of the transfer reaction 14 given in Table 7, which contains furthermore the quantities obtained with the equations 15 to 18.

Table 6. Logarithms of formation constants and enthalpy changes (kcal/mole) at $\mu = 1.0$ (KNO₃) and 20°C

n	Protonation of H ₂ N—(CH ₂) _n —NH ₂		Protonation of CH ₃ —(CH ₂) _n —NH ₂		Methylmercuration of R—S—(CH ₂) _n —S—R					
	pK ₁	pK ₂	—ΔH ₁	—ΔH ₂	pK	—ΔH	pK ₁	pK ₂	—ΔH ₁	—ΔH ₂
2	10.226 ± 0.01	7.485 ± 0.01	12.4 ± 0.3	10.8 ± 0.3	10.960 ± 0.01	10.8 ± 0.3	4.26 ± 0.05	2.83 ± 0.1	6.85 ± 0.5	4.5 ± 0.5
3	10.832 ± 0.01	9.125 ± 0.01	13.15 ± 0.3	12.85 ± 0.3	11.005 ± 0.01	13.05 ± 0.3	3.81 ± 0.05	2.70 ± 0.15	6.78 ± 0.5	6.0 ± 0.5
4	11.122 ± 0.01	9.858 ± 0.01	13.1 ± 0.3	13.05 ± 0.3	11.041 ± 0.01	13.35 ± 0.3	—	—	—	—
5	11.258 ± 0.01	10.173 ± 0.01	13.2 ± 0.3	13.2 ± 0.3	11.046 ± 0.01	13.3 ± 0.3	4.09 ± 0.05	3.28 ± 0.1	6.82 ± 0.5	7.8 ± 0.5

Table 7. Thermodynamic quantities for reaction 13 (kcal/mole), $\mu = 1.0$, (KNO₃), 20°C. ϵ_e is to be compared with the bulk dielectric constant: $\epsilon = 80.36$ and $\delta\epsilon_e/\delta T$ with $\delta\epsilon/\delta T = -0.368$; $\delta \ln \epsilon_e/\delta \ln T = -1.34$

n	Pairs of type I			TS _{st}	A _{el}	a (Å)	ϵ_e	— $\delta\epsilon_e/\delta T$	$\frac{\delta \ln \epsilon_e}{\delta \ln T}$
	ΔG	ΔH	ΔH						
2	—3.69 ± 0.03	—1.6 ± 0.6	—1.6 ± 0.6	0.81	2.88 ± 0.03	5.35	22	0.034	0.45
3	—2.30 ± 0.03	+0.2 ± 0.6	+0.2 ± 0.6	0.81	1.49 ± 0.03	6.60	34	0.13	1.13
4	—1.71 ± 0.03	+0.3 ± 0.6	+0.3 ± 0.6	0.81	0.90 ± 0.03	7.90	47	0.21	1.33
5	—1.46 ± 0.03	+0.1 ± 0.6	+0.1 ± 0.6	0.81	0.65 ± 0.03	9.20	55	0.22	1.16
Pairs of type II									
2	—4.68 ± 0.03	—1.6 ± 0.6	—1.6 ± 0.6	0.40	4.28 ± 0.03	4.50	17	0.036	0.63
3	—2.54 ± 0.03	—0.1 ± 0.6	—0.1 ± 0.6	0.40	2.14 ± 0.03	5.75	27	0.09	0.96
4	—1.59 ± 0.03	+0.2 ± 0.6	+0.2 ± 0.6	0.40	1.19 ± 0.03	7.00	40	0.16	1.17
5	—1.18 ± 0.03	+0.1 ± 0.6	+0.1 ± 0.6	0.40	0.78 ± 0.03	8.30	51	0.19	1.13
Pairs of type III									
2	—1.93 ± 0.2	—2.3 ± 1.0	—2.3 ± 1.0	0.81	1.12 ± 0.2	8.65	~35	—	—
3	—1.50 ± 0.3	—0.8 ± 1.0	—0.8 ± 1.0	0.81	0.69 ± 0.3	9.95	~50	—	—
5	—1.09 ± 0.2	+1.0 ± 1.0	+1.0 ± 1.0	0.81	0.28 ± 0.2	12.35	~90	—	—

In *Figure 1*, the electrostatic work A_{el} has been plotted as a function of the distance 'a'. It is very satisfactory that the data from base pairs of types I and II apparently form a single smooth curve as it should be, if the assumptions made are correct. However, the data obtained with the methylmercury complexes of the dithioethers (pairs type III) do not fit in as nicely. The small deviations are almost certainly caused by chelation. The methylmercury cation coordinates only one single ligand strongly. However, the formation of weak 1:2-complexes is noticeable in many cases³¹. Therefore it is to be suspected that the dithioethers form chelates with CH_3Hg^+ which makes pK_1 larger than it would be otherwise and pK_2 smaller. The deviation from the expected values should be largest if the ring formed is five-membered ($n = 2$) and should become smaller with increasing ring size, and the experimental results (*Figure 1*) are in harmony with this expectation.

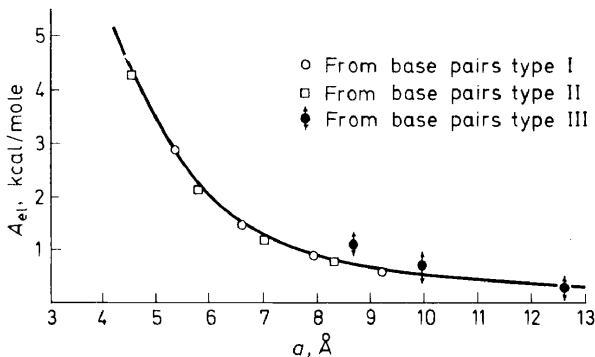


Figure 1. Electric work to be gained if a positive electronic charge situated on one end of an unbranched chain of CH_2 -groups is removed from another such charge situated on the other end of the chain at a distance of $a \text{ \AA}$.

In *Figure 2* the effective dielectric constant ϵ_e obtained from A_{el} by means of equation 16 has been plotted as a function of the distance 'a'. It is interesting to compare the experimental values with the local dielectric constant ϵ'_e obtained theoretically from models^{35,36}. According to equation 12 ϵ'_e should be smaller than ϵ_e which is in conspicuous contrast to our results. However, this deviation is not unexpected. In order to investigate the dielectric shielding experimentally, a carrier for the charges influencing one another was required. A_{el} is the electrostatic work needed to bring the charge $+e$ from infinity up to a distance 'a' from another charge $+e$, but the two charges are sitting at the ends of a zigzag chain of n CH_2 -groups after this has been done. We can imagine that a part of the solvent between the two charges is replaced by a hydrocarbon medium of much lower polarizability. That this actually is one of the causes of the small values found for ϵ_e will be made clear in the next section by demonstrating that the effective dielectric constant ϵ_e decreases with increasing bulkiness of the organic part of the molecule used to carry the charges whose electrostatic influence is investigated.

Another comparison is also of interest. Born's equation 19 for the free energy of hydration of gaseous ions of charge ν and radius r produces much

too negative values⁴⁰ if crystal radii and the macro dielectric constant ϵ of the solvent are used.

$$\Delta G_{\text{hyd}} = (e^2 v / 2r) (1 - 1/\epsilon) N \quad (19)$$

In order to get better agreement with experimental values, it has become customary to use effective radii r_e in 19 which are considerably larger than the crystal radii⁴¹. Noyes⁴², on the other hand, proposed to correct 19 by introducing an effective dielectric constant which is much smaller than the macro constant. These data, ϵ_e^N , are shown on *Figure 2* at the lower left hand corner, plotted as a function of the crystal radius of the ion. Most people consider that the Noyes method produces too low values for the effective dielectric constant.

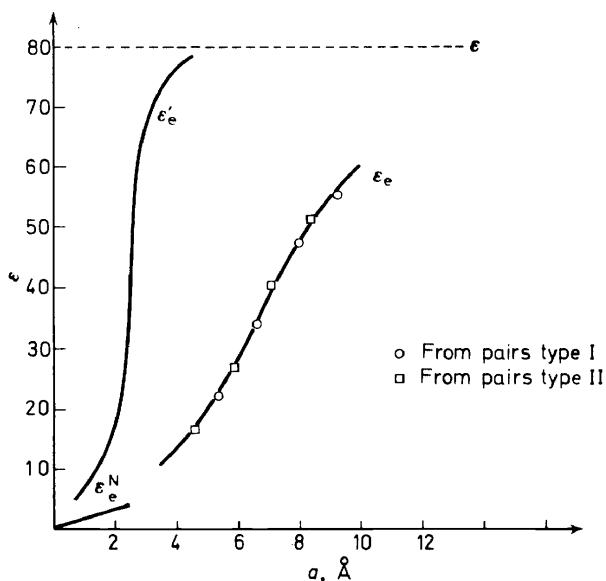


Figure 2. Effective dielectric constant ϵ_e .

Because of the organic molecule needed to carry the charges the interaction of which is to be studied by means of the proton transfer 14, the results hardly allow us to draw any definite conclusions concerning the effective dielectric constant to be used in association processes of ions of opposite charges (see section 7 of this paper 327). However, the thermodynamic functions of reaction 14 not only furnish values for ϵ_e (equations 15 and 16), but also for the temperature coefficient of the effective dielectric constant (equation 18). Up to the present, no information whatsoever seems to be available on that quantity.

Again, the proton transfer 14 will not furnish numbers for $\delta\epsilon_e/\delta T$ which can be used at once for an evaluation of ΔH of ion associations (equation 10). But the relation of the quantities ϵ_e and $\delta\epsilon_e/\delta T$ is most interesting and in this respect the experience gained by means of process 14 is remarkable. Both

quantities will depend on the strength of the electric field in the neighbourhood of the charges and it is to be expected that a diminution of ϵ_e will be accompanied by a lowering of $-\delta\epsilon_e/\delta T$. That this actually is so can be seen from *Figure 3* in spite of the relatively large uncertainties (lengths of the vertical lines) of the experimental values. Furthermore, there is no doubt that the quantity $-\delta\epsilon_e/\delta T$ decreases relatively more than ϵ_e , with the consequence that $\delta \ln \epsilon_e/\delta \ln T$ becomes less negative the stronger the electrostriction (*Table 7*). Therefore, an ion association will be much less endothermic than predicted by equation 10, using the bulk dielectric constant and its temperature coefficient.

This phenomenon actually is observed (see page 315) and we now have an explanation for it.

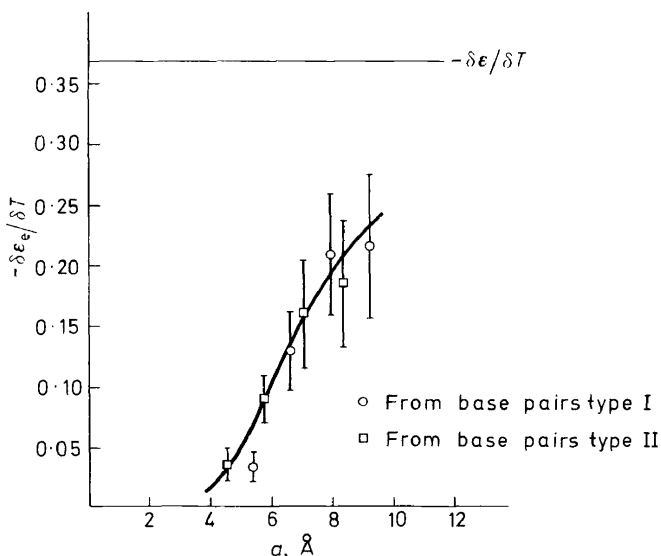


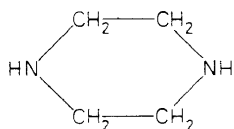
Figure 3. Temperature dependence of effective dielectric constant ϵ_e .

6. DIELECTRIC SHIELDING IN STRONG ELECTRIC FIELDS

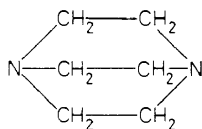
Figures 2 and 3 demonstrate that the effective dielectric constant and its temperature coefficient diminish to an extraordinary extent in an increasing electrostatic field. Unfortunately no data are available for distances below 4 Å of the two interacting positive ammonium groups, because of the impossibility of carrying out measurements with $\text{H}_2\text{N}-\text{CH}_2-\text{NH}_2$, which is unstable to hydrolysis. However, it is possible to increase the strength of the electric field to which one of the charges exposes the other charge by making the organic part of the charge carrier more bulky. In the mean the medium between the two charges will become less polarizable by doing so.

CONTRIBUTIONS TO ION ASSOCIATION IN SOLUTION

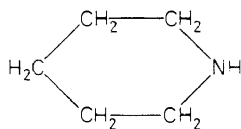
In the diprotonated diethylenediamine I (piperazine) and triethylenediamine II the charges not only are somewhat closer than in H_2en^{2+} , they are also dielectrically shielded from one another to a smaller extent.



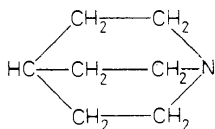
(I)



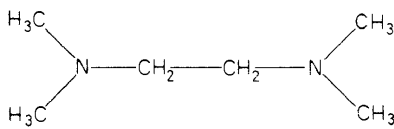
(II)



(III)



(IV)



(V)

By comparing the first step of protonation of I^{43} or II^{44} with the second step, we obtain data for the interaction of two $+e$ -charges at the intramolecular distance of the two acidic protons (base pair type I). Two base pairs of type II are obtained by comparing III^{45} or IV^{38} with the respective first protonation products of I or II; the two interacting charges being now at a distance proton-nitrogen. The results listed in *Table 8* are most interesting. The increase in bulkiness of the hydrocarbon part between the two charges causes a strong increase of the electrostatic energy A_{e1} which is caused by a decrease of the effective dielectric constant ϵ_e . Again $-\delta\epsilon_e/\delta T$ decreases relatively more than ϵ_e , so that $\delta \ln \epsilon_e/\delta \ln T$ becomes less negative and process 14 more exothermic.

In reaction 14 two charges of equal sign are separated from one another, which is to be compared with the approach of two opposite charges (ion association), which also causes an intensity decrease of the electric field to which the solvent is exposed. These processes are endothermic, if the electrostriction is small in magnitude (*Table 7*, pair type I, $n = 3, 4, 5$ and pair type II, $n = 4, 5$), but become exothermic with increasing electrostriction when the quantity $-(\delta \ln \epsilon_e/\delta \ln T)$ drops below 1 (equation 18). The electrostriction increases (ϵ_e and $-\delta\epsilon_e/\delta T$ decrease) when the number of carbon atoms n in $H_3N-(CH_2)_n-NH_3$ becomes smaller (*Table 7*) and when the bulkiness of the organic part of the charge carrier gets larger (*Table 8*). If the protonated form of II is compared with the protonated form of V (*Table 8*, lines 3 and 5), it is recognized that the increase of the organic part between the charges is much more effective in lowering ϵ_e and $-\delta\epsilon_e/\delta T$ than an increase outside the charges, as would be expected.

The electrostriction may be increased also by placing more than two charges on the charge carrier. Their influence on ϵ_e and $\delta\epsilon_e/\delta T$ can be estimated

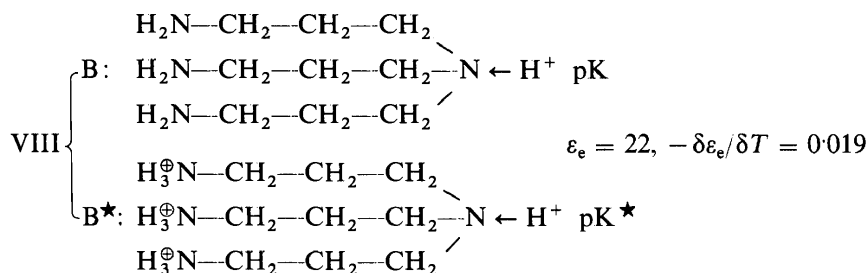
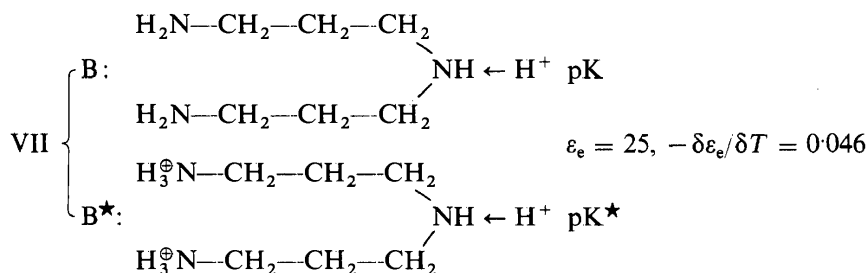
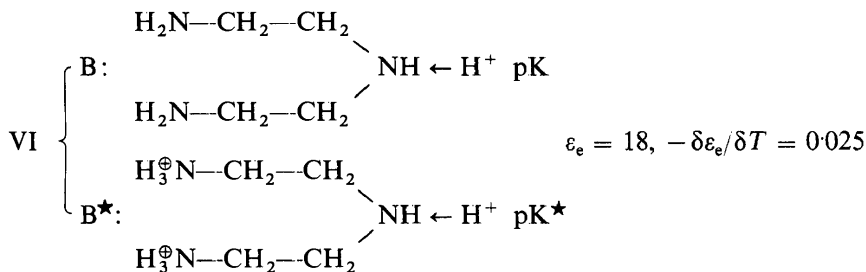
Table 8. Free energy and enthalpy changes in the proton transfer from base B* to base B (kcal/mole), $\mu = 0.1$, 25°C. ϵ_e , $\delta\epsilon_e/\delta T$ and $\delta \ln \epsilon_e/\delta \ln T$ are to be compared with these quantities of the bulk solvent $\epsilon = 78.54$; $\delta\epsilon/\delta T = -0.361$; $\delta \ln \epsilon/\delta \ln T = -1.37$

B	B*	Ref.	Pair type	$-\Delta G - \Delta H$	TS_{st}	A_{el}	$a(\text{\AA})$	ϵ_e	$-\frac{\delta\epsilon_e}{\delta T}$	$\frac{\delta \ln \epsilon_e}{\delta \ln T}$
HN=(CH ₂ -CH ₂) ₂ =N	H [⊖] N=(CH ₂ -CH ₂) ₂ =NH	43	I	5.62	3.05	0.82	4.80	4.75	14	0.017
H ₂ C=(CH ₂ -CH ₂) ₂ =N	H [⊖] N=(CH ₂ -CH ₂) ₂ =NH	43, 45	II	7.54	5.67	0.41	7.13	3.8	12	0.008
N=(CH ₂ -CH ₂) ₃ =N	NH [⊖] ≡(CH ₂ -CH ₂) ₃ =N	44	I	7.94	4.29	0.82	7.15	4.5	10	0.014
HC≡(CH ₂ -CH ₂) ₃ =N	HN [⊖] ≡(CH ₂ -CH ₂) ₃ =N	44, 38	II	10.69	8.29	0.41	10.28	3.5	9	0.006
(CH ₃) ₂ N-CH ₂ -CH ₂ -N(CH ₃) ₂	(CH ₃) ₂ N [⊖] -CH ₂ -CH ₂ -N(CH ₃) ₂	50	I	4.30	0.76	0.82	3.48	5.35	18	0.047
(H ₂ N-CH ₂ -CH ₂) ₂ NH	(H [⊖] N-CH ₂ -CH ₂) ₂ NH	47	I	7.55	4.00	0.66	6.89	5.35	18	0.025
(H ₂ N-CH ₂ -CH ₂ -CH ₂) ₂ NH	(H [⊖] N-CH ₂ -CH ₂ -CH ₂) ₂ NH	47	I	4.00	1.82	0	4.00	6.6	25	0.046
(H ₂ N-CH ₂ -CH ₂ -CH ₂) ₃ N	(H [⊖] N-CH ₂ -CH ₂ -CH ₂) ₃ N	48	I	6.70	5.02	0	6.70	6.6	22	0.019
[Ac ₂ =N-C ₂ H ₄ -N=Ac ₂] ⁴⁻	[Ac ₂ =N [⊖] -C ₂ H ₄ -N=Ac ₂] ³⁻	49	I	5.55	1.33	0.81	4.74	5.35	13	0.031
[Ac ₂ =N-C ₆ H ₁₀ -N=Ac ₂] ⁴⁻	[Ac ₂ =N [⊖] -C ₆ H ₁₀ -N=Ac ₂] ³⁻	49	I	8.34	4.59	0.81	7.52	5.0	9	0.012
PO ₃ ³⁻	HPO ₄ ²⁻	51	I	6.47	2.70	0.58	5.89	3.8	15	0.027
HPO ₃ ²⁻	H ₂ PO ₄ ⁻	51	I	6.93	2.68	0.48	6.45	3.8	14	0.026
PO ₄ ³⁻	SO ₄ ²⁻	51	II	13.6	8.9	0	13.6	2.2	11	0.013

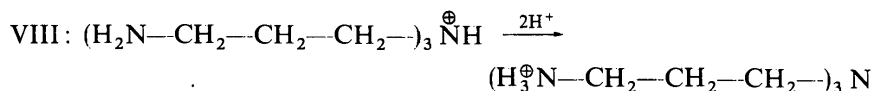
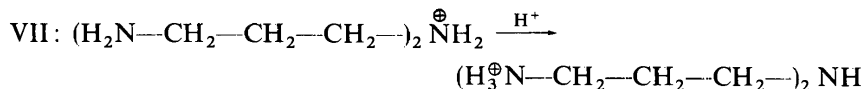
Upper: $\mu = 0.1$, 20°C; lower: $\mu = 0.0$, 25°C.

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by comparing the basicity of the members of pairs VI, VII and VIII, wherein the central nitrogen of B is to be protonated as well as that of B*:



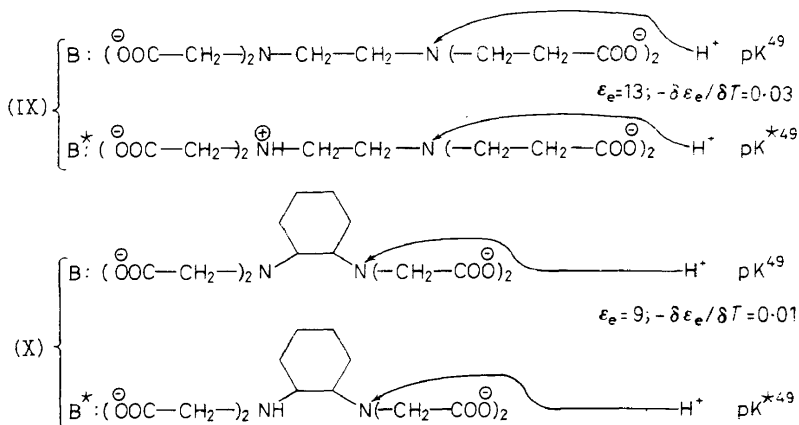
The central nitrogen atoms of VII and of VIII are the most basic of the non-protonated triamine and tetramine because they are secondary and tertiary amino groups respectively⁴⁶. The proton again is bonded by the central N in the third protonation step of VII and the fourth protonation step of VIII. The central nitrogen becomes available again in a tautomeric change, induced by the repulsion of charges, which takes place when the second proton is added:



In order to obtain the thermodynamic functions for the proton transfer 14 from B^* to B , we simply have to subtract ΔG (ΔH) of the third protonation step (pair VII)⁴⁷ or the fourth protonation step (pair VIII)⁴⁸ from ΔG (ΔH) of the first protonation step. Again we obtain A_{el} from 15, S_{st} being zero, and ϵ_e from 16 after introducing a factor of two (two e -charges on B^* in pair VII) or three (three charges on B^* in pair VIII). Equation 18 is applicable without any change. From the results (Table 8) we learn that three charges at the ends of chains of three CH_2 -groups (pair VIII) have approximately the same influence on ϵ_e and $\delta\epsilon_e/\delta T$ as a single charge at the end of the shorter ethylene chain (Table 7, line 1).

For bis-(β -aminoethyl)-amine VI⁴⁷, it has been assumed that the three nitrogens all have the same 'internal basicity', which leads to a statistical entropy term in 15 of $S_{st} = R \ln 3$. The result (line 6, Table 8) is as expected: two ammonium charges separated by an ethylene bridge reduce ϵ_e and $-\delta\epsilon_e/\delta T$ considerably more than a single charge at the same distance (line 1, Table 7).

The anions of EDTA (IX) and DCTA (X) are also symmetrical amine bases which form pairs B and B^* of type I.



The positive charges of the protons whose electrostatic interaction gives rise to the basicity difference ($pK - pK^*$) approach one another here in the additional field of the four negative carboxylate groups. This must cause a more intense electrostriction of the solvent and a comparison of IX (line 9, Table 8) with V⁵⁰, which is also a N,N' -tetrasubstituted ethylene diamine (line 5, Table 8), reveals that ϵ_e as well as $-\delta\epsilon_e/\delta T$ have indeed become considerably smaller. Also the results obtained with pair X are as expected: the two nitrogens are somewhat closer than in IX, they are separated by a more bulky organic carrier and the four COO^- groups are restricted to a smaller area, with the effect that ϵ_e drops to a very low value and also the temperature coefficient of ϵ_e is extraordinarily small.

The reduced basicity of HPO_4^{2-} with respect to PO_4^{3-} and of H_2PO_4 with respect to HPO_4^{2-} may be considered as being caused by electrostatic forces only: the second proton has to be approached in the additional field of the

first and the third proton in the additional field of the second. This constitutes the two second last pairs of type I in *Table 8* which have to be evaluated with $S_{st} = R \ln 8/3$ and $R \ln 9/4$ respectively in equation 15. The assumption that the 'internal basicity' of the oxygens remaining unprotonated does not change from PO_4^{3-} to HPO_4^{2-} and H_2PO_4^- is of course difficult to justify. However, the results obtained for ϵ_e and its temperature coefficient are very reasonable indeed.

The bases PO_4^{3-} and SO_4^{2-} differ from each other by the nuclear charge of the central atom and constitute a pair of type II (bottom line, *Table 8*). On protonation of SO_4^{2-} , the hydrogen ion has to be brought up within a distance of only 2.2 Å of this additional charge and it is reasonable again to find very low values of ϵ_e as well as of its temperature coefficient.

7. THE THERMODYNAMIC FUNCTIONS OF COMPLEX FORMATION

Before finishing we will consider a general association process taking place in aqueous solution with reactants which may be ions or uncharged dipoles or multipoles and atomic or molecular species of any kind. Charges of opposite or like signs will approach one another during such a reaction and an electrostatic energy A_{ei} is to be gained, which has to be formulated as a sum according to 20:

$$A_{ei} = N \sum_i \frac{e^2 z_+ z_-}{a_i \epsilon_{ei}} = (1/\epsilon_e) \text{ constant} \quad (20)$$

z_+ and z_- are the charges on the individual atoms of the associating ions and molecules which are brought up to distances a_i from one another. The solvent again will be treated as a structureless but non-homogeneous medium in using local dielectric constants. For each of the pairs of charges in the sum of 20 we need an individual effective dielectric constant ϵ_{ei} to account for their interaction and these are replaced by a mean value ϵ_e in the expression at the RHS of 20.

Equations 21 to 24 are obtained for the changes in free energy, entropy and enthalpy of the association process:

$$\Delta G = -T(\Delta S_t + \Delta S_c + \Delta S_r) - A_{ei} - E_n \quad (21)$$

$$\Delta S = (\Delta S_t + \Delta S_c + \Delta S_r) - A_{ei}(1/\epsilon_e)(\delta\epsilon_e/\delta T) \quad (22)$$

$$\Delta H = -A_{ei}(1 + \delta \ln \epsilon_e / \delta \ln T) - E_n \quad (23)$$

The entropy change is composed of several parts. The changes of translational entropy ΔS_t will be negative for an association reaction. On coordination flexible molecular reactants, especially chelating ligands, will lose their flexibility to a large extent which is accounted for by the conformational entropy change ΔS_c which again will be a negative quantity. The reactants furthermore will no longer be able to rotate independently in the adduct and therefore the change in rotational entropy ΔS_r is also negative. Changes in vibrational entropy are probably negligible and a fourth quantity ΔS_v , taking care of these, has been omitted from the first bracket on the right of 21 and 22.

The term E_n accounts for non-electrostatic interactions between the reactants, such as covalency and ligand field stabilization effects, and it is assumed that this quantity is independent of temperature.

Unfortunately, all the quantities in 21 to 23 are difficult to assess. We are mainly interested in the electrostatic contribution A_{e1} and the non-electrostatic contribution E_n . However, neither ΔG nor ΔH is a simple function of these quantities.

Let us have a look at the entropy terms in 21. The translational entropy of a solute species, which will be solvated to an unknown extent, certainly cannot be obtained simply with the Sackur-Tetrode equation. It has become customary⁵² to use instead of ΔS_t the cratic entropy⁵³ ($nR \ln 55 = n \times 8$ e.u., n being the difference of the number of product and reactant molecules in the chemical equation). However, the cratic entropy is a mixing and not a translational entropy.

From the magnitude of the chelate effect⁵⁴ I would like to conclude that ΔS_t for a 1:1 association must be considerably larger than eight entropy units. The chelate effect for a bidentate ligand Z has been defined as 24

$$\text{Chel} = \log K_{MZ} - \log \beta_{MA_2} \quad (24)$$

where K_{MZ} is the stability of the chelate MZ and β_{MA_2} the product $K_1 K_2$ of the individual stability constants of MA and MA_2 with a unidentate ligand A ; Z and A having like ligand atoms. An equivalent equation is

$$2.3 RT \text{Chel} = \Delta G_{MA_2} - \Delta G_{MZ} \quad (25)$$

which can be combined with 21. In doing so, we may neglect A_{e1} , if the ligands Z and A are uncharged

$$(A_{e1})_{MZ} = (A_{e1})_{MA_2} \approx 0 \quad (26)$$

Furthermore, the same bonds are formed between the metal atom and the ligand atoms of MZ and MA_2 respectively, which leads to

$$(E_n)_{MZ} = (E_n)_{MA_2} \quad (27)$$

Equations 26 and 27 are equivalent to the statement that Chel is an entropy effect

$$2.3 R \text{Chel} = \{(\Delta S_t)_{MZ} - (\Delta S_t)_{MA_2}\} + \{(\Delta S_c)_{MZ} - (\Delta S_c)_{MA_2}\} + \{(\Delta S_r)_{MZ} - (\Delta S_r)_{MA_2}\} \quad (28)$$

Considering that $(\Delta S_t)_{MZ} = (S_t)_{MZ} - (S_t)_M - (S_t)_Z$ (the difference of the translational entropies of MZ , M , Z) and $(\Delta S_t)_{MA_2} = (S_t)_{MA_2} - (S_t)_M - 2(S_t)_A$, we recognize that the quantity within the first brace of 28 is positive and constitutes a mean value of translational entropy S_t of a solute particle.

The differences within the second and third braces on the other hand are negative quantities. The chelating agent Z will lose more flexibility on coordination than the unidentate ligand A , and the more the longer the carbon chain connecting the two ligand atoms of Z . The chelate effect therefore decreases with the size of the chelate ring formed. There are hundreds of examples which demonstrate that the largest stability increase by chelation is achieved with a five-membered chelate ring; a four-membered ring being

probably strained, so that 27 is no longer valid. The stability of the complexes with uncharged chelating polyamines furthermore shows unambiguously that the stability increase gained by chelation is essentially due to an increased entropy term of the Gibbs–Helmholtz equation.

Equation 28, therefore, has a reasonably good experimental basis for uncharged ligands, and can be used for an estimation of the translational entropy S_t , which is identical with the difference $(\Delta S_t)_{MZ} - (\Delta S_t)_{MA_2}$. According to 28, the chelate effect can never be larger than $S_t/2.3R$. With ethylenediamine for Z, in comparison with ammonia or an aliphatic amine for A, the chelate effect amounts to two or three units. However, Chel can become as large as four or five units with rigid chelating agents such as phenanthroline in comparison with pyridine. Rigidity of the chelating ligand reduces the negative value of the difference within the second brace in 28. From these experimental chelate effects we conclude that the translational entropy S_t of a solute particle in aqueous solution must be of the order of magnitude of 30 entropy units and is therefore about as large as the translational entropy of a gas molecule.

Also the complexes of negatively charged ligands can be stabilized enormously by chelation. However, the magnitude of the stability increase is now very much more difficult to interpret because of the importance of the electrostatic energy terms. Certainly, equation 26 is now no longer valid, which influences not only ΔG of the exchange of two A by Z but also ΔH of this process and indeed, it is found experimentally that Chel (equation 24) is now no longer only an entropy effect⁵⁵.

A statement that the stability increase achieved by chelation was to a large extent a cratic effect⁵⁶ and would almost disappear by using unitary quantities, has caused considerable confusion⁵⁷. Using unitary quantities is equivalent to expressing the concentrations in mole fractions. Now, the chelate effect (equation 24) has the dimension of the logarithm of a concentration and its numerical value depends on the definition of the concentration unit. The value is very much smaller (by $\log 55 = 1.7$) when mole fractions are used instead of mole per litre, just as it is very much larger (by $\log 10^3$) when the concentrations are expressed in millimoles per litre. By no means does the chelate effect disappear through using unitary quantities; it is just measured by a very much larger unit and becomes numerically smaller. The translational entropy depends on the volume which the molecules have at their disposal (Sackur–Tetrode equation) and the numerical value of the difference ΔS_t in equation 28 depends therefore on the reference state.

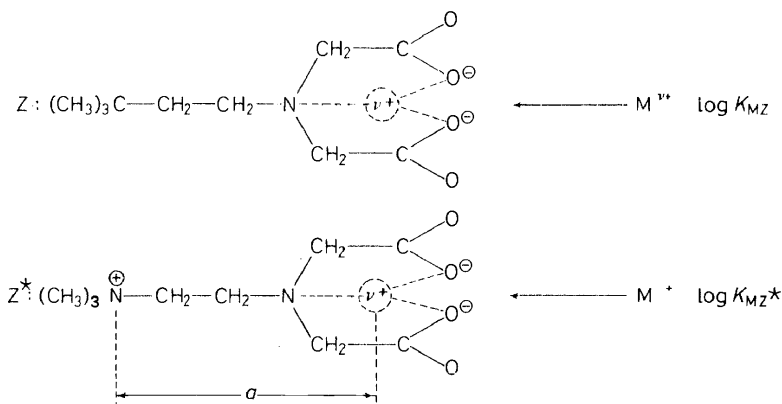
Finally, what is to be said concerning the contributions of the electrostatic energy A_{e1} and the non-electrostatic term E_n to ΔG on the one hand and to ΔH on the other? From 21 we learn that A_{e1} and E_n are of equal importance for the free energy change, whereas for the enthalpy change 23, A_{e1} has to be multiplied with a factor which may be positive or negative. This factor contains the effective dielectric constant as well as its temperature coefficient, both of which are very difficult to assess.

From experience (section 2) we know that associations are either slightly exothermic or slightly endothermic when the reaction is caused mainly by Coulombic forces (which was decided by the selectivity criterion, section 1). As a mean we can assume ΔH to be around zero when no covalency is

involved ($E_n = 0$), and therefore—according to 23: $\delta \ln \epsilon_e / \delta \ln T \approx -1$. With reasonable entropy terms in 21 an approximate value for A_{e1} is found, and with 20 we obtain the result that an effective dielectric constant of about 30 does account for many observed ΔG s and a value around -0.1 for $\delta \epsilon_e / \delta T$ is needed to account for the ΔH -values of common A-character associations (Reaction 11 may serve as an example, page 315). In the adduct formed, the reactants of opposite charge are about 2 to 3 Å apart and glancing now at *Figures 2 and 3* we recognize a conspicuous discrepancy.

The method outlined in section 5 apparently furnishes values for ϵ_e and its negative temperature coefficient which are substantially too small to be useful in common ion association processes. To a large extent this is due to the organic molecular carrier needed to investigate the interaction of charges by means of the proton transfer 14. There is of course no organic molecule between the associating ions forming an adduct and it is understandable that ϵ_e as well as $-\delta \epsilon_e / \delta T$ will be larger than the data presented in *Figures 2 and 3*.

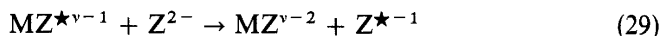
But, in addition to the influence of the organic carrier, there must be still another reason for the discrepancy between the values for ϵ_e and $\delta \epsilon_e / \delta T$ found with base pairs and those needed to account for the thermodynamic functions of A-character associations. The electrostriction exerted on the solvent (characterized by ϵ_e and $\delta \epsilon_e / \delta T$) apparently depends not only on the magnitude of the charge of the ion influencing the solvent and its radius but also on the structure of the solvation shell as well. The various ions seem to be shielded dielectrically in a very individual manner. This is demonstrated clearly by a study of the influence of a charge situated on a chelating ligand on the stability of its metal complexes. The anions of the following two substituted iminodiacetic acids Z and Z^* have been compared in determining the stability of the adducts with some cations⁵⁸.



The ligands Z and Z^* are a pair of bases as described in section 5. However, they can bind not only the proton but also metal cations M^{v+} with completely identical donor groups. The difference ($\log K_{MZ} - \log K_{MZ^*}$) corresponds to the quantity ΔpK of base pairs type II and is proportional to the free energy

CONTRIBUTIONS TO ION ASSOCIATION IN SOLUTION

change of the transfer of M^{v+} from the complex with $Z^{\star-1}$ to the ligand Z^{2-}



and in analogy with 15 we get

$$\Delta G_{29} = -2.305 RT \Delta \log K = -A_{e1} \quad (30)$$

There is no statistical term to be added on the RHS side; and no translational entropy, which is such a questionable quantity, brings in any uncertainty. For the electrostatic energy we write

$$A_{e1} = Ne^2v/a\epsilon_e \quad (31)$$

The intramolecular distance 'a' between the site of the metal cation within the complex and the nitrogen nucleus of the quaternary ammonium group is obtained from models and so the quantity ϵ_e can be calculated. The results are collected in *Table 9*.

Table 9. Free energy and some enthalpy changes in the metal transfer process between ligands Z and Z^{\star} (reaction 29): ionic strength $\mu = 0.1$; 20°C; kcal/mole

M^{v+}	$\Delta \log K$	ΔG	ΔH	a (Å)	ϵ_e	$-\delta\epsilon_e/\delta T$	$\frac{\delta \ln \epsilon_e}{\delta \ln T}$
H ⁺	4.8	-6.4	-4.8	4.5	12	0.01	-0.255
Mg ²⁺	2.2	-3.0	+0.3	5.1	44	0.17	-1.11
Ca ²⁺	1.8	-2.4	n.d.	5.4	51	---	---
Mn ²⁺	2.7	-3.6	n.d.	5.2	35	---	---
Ni ²⁺	2.7	-3.6	n.d.	5.1	36	---	---
Cu ²⁺	3.8	-5.1	-2.2	5.1	25	0.05	-0.57
Zn ²⁺	2.6	-3.5	n.d.	5.1	37	---	---
Cd ²⁺	2.5	-3.4	n.d.	5.3	37	---	---
Pb ²⁺	2.8	-3.8	n.d.	5.5	32	---	---

n.d. = not determined

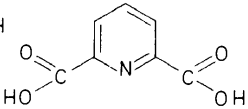
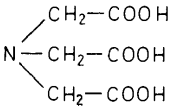
The ΔG s are not very accurate (± 0.2 kcal/mole) and there are uncertainties also in the distance 'a'. But even if it is admitted that the ϵ_e -values obtained are uncertain to about ten per cent, it is quite obvious that the various cations behave very individually with respect to the effective dielectric constant. Different cations apparently have a very different 'order producing capacity' with respect to the surrounding solvent, which is reflected also in their free energy of hydration. Most surprising is the result that considerably more energy is needed to bring up the singly charged hydrogen ion within a certain distance of the positive quaternary ammonium group than to approach any of the doubly charged metal cations.

The charge of A-character metal cations seems to be especially well shielded dielectrically. The charge of the hydrogen ion on the other hand is shielded to an extraordinarily small extent, perhaps because the proton fits exactly into the water structure thus causing formation of an iceberg around it, which may be of special rigidity. This makes it understandable that the experimental values for ϵ_e obtained from the proton transfer process 14 cannot *per se* be used for complex formation of metal ions.

The enthalpy change of 29 has only been determined⁵⁹ for the transfer of the proton as well as the transfer of the metal ions Mg^{2+} and Cu^{2+} . From ΔH again the temperature coefficient of the effective dielectric constant has been obtained (equation 18) and the results (Table 9) demonstrate anew that $\delta\epsilon_e/\delta T$ deviates relatively more from the normal value $\delta\epsilon/\delta T (= -0.36)$ the more ϵ_e deviates from the bulk dielectric constant ϵ , with the consequence that with increasing electrostriction the quantity $(-\delta \ln \epsilon_e/\delta \ln T)$ decreases and the reaction becomes more exothermic. This seems to be quite generally so. The transfer of Mg^{2+} in 29 is slightly endothermic, but the transfer of Cu^{2+} is somewhat and the transfer of H^+ is considerably exothermic. It is remarkable that this parallels generally the complex formation of these three cations with anionic ligands although the covalency contributions cancel out in process 29.

A very intimate knowledge of the structure of the solvent in the vicinity of the ions seems to be needed for a full understanding of the thermodynamic functions of complex formation in aqueous solution.

Table 10. A-character associations which are ΔH stabilized, kcal/mole

$HOOC-CH_2-O-CH_2-COOH$ H_2 (digl)	 H_2 (dipic)	 H_3X	EDTA = H_4Y
$HOOC-CH_2-NH-CH_2-COOH$ H_2 (ida)			

Reaction	μ	ΔG	ΔH	$T \Delta S$	$t^\circ C$	Ref.
$Lu^{3+} + digl^{2-} \rightarrow Lu(digl)^+$	1	- 7.71	+ 1.23	+ 8.97	} 25	60
$+ digl^{2-} \rightarrow Lu(digl)_2^-$	1	- 6.70	- 0.45	+ 6.23		
$+ digl^{2-} \rightarrow Lu(digl)_3^{3-}$	1	- 3.48	- 4.60	- 1.05		
$Lu^{3+} + dipic^{2-} \rightarrow Lu(dipic)^+$	0.5	- 12.27	- 2.21	+ 10.05	} 20	62
$+ dipic^{2-} \rightarrow Lu(dipic)_2^-$	0.5	- 10.54	- 3.82	+ 6.71		
$+ dipic^{2-} \rightarrow Lu(dipic)_3^{3-}$	0.5	- 6.28	- 6.65	- 0.37		
$GdY^- + ida^{2-} \rightarrow GdY(ida)^{3-}$	0.1	- 5.77	- 6.61	- 0.84	} 20	62
$TbY^- + ida^{2-} \rightarrow TbY(ida)^{3-}$	0.1	- 5.34	- 8.10	- 2.76		
$GdY^- + X^{3-} \rightarrow GdY(X)^{4-}$	0.1	- 6.52	- 7.92	- 1.40		
$TbY^- + X^{3-} \rightarrow TbY(X)^{4-}$	0.1	- 6.24	- 8.49	- 2.25		

One more word should be said concerning the rule stating that electrostatic adducts are mainly entropy stabilized, whereas covalent complexes are enthalpy stabilized. Equation 23 raises some doubt concerning the general validity of this rule. The factor with which A_{e1} has to be multiplied in order to obtain ΔH is bound to become positive in strong electric fields because of the stronger relative decrease of $-\delta\epsilon_e/\delta T$ in comparison to ϵ_e . We expect therefore exothermic associations with highly charged reactants. This actually proves to be so. Examples are the complexes of many A-character metal ions with the anion of EDTA. Even the calcium-EDTA-complex is produced in a reaction which is exothermic by 6.5 kcal/mole and it certainly

would be wrong to assume that this is due to the formation of covalent bonds.

Further examples are given in *Table 10*. The complexes of the rare earth cations—which are d^0 and of pronounced A-character—with the doubly negative anions of diglycolic acid and dipicolinic acid⁶⁰, are very informative. The 1:1-adduct is almost entirely ΔS -stabilized; the addition of the second ligand, however, is already appreciably exothermic and the formation of ML_3^{3-} from ML_2^- is caused by a large negative ΔH , while ΔS is unfavourable. Certainly, the rare earth cation is not acquiring more and more B-character from step to step in the complexes ML^+ , ML_2^- and ML_3^{3-} . The 1:2-complex ML_2^- does not add any chloride, cyanide or ammonia and does not react with sulphur donors. The selectivity criterion and the ΔS - ΔH -criterion, therefore, do not give the same answer with respect to the third step.

The explanation is obvious. In the third step the two reactants ML_2^- and L^{3-} are both anions and repel one another at longer distances. At these distances A_{e1} is negative and $-(\delta \ln \epsilon_e / \delta \ln T)$ will probably be greater than one (little electrostriction), so that the approach of the two anions is exothermic as long as they are repelling one another. At shorter distances the repelling forces give way to attraction and A_{e1} becomes positive, but $-(\delta \ln \epsilon_e / \delta \ln T)$ will now become smaller than one, so that ΔH again is negative. The large electrostriction in the range of attraction between the two anions is caused, of course, by an almost complete orientation of the water molecules between the many close ionic charges to a rigid solvent structure, making ϵ_e small and its temperature coefficient almost zero. The electrostatic association of two anions resembles to some extent the formation of an adduct in the gas phase, as in both cases the electrostatic attraction forces depend little on temperature. For the lanthanide complexes (for which E_n is negligible) it is generally observed⁶¹ that the more exothermic the complex formation, the less positive is the entropy change, which is explained by equations 21 and 22.

The lower part of *Table 10* contains further examples of associations between an anionic complex of a 'hard' metal and a 'hard' anionic ligand⁶². Again it is found that these reactions are strongly exothermic and proceed only because of a dominant negative ΔH , whereas the entropy change is unfavourable. All of the reactions of *Table 10* are A-character associations which do not follow the general rule, the adducts formed being enthalpy and not entropy stabilized.

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